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PAPER

# Selective aerobic oxidation of *para*-xylene in sub- and supercritical water. Part 2. The discovery of better catalysts†

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An extensive and systematic study has been carried out on the catalytic effect of more than 20 elements on the aerobic oxidation of *p*-xylene to terephthalic acid in super- and subcritical water. Reactions have been performed in a continuous reactor under catalyst unsaturated conditions. Reaction product, by-products and intermediates have been quantified as well as the burn (the amount of $CO_2$ originating from total oxidation of *p*-xylene). $CuBr_2$ has been found to be a superior catalyst to $MnBr_2$, which has been widely used in the literature for this reaction in water at high temperatures. At catalyst unsaturated conditions (*i.e.* with low concentrations of catalyst), $MnBr_2$ gives a terephthalic acid yield of 36.1% whereas $CuBr_2$ enhances this value to 55.6%. A strong synergistic effect has been found between $CuBr_2$ and other metals and sources of bromide. Indeed, we show that Cu/Co/Br, Cu/Co/$NH_4$/Br and other mixtures give better results than $CuBr_2$ reaching a terephthalic acid yield of 70.5% for the four component catalyst. The compositions of the catalyst as well as the reactor temperature have been optimized and their effects on the analyzed compounds are discussed. A substantial amount of additional data is included in the electronic supplementary information.

## Introduction

Terephthalic acid (TA) is an important commodity chemical. It is an intermediate of polyethylene terephthalate, which is used for making plastics, textiles and other polymeric products. Most of the TA produced in the world is made by catalytic aerobic oxidation of *p*-xylene (pX) using acetic acid as the solvent. Over the past few years, attempts have been made by our group[1–5] and others[6–14] to substitute acetic acid by supercritical water (SCW) and high temperature water (HTW) because of the potential economic and environmental advantages that water offers.[15] In addition, the unusual properties of water ($T_c$ = 374 °C, $p_c$ = 221 bar) at near- and supercritical conditions[16] allows it to be used as a reaction medium for a range of other chemical transformations.[17–21]

This paper is the second of two describing our research on the aerobic, homogeneously catalyzed autoxidation of *p*-xylene in sub- and super-critical water. The first paper[22] contrasted the different behaviour of *para*- and *ortho*-xylene under uncatalyzed, bromide-catalyzed, and Co/Br and Mn/Br-catalyzed conditions and we described the impact that water has on the catalyst activity and yields of the different products and by-products of this reaction (especially $CO_2$ and benzoic acid). In this paper we describe improved catalysts for HTW and SCW over those that have already been reported.

Commercial manufacture of TA started in 1951 using Co acetate and Co/Mn mixtures in acetic acid. Since then, a huge effort has been made to improve the efficiency of this process.[23] The order of catalyst activity for the formation of *p*-toluic acid (PTA) is Co(II) ≫ Mn(II) > Ni(II) with the remaining first row transition elements having no activity.[24] In 1954 a major breakthrough occurred with the discovery of metal/bromide catalysts especially the combination of Co and Mn acetates with bromide.[25] The metal/bromide catalysts greatly improve the selectivity and yield for converting pX to TA. The order of catalyst activity for the formation of *p*-toluic acid of the metallic bromides is Co(II) > Mn ≫ Ni.[24] The combination Co/Mn/Br

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† Electronic supplementary information (ESI) available: Full experimental details, including the configuration of the reactor, Fig. S1; additional experimental data, Tables S1–S18; and an analysis of the colour of some samples, Fig. S2 and Table S19–S20. See DOI: 10.1039/c1gc15138j

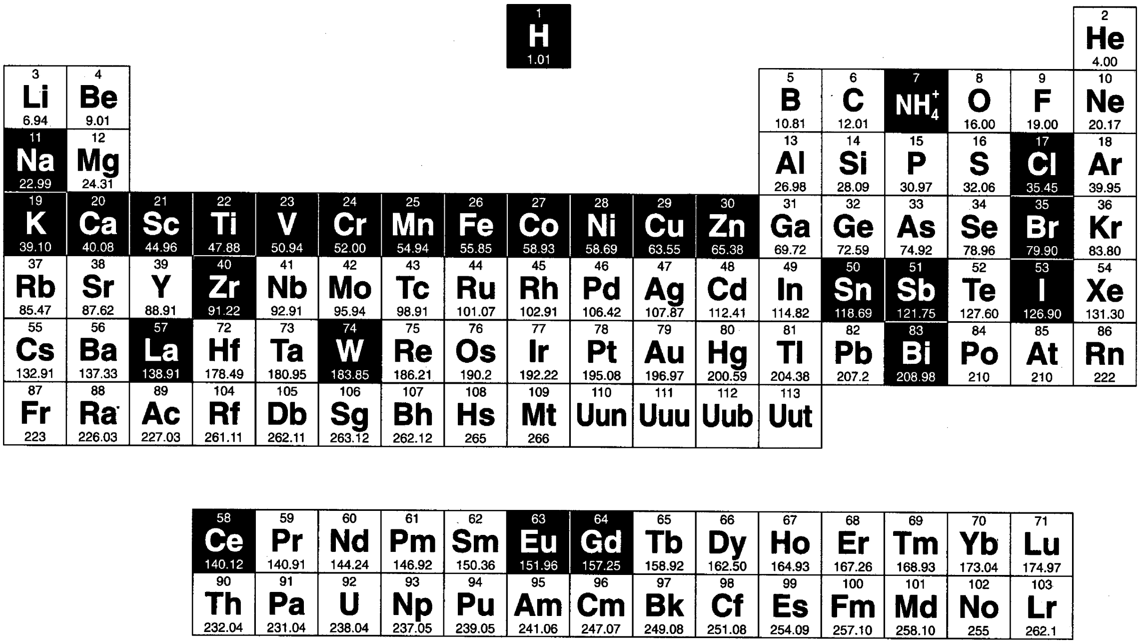


**Fig. 1** Summary of all of the elements plus $NH_4^+$ used in this study. Most metals were used as the halide salts. Non-redox active metal ions, *e.g.* $Na^+$ or $Ca^{2+}$, were used to vary the concentration of $Br^-$ relative to the redox active metals. W, Ti, V were evaluated but, due to the unavailability or instability of their bromide salts in water, $NaWO_4$, titanium(IV) bis(ammonium lactate) dihydroxide and $NH_4VO_3$ were used instead. Combinations of these W, Ti and V salts with different sources of bromide are reported in the ESI;† however the results were poor. Some metals such Bi and Sb could not been evaluated because their bromide salts are not soluble in water. $SnBr_2$ is soluble in water only at low concentrations. $BiBr_3$ and $SbBr_3$ hydrolysed in water to BiOBr or SbOBr and HBr.[32]

performs much better than its parts separately. This synergistic effect gives a scientific explanation of the superior activity of this catalyst for the TA manufacture. All these discoveries have led to the current technology for converting pX to TA.

Although the Co/Mn/Br combination in acetic acid is the most extensively investigated catalyst, many other combinations of metal with bromide have been reported.[23] Ni can be substituted for Co; Ni/Mn/Br is as active as Co/Mn/Br[26] and Ce can be substituted for Mn although it is less active.[27] Combinations of more than two metals have also been attempted incorporating Zr(IV), Hf(IV), Zn(II) and other metals in the catalyst configuration.[23] Mixed halogen catalysts have also been reported[28–30] as well as metal/NHPI combinations[31] (NHPI = *N*-hydroxyphthalamide).

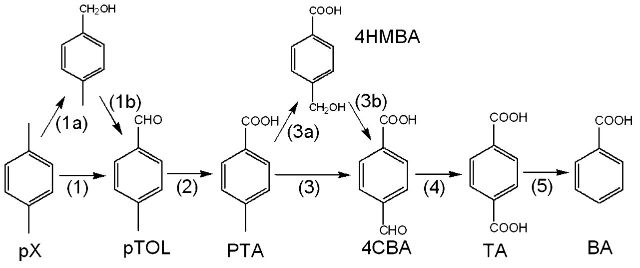
In 1998, Holliday *et al.*[6] demonstrated that selective batch oxidation of methylaromatics is possible on a small scale in HTW. Since then, there has been a number of papers by different research groups reporting oxidation of pX using water as a solvent.[1–14] However, very little research has been carried out to optimize the nature of the catalysts. Dunn *et al.*[9,10] established that $MnBr_2$ was more effective in HTW than Co/Mn/Br, the most commonly used catalyst in acetic acid. Interestingly, it was also observed to be more active than Mn/Zr/Br, Co/Mn/Hf/Br or Mn/Ni/Zr/Br. Most of the subsequent research conducted on this reaction in water has used $MnBr_2$ as catalyst.

In this paper, we present a systematic study of the effect of different inorganic salts used as catalysts in the continuous oxidation of pX to TA in SCW and HTW. The primary objective has been to find the most active catalyst for this reaction and we have done this by investigating a wide range of elements, see Fig. 1. Particularly significant is the fact that copper in metal/bromide catalyst is generally strongly antagonistic, *i.e.* it strongly inhibits the rate of reaction in acetic acid.[23] Here we report that Cu is one of the best catalysts in HTW.

This paper summarizes the key points from several person years of research undertaken at the University of Nottingham. Additional data are given in the ESI.†

## Results

Oxidation of TA in acetic acid follows a sequence of partially oxidized intermediates: *para*-xylene (pX) → 4-methylbenzaldehyde (*p*-tolualdehyde, pTOL) → *p*-toluic acid (PTA) → 4-carboxybenzaldehyde (4CBA) → TA; see Scheme 1. Reaction 1a and 3a to the benzylic alcohols are minor reactions. Small amounts of benzoic acid (BA) are also detected, which probably comes from decarboxylation of TA or one of its precursors.[22]



**Scheme 1** Sequence of intermediates of the oxidation of pX to TA in acetic acid. Reaction 5 is only one possible route to BA.[15]

All the experiments were conducted using tubular continuous flow reactors, the details of which are reported elsewhere.[3] A simplified diagram is shown in Fig. 2. An aqueous solution of hydrogen peroxide was passed through a pre-heater where it decomposed to a mixture $O_2$/SCW before entering the reactor. The pX and a cold aqueous solution of catalyst are continuously pumped into the reactor where they contact the $O_2$/SCW. At the reactor outlet, the mixture was quenched with aqueous NaOH to prevent precipitation of TA. The products were analyzed by HPLC and the $CO_2$ yield was measured by acid titration of the carbonate in solution. Unless otherwise stated, the reactions were carried out at a pressure of 230 bar and at temperature of 380 °C. The inlet pipes of the pX and catalyst feeds protruded into the reactor unless specified otherwise. More details of the equipment and procedures can be found in the ESI.†

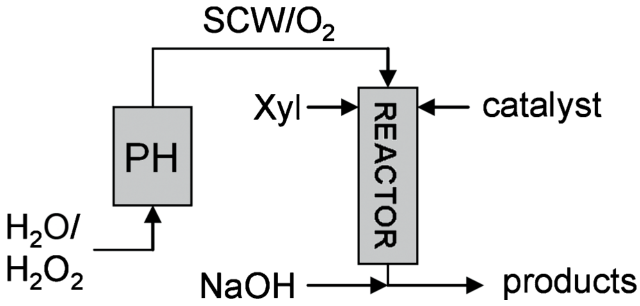


**Fig. 2** Schematic of the continuous reactor used in this work; PH is the preheater.

Reproducibility of yields in runs performed within a few days of each other was better than 1%. However, the work presented in this paper is the result of a project that lasted for several years and with many experimenters. Over this time, the $CO_2$ yield was found to vary by several percentage units. This does not change the conclusions of this work because the relative trends were maintained in any set of experiments done within a given period. The reproducibility of the TA yield and selectivity remained good over this time. Generally the error is ±1% for TA selectivity and ±2% for TA yield. BA yield reproducibility was lower: ±5%.

When evaluating the relative activity of various catalysts in homogeneous oxidation, it is important that the solution should be not "catalyst saturated"; *i.e.* the catalyst concentration should be lower than that needed to give the maximum yield. Seeking improved catalysts when the system is catalyst saturated often gives negative results because the high catalyst concentration "masks" the intrinsic catalytic activity.[39] In this study we have deliberately tested the relative activity of different catalysts under 'catalyst unsaturated' conditions with lower than optimum yields. Thus, the typical catalyst concentrations in the reactor were 2.6 mM, *ca.* 25% of those we have used previously.[1–5] In our discussion, each catalyst is designated by the sum of its cations and anions and the concentration of each species is expressed as multiples of this concentration. For example, if equal amounts of $CoBr_2$ and $MnBr_2$ were added, the catalyst formulation would be Co/Mn/Br with the relative amounts: 0.5/0.5/2.0 and concentrations of the species would be 1.3/1.3/5.2 mM. Apart from pX and *p*-tolualcohol, the concentrations of the six other species shown in Scheme 1 were quantified by HPLC. The selectivity for each compound was calculated as the concentration of that compound divided by the sum of those of the six aromatic compounds. The yield of TA, $Y_{TA}$, was calculated by eqn (1)

$$Y_{\mathrm{TA}} = 100\frac{[\mathrm{TA}]}{[\mathrm{pX}]} \tag{1}$$

where [pX] is the molar concentration of pX in the sample if the conversion had been 0. *i.e.* allowing for dilution. $[\mathrm{pX}] = (F_{\mathrm{pX}}\rho_{\mathrm{pX}})/(F_{\mathrm{total}}M_{\mathrm{pX}})$, where $F_{\mathrm{pX}}$, $F_{\mathrm{total}}$ are the flowrates of pX and the total flow after quench; $\rho_{\mathrm{pX}}$ and $M_{\mathrm{pX}}$ are the density and molar mass of pX respectively. The $CO_2$ yield originating from total combustion was calculated from the carbonate concentration obtained from titration by the eqn (2), with [BA] being subtracted to avoid counting the $CO_2$ molecules arising from decarboxylation. There are eight carbon atoms in *p*-xylene hence the factor of 8 in eqn (2).

$$Y_{\mathrm{CO_2}} = 100\frac{[\mathrm{CO_3}^{2-}]-[\mathrm{BA}]}{8[\mathrm{pX}]} \tag{2}$$

Finally, we define "burn" as shown in eqn (3):

$$\mathrm{Burn} = Y_{\mathrm{CO_2}}/Y_{\mathrm{TA}} \tag{3}$$

*i.e.* the amount of $CO_2$ relative to the yield of the main product, TA. The burn is a measure of the amount of pX that is lost through combustion.

## 1. Search for the best redox metal(s) as catalyst

**Scope of this paper.** Redox catalysts usually contain metals with variable valence, *i.e.* the transition metals. With homogeneous oxidation catalysts the two valencies normally differ by one unit, *e.g.* Co(II) and Co(III). A wide range of different metallic bromide solutions have been used as catalysts in our experiments. Fig. 3 illustrates the catalytic activity of different metallic bromides for this reaction in supercritical water.

**Pure metal bromides.** Table 1 summarizes the data quantitatively for the pure metal bromides. The following points are clear from Fig. 3 and Table 1. (a) The $CuBr_2$ catalyst gives the highest TA yield and selectivity of the simple metal bromides investigated. It also gives the lowest 4CBA and PTA selectivities and no detectable amounts of HMBA and pTOL. (b) Under unsaturated conditions, the order of activity of metals according to the highest TA yield and selectivity is Cu(II) > Fe(III) > Mn(II) > Co(II) >other metals. These results are consistent with the observation by Savage *et al.*[9] and our group[22] that $MnBr_2$ is better catalyst in SCW than $CoBr_2$. (c) $MnBr_2$ is not the optimal catalyst since $FeBr_3$ and $CuBr_2$ perform better. (d) Of the metal bromides, Co/Br is the best catalyst in acetic acid but, in SCW, TA yield and selectivities are significantly lower than several other metals. (e) The $CO_2$ yield for $CuBr_2$, 24.4%, is higher than for $MnBr_2$, which only gives 18.1%. Even so, the burn is lower with Cu because the $CO_2$ yield is related to the amount of TA produced. (f) Taking this into account, $CuBr_2$ is also the best catalyst from the point of view of burn. (g) $ZrBr_4$ gives a lower TA yield than $MnBr_2$ but the selectivity is better. $ZrBr_4$ is believed to hydrolyze to $ZrO_2$ and HBr and to precipitate in

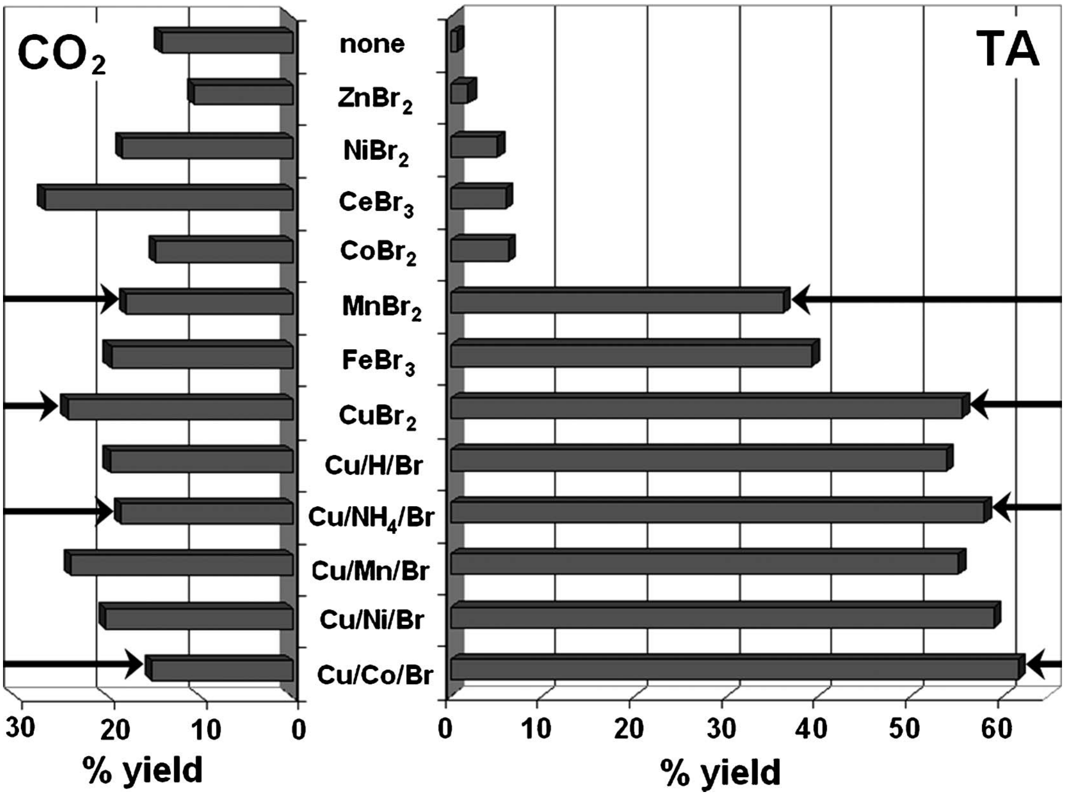


**Fig. 3** TA and $CO_2$ yields for selected catalysts evaluated at the same unsaturated concentration. The arrows highlight the most important catalysts. It can be seen that the metal has a more dramatic effect on the TA than on the $CO_2$ yields. All reactions carried out at 230 bar and 380 °C.

**Table 1** Catalytic activity of different metallic bromides in the oxidation of pX to TA in supercritical water

| | | | | Yield, mol (%) | | | Selectivity | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Entry | Catalyst | [catalyst]/2.6 mM | Br : metals mol/mol | $CO_2$ | TA | Burn | TA | PTA | 4-CBA | HMBA | pTOL | BA |
| 1 | none | — | — | 14.3 | 0.6 | 23.8 | 8.4 | 73.3 | 4.7 | 1.8 | 9.9 | 1.9 |
| 2 | Zn/Br | 1.0/2.0 | 2.0 | 10.7 | 1.9 | 5.63 | 14.5 | 47.0 | 25.0 | 2.3 | 6.6 | 4.7 |
| 3 | La/Br | 0.66/2 | 3.0 | 13.4 | 2.5 | 5.36 | 12.3 | 61.7 | 11.2 | 2.5 | 9.6 | 2.7 |
| 4 | Eu/Br | 1.0/3.0 | 3.0 | 22.8 | 4.8 | 4.75 | 13.4 | 48.9 | 14.9 | 2.7 | 17.0 | 3.1 |
| 5[a] | Zr/Br | 1.0/4.0 | 4.0 | 26.4 | 17.1 | 1.54 | 56.2 | 30.8 | 2.8 | 1.5 | 0.6 | 8.0 |
| 6 | Ni/Br | 1.0/2.0 | 2.0 | 18.5 | 5.0 | 3.70 | 18.9 | 52.4 | 19.2 | 2.2 | 3.7 | 3.6 |
| 7 | Ce/Br | 1.0/3.0 | 3.0 | 27.1 | 6.0 | 4.52 | 22.7 | 59.9 | 8.9 | 2.1 | 3.1 | 3.4 |
| 8 | Gd/Br | 1.0/3.0 | 3.0 | 25.1 | 6.5 | 3.86 | 19.2 | 57.2 | 13.0 | 3.2 | 4.2 | 3.2 |
| 9 | Co/Br | 1.0/2.0 | 2.0 | 14.8 | 6.3 | 2.35 | 19.4 | 56.4 | 15.8 | 2.6 | 3.0 | 2.8 |
| 10 | Mn/Br | 1.0/2.0 | 2.0 | 18.1 | 36.1 | 0.50 | 51.3 | 34.9 | 6.3 | 1.4 | 0.0 | 6.0 |
| 11[b] | Fe/Br | 1.0/3.0 | 3.0 | 19.8 | 39.3 | 0.50 | 75.3 | 9.9 | 3.2 | 0.0 | 4.8 | 6.8 |
| 12 | Cu/Br | 1.0/2.0 | 2.0 | 24.4 | 55.6 | 0.44 | 86.4 | 5.9 | 1.2 | 0.0 | 0.0 | 6.5 |

[a] $ZrBr_4$ is likely to hydrolyze to $ZrO_2$ + 4HBr. Catalytic activity is probably due only to the 10.4mM HBr released (see Table 1 in the first paper of this series[22]). [b] $FeBr_3$ caused blockages in the pipes so it was tried using a different reactor configuration: pX and catalyst streams were premixed in a T piece before entering the reactor.

the reactor, as happens in acetic acid.[33] The rest of the bromides evaluated gave poor TA yields and selectivities.

**Search for the best source of bromide.** In acetic acid, the presence of bromide greatly boosts the activity and selectivity to TA in the oxidation of pX.[24] The source of bromide in acetic acid results in only small differences in TA yield or selectivity. In SCW, the high sensitivity of the reaction to the bromide concentration has been reported in several cases.[1,5,9,22] However, until now, the source of bromide used in all SCW reactions has been the bromide of the redox metal. In the oxidation of *o*-xylene, Fraga-Dubreuil *et al.*[5] have already demonstrated that addition of HBr to $MnBr_2$ enhances the solubility of Mn and hence increases its activity. However, adding bromide as a mixture of HBr and NaBr was much less effective (Table S2 in the ESI†). Attempts to reduce the amount of bromide by substituting chloride or iodide also gave lower activity (Table S4).

However the real surprise came when HBr was used to keep the absolute concentration of bromide constant while the concentration of Cu(II) was decreased. Entry 1 of Table 2 shows

**Table 2** Catalytic activity using different combinations of $CuBr_2$ + $MBr_n$ as catalyst[a]

| Entry | Catalyst[b] | [catalyst]/2.6 mM | Br : metals mol/mol | Yield, mol (%) |  | Burn | Selectivity[c] |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  | $CO_2$ | TA |  | TA | PTA | 4-CBA | HMBA | BA |
| 1 | Cu/H/Br | 0.15/1.7/2 | 13.3 | 19.9 | 53.9 | 0.37 | 90.8 | 1.4 | 0.2 | 0.0 | 7.6 |
| 2 | $Cu/NH_4/Br$ | 0.15/1.7/2 | 13.3 | 18.7 | 58.0 | 0.32 | 92.1 | 0.0 | 0.0 | 0.0 | 7.9 |
| 3 | Cu/Mn/Br | 0.15/0.85/2 | 2.0 | 23.5 | 55.2 | 0.43 | 91.3 | 0.6 | 0.0 | 0.0 | 8.1 |
| 4 | Cu/Co/Br | 0.15/0.85/2 | 2.0 | 15.3 | 61.7 | 0.25 | 92.1 | 0.0 | 0.0 | 0.0 | 7.9 |
| 5 | Cu/Fe/Br | 0.15/0.57/2.1 | 2.9 | 19.9 | 41.2 | 0.48 | 72.3 | 15.4 | 3.3 | 0.0 | 9.0 |
| 6 | Cu/Ni/Br | 0.15/0.85/2 | 2.0 | 19.6 | 59.0 | 0.33 | 89.7 | 0.7 | 0.0 | 0.1 | 9.5 |
| 7 | Cu/Zn/Br | 0.15/0.85/2 | 2.0 | 17.5 | 46.8 | 0.37 | 70.3 | 13.8 | 2.5 | 1.1 | 12.3 |
| 8 | Cu/La/Br | 0.1/0.9/2.9 | 2.9 | 23.4 | 57.5 | 0.41 | 90.8 | 0.0 | 0.0 | 0.0 | 9.2 |
| 9 | Cu/Eu/Br | 0.1/0.9/2.9 | 2.9 | 21.6 | 56.2 | 0.38 | 90.4 | 0.0 | 0.0 | 0.0 | 9.6 |

[a] Data for additional Cu/M/Br, M = Na, K, Ca, are given in Table S3 in the ESI. [b] Concentration of metals is 2.6 mM in every case except in entries 1 and 2 that is 0.39 mM and in entry 5 that is 1.9 mM. [c] Selectivity for pTOL was 0 in all cases.

that more than a six-fold reduction in concentration of Cu gave a better catalytic performance than $CuBr_2$ itself. Furthermore replacing HBr by $NH_4Br$ gave even better results, see Fig. 3 and Table 2, entry 2. BA is the only aromatic by-product present in significant quantities and no 4CBA was detected. The burn is also low, giving so far the smallest amount of $CO_2$ per unit of TA produced. $NH_4Br$ is therefore an interesting candidate as source of bromide. Additional results are summarized in Table S3 in the ESI†.

Unlike in acetic acid, the effect on TA yields of adding non-redox metal bromides to $CuBr_2$ was very large in HTW ranging from 21 to 58% following the order $NH_4Br$ > HBr > $ZnBr_2$ > $CaBr_2$ > NaBr > KBr; see Tables 2 and S3.

**Synergistic effects between Cu and other metals.** From the results in the previous sections, Cu appears to be an especially active catalyst, possibly playing the same role as Co in the acetic acid-based reaction. The next step was to search for synergistic effects between Cu and other metals in SCW. Table 2 shows the effects of combining $CuBr_2$ with other metallic bromides. Catalyst configurations are Cu/M/Br where the bromide concentration was kept constant at 2 × 2.6 mM and Cu concentration is 0.15 × 2.6 mM, except in entries 5, 8 and 9. When M was either Co or Ni, a better TA selectivity and yield were obtained than for $CuBr_2$ alone. La and Eu also gave better TA yields and selectivities but the Br concentration is also higher because of the stoichiometry of $MBr_3$. No 4CBA was detected for the best combinations (M = Mn, Co, Ni, Eu or La). Cu/Co/Br gave the highest TA yields obtained so far under catalyst unsaturated conditions, as well as high selectivity and low burn. We also investigated whether adding a third metal to Cu/Co/Br would give additional benefits. Table S6 in the ESI† shows the results for a range of Cu/M/M′/Br, where M, M′ = Co, Ni, Mn, Fe, La or Zn. None of them gave as good a performance as Cu/Co/Br in terms of TA yield, TA selectivity and low burn together. Some Ni-containing catalysts gave a higher TA yield but also higher burn. Cu/Co/Zn/Br gave low burn and might be worth investigating further. Some Fe-based compositions (Table S7) and a number of binary and ternary mixtures which did not contain Cu were also studied, see Table S8. These included Mn, Fe, Ni, Zn and Ce. None came close to the performance of the Cu-based catalysts.

Synergy occurs when the resultant effect of combining the components is greater than the sum of its parts. Examination of Tables 1 and 2 suggests synergism between Cu and other components. A more detailed study reveals synergistic effect between Cu and Co, Mn, Ni, Zn, HBr and $NH_4Br$. Details can be found in the ESI (Table S10).†

The experiments described above have demonstrated the high activity of Cu for the oxidation of pX to TA when this metal is in solution, *i.e.* it acts as a homogenous catalyst. An additional study using solid metallic Cu plus HBr as the catalyst was also carried out. The results showed that the reaction could be catalysed by Cu(II) formed *in situ* by dissolution of copper metal by HBr. Details of these experiments are also given in the ESI, Table S18.†

**Co-oxidation of *p*-xylene with selected substrates.** One of the former commercial scale methods for TA manufacture catalyzed by cobalt(II) acetate, was conducted by co-oxidizing pX with acetaldehyde, which is oxidized readily to peroxyacetic acid.[34] This acid is known to oxidize Co(II) rapidly to Co(III).[15] Without the co-oxidant, the pX is oxidized chiefly to *p*-toluic acid. The formation of the additional Co(III) in the presence of acetaldehyde drives the reaction to high TA yields. Since co-oxidation has been used commercially in acetic acid,[34] we evaluated this approach to see whether it would be beneficial for the oxidation of pX in SCW. Benzaldehyde can also serve as an effective co-oxidant since it will form peroxybenzoic acid quickly and selectively.[35] However we found that the co-oxidation of pX with benzaldehyde did not improve the TA yield with either Cu/Br or Cu/Co/Br catalysts. GC analysis after the experiments confirmed that most of the benzaldehyde had been consumed. Similarly the use of other co-oxidants such as phenol, isopropanol, methanol or toluene was also unsuccessful. Details of these experiments are given in the ESI, Table S11.†

## 2. Catalyst optimization

In the first part of this paper, we described the discovery of Cu/Co/Br as a new homogeneous catalyst for the oxidation of pX to TA in SCW. After the discovery of such a catalyst, it can be optimized further in the following ways:

*1. Catalyst Concentration.* The activity of the oxidation system normally increases with increased catalyst concentration until the system is 'catalyst saturated' whereupon the activity either remains constant or decreases.[39] Often the yield with metal/bromide catalysts also increases with catalyst concentration because the system becomes more selective towards the desired aromatic acid, *i.e.* mechanisms leading to the total destruction of the aromatic ring to $CO_2$ are decreased.[23]

*2. M : Br ratio.* In acetic acid, the activity of the system usually increases as this ratio increases, reaches a maximum and then decreases. There are reports of the selectivity of the system changing as well.[23]

*3. M′ : M″ ratio.* Variation of this ratio in Co/Mn/Br and Co/Mn/Zr/Br catalysts has a strong influence on activity during pX oxidation in acetic acid.[24] It can also affect amount of ring degradation using a Co/Mn/Br catalyst in acetic acid.[36] Changing the Cu : Co ratio in the Cu/Co/Br catalyst in acetic acid changed the relative rates of pX and PTA acid oxidation[37]

*4. Temperature.* Temperature will affect to the reaction rate but it can also affect the extent of decarboxylation[38] and ring degradation.[22]

Here we describe the first stages in optimizing the new Cu/Co/Br catalyst using these approaches. We also discuss the influence of temperature on the reaction.

**Effect of catalyst concentration.** Without any catalyst present and assuming no leaching of the metals from the reactor walls, the TA yield is only 0.6%. Cu is an especially active catalyst, by adding just 0.39 mM of $CuBr_2$, the TA yield jumps from 0.6 to 12.2% (by a factor of 20), see Table S3. Increasing the concentration to 2.57 mM, the yield increases to 55.6%, see Table 1. When only 0.18 mM of $CuBr_2$ is combined with 1.09 mM of $CoBr_2$ one obtains 60% TA yield and 88.5% selectivity. However, four times more catalyst only increases the TA yield to 65.1%, indicating that the catalyst is close to saturation, see Table S12. More active catalysts such as the Cu-based ones become saturated at lower concentrations. This fact has a crucial importance on the optimum design of a viable process using such catalysts.

**Effect of Cu : Co ratio.** Fig. 4 shows the effect on several reaction products of varying the Cu : Co ratio in the Cu/Co/Br catalyst. The combined concentration of the metals and of the bromide were kept at 2.6 and 5.2 mM respectively. The figure again reveals the high activity of Cu. At a concentration of 2.6 mM $CoBr_2$ gives only a 8.8% TA yield. Addition of an amount of Cu so that the Cu : Co ratio is only 0.010 mol/mol (*i.e.* the Cu concentration is only 0.026 mM) boosts the TA yield to 55%. Thus the TA and $CO_2$ yields are sensitive to very small changes in the Cu:Co ratio at low Cu proportions. The TA yield reaches a maximum value of 65% at a Cu : Co ratio of 0.1 : 0.9 and then quickly decreases as the proportion of Cu is raised further. Also the $CO_2$ yield reaches a minimum at this point. This change in activity can be also seen by observing the changes in the selectivity to the intermediates, such as *p*-toluic acid. On the other hand, the BA yield remains constant over the whole range.

A similar trend is observed for other catalyst combinations such as Cu/Mn/Br. The yield is higher when there is an excess of Mn over Cu and the $CO_2$ yield is lower. Details of all these experiments can be found in the ESI, Table S13.†

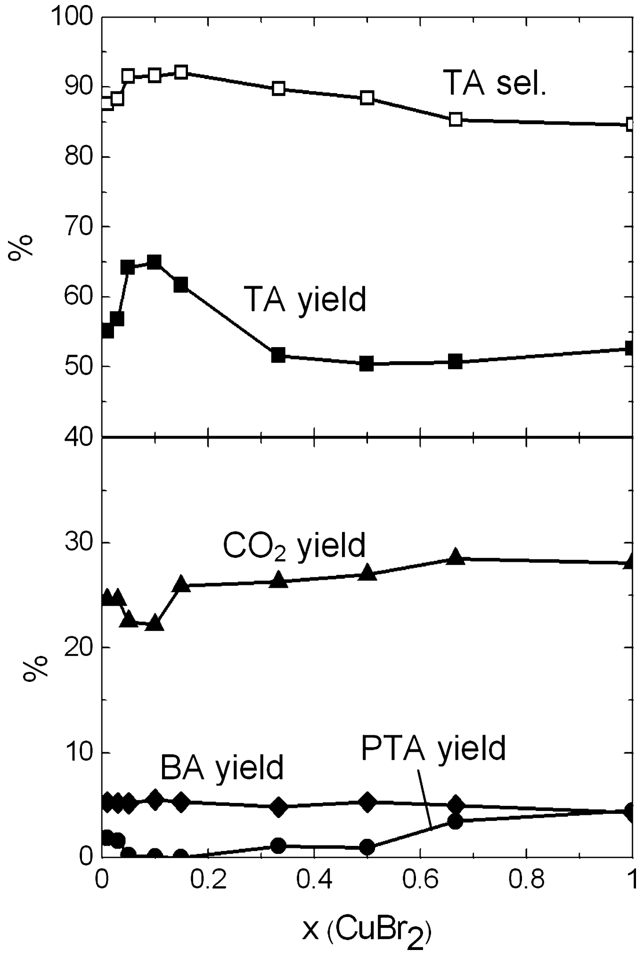


**Fig. 4** Effect of varying the $Cu^{2+}$ content of the Cu/Co/Br catalyst on the % yields of TA, BA, PTA and $CO_2$ and the % TA selectivity. During the experiment the $Br^-$ was held constant at 5.2 mM. $x(CuBr_2)$ is the molar fraction of $CuBr_2$: $x(CuBr_2) = n_{CuBr_2}/(n_{CuBr_2} + n_{CoBr_2})$.

**Effect of temperature.** The effect of temperature on the performance of the Cu/Co/Br catalyst is shown in Fig. 5. Concentration is (0.1/0.9/2.0) × 2.6 mM which was shown to be the optimum ratio in the previous section. There are maxima in TA yield and selectivity at 330 °C. However, yields of $CO_2$ and BA increase monotonically with temperature. There is, therefore, a compromise between highest TA yield and lowest $CO_2$ and BA yields, with the optimum point at subcritical temperatures (330 °C).

Several further examples comparing catalyst performance at 330 and 380 °C can be found in the ESI.† In general, yields for Cu-containing catalysts are always higher at 330 °C with correspondingly lower yields of $CO_2$ and BA. However, if $NH_4Br$ is added to increase Br : metals ratio, the opposite effect is observed; see Table S14.

As expected, a less active catalyst, like $EuBr_3$, usually shows better activity at the highest temperature but the loss to BA is always lower at 330 than at 380 °C.

**Variation of $CoBr_2$ & $NH_4Br$ in the Cu/Co/$NH_4$/Br catalyst.** We have seen that the variation of the Cu : Co ratio, Fig. 4, and the presence of $NH_4Br$, Table 2, both have a positive effect on the TA yield and decrease the formation of $CO_2$. A study

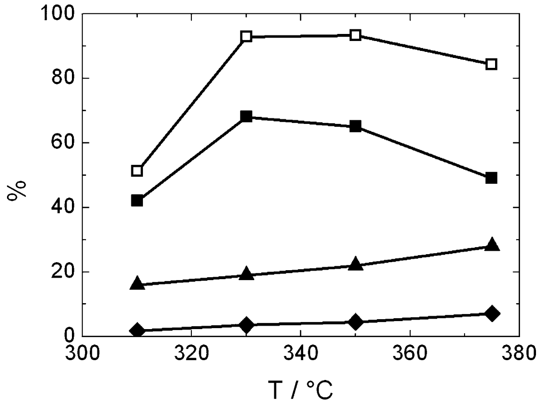


**Fig. 5** Effect of reactor temperature on the yields TA, $CO_2$ and BA and the TA selectivity using a Cu/Co/Br catalyst in SCW. These experiments were carried out using Cu/Co/Br = (0.1/0.9/2.0) and a slightly different reactor configuration: inlet catalyst pipe is 1/8″ instead of 1/16″. (□) TA selectivity, (■) TA yield, (▲) $CO_2$ yield, (◆) BA yield.

was subsequently performed on the incremental substitution of $CoBr_2$ by $NH_4Br$ in a Cu/Co/$NH_4$/Br catalyst. It would be beneficial to reduce the amount of $CoBr_2$ in the catalyst formulation in favour of $NH_4Br$ for the following reasons: (1) $NH_4Br$ is less expensive; (2) $CoBr_2$ is more prone to precipitation in SCW due to hydrolysis.

The Cu and Br concentrations were held constant at 0.385 and 5.13mM respectively. The $CoBr_2$:$NH_4Br$ ratio was varied in the way that Co concentration is 25, 50 and 75% of the original value in the Cu/Co/Br catalyst; that is 0.21, 0.43 and 0.64 mM respectively. Two temperatures were studied: 330 and 380 °C. Fig. 6 shows the results obtained. Details of all these experiments can be found in the ESI, Table S15.†

The shape of the curves is different at the two temperatures. At 380 °C a clear maximum in TA yield is obtained for [Co] = 0.43 mM with a similar $CO_2$ yield as for the Cu/Co/Br catalyst without $NH_4Br$. The TA selectivity does not change significantly. At 330 °C no local maxima are observed. However it is noticeable how even a low proportion of $CoBr_2$ is able to enhance greatly the performance of the Cu/$NH_4$/Br catalyst, which is not very active at this temperature. The initial TA yield of 44% rose to 62% upon substitution of just the 25% of $NH_4Br$ by $CoBr_2$, with the $CO_2$ yield decreasing from 21% to 19%. The BA selectivity does not vary significantly for any of the temperatures studied. These results demonstrate a beneficial effect on combining $CoBr_2$ and $NH_4Br$ in the presence of $CuBr_2$.

**Effect of Br : metals ratio.** Table 3 shows the effect of adding extra bromide as HBr or $NH_4Br$ to selected catalysts at 380 and 330 °C. In entries 1 and 2, HBr is added to $MnBr_2$, the "traditional" catalyst, and to Cu/Co/Br, the newly discovered catalyst. In entries 3 and 4 $NH_4Br$ is added to the formulation Cu/Co/$NH_4$/Br at the proportion where the maximum in TA yield was found in the previous section.

Several trends were observed: (1) apart from entry 4, the TA yield decreases when small amounts of Br are added and then slightly increases if more Br is added (probably due to the activity of the Br catalyst itself); (2) the $CO_2$ yield generally increases upon $Br^-$ addition; and (3) the BA selectivity decreases upon Br addition.

Entries 1 to 3 show that Br addition has negative effect on catalyst performance. The higher TA yield observed when 8 × 2.6 mM of Br is added to $MnBr_2$ is probably due to the activity of HBr itself. Entry 2 shows that the optimum Br : metals ratio is 2. The same tendency is observed when $NH_4Br$ is used as source of Br instead.

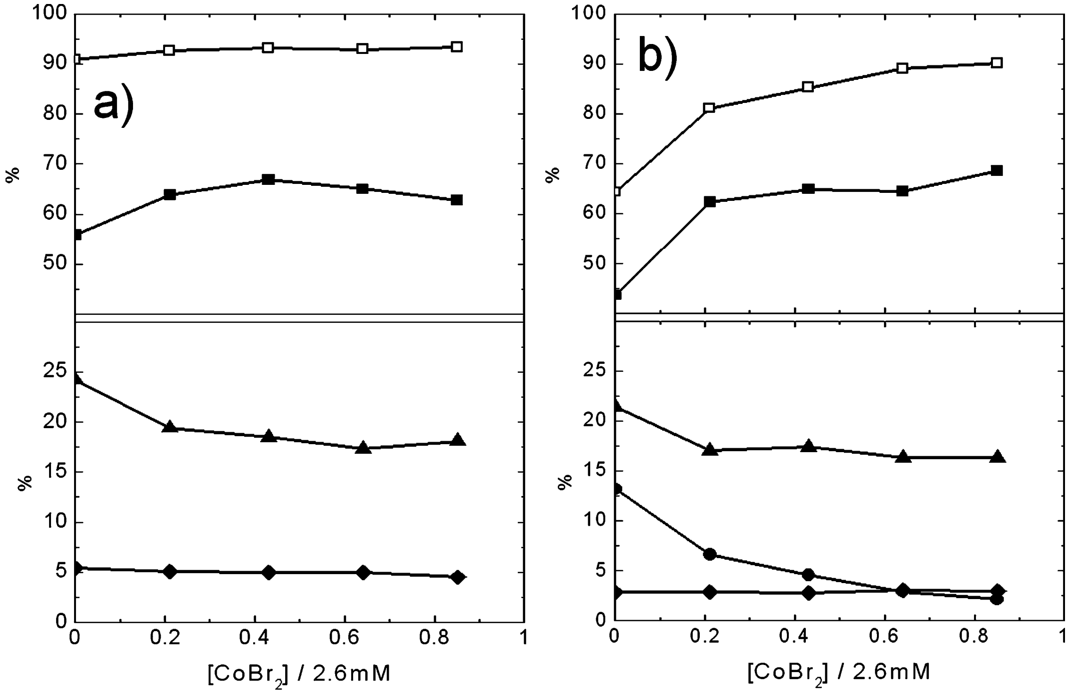


**Fig. 6** Effect of varying the relative concentration of $CoBr_2$ and $NH_4Br$ in the Cu/Co/$NH_4$/Br catalyst at (a) 380 and (b) 330 °C. (□) TA selectivity, (■) TA yield, (▲) $CO_2$ yield, (◆) BA yield, (●) PTA yield.

**Table 3** Effect of increasing Br : metals ratio for some selected catalysts at 380 °C

| | | | | Yield, mol (%) | | | Selectivity | |
|---|---|---|---|---|---|---|---|---|
| Entry | Catalyst[a] | Br added[a] | Br : metals mol/mol | $CO_2$ | TA | Burn | TA | BA |
| 1 | Mn/Br (1.0/2.0) | — | 2 | 18.1 | 36.1 | 0.50 | 51.3 | 6.0 |
| | | HBr (1.0) | 3 | 14.2 | 22.7 | 0.63 | 39.8 | 3.7 |
| | | HBr (8.0) | 10 | 25.2 | 46.9 | 0.54 | 96.2 | 3.0 |
| 2 | Cu/Co/Br | — | 2 | 22.0 | 60.0 | 0.37 | 88.5 | 10.2 |
| | (0.07/0.42/1.0) | HBr (0.5) | 3 | 24.4 | 53.7 | 0.45 | 91.1 | 7.2 |
| | | HBr (1.0) | 4 | 23.6 | 55.9 | 0.42 | 93.9 | 6.1 |
| 3 | Cu/Co/NH4/Br | — | 3.4 | 17.9 | 66.8 | 0.27 | 93.1 | 6.9 |
| | (0.15/0.43/0.85/2.0) | $NH_4Br$ (1.0) | 5.2 | 23.3 | 60.1 | 0.39 | 91.6 | 8.4 |
| | | $NH_4Br$ (2.0) | 6.9 | 23.6 | 63.0 | 0.37 | 92.4 | 7.6 |
| 4[b] | Cu/Co/NH4/Br | — | 3.4 | 17.0 | 64.9 | 0.26 | 85.2 | 3.7 |
| | (0.15/0.43/0.85/2.0) | $NH_4Br$ (1.0) | 5.2 | 17.8 | 70.5 | 0.25 | 91.6 | 4.2 |
| | | $NH_4Br$ (2.0) | 6.9 | 17.4 | 70.2 | 0.25 | 92.6 | 4.0 |

[a] The numbers between brackets indicate the concentration of every species relative to 2.6 mM. [b] Temperature was 330 °C

Entry 4 is an exception to the general trend. Addition of 2.6 mM $NH_4Br$ increases TA yield to the highest values presented in this series of papers. Further addition of bromide does not affect greatly the performance. Notice that the $CO_2$ yield and BA selectivity remain almost constant in every case.

## Discussion

Some of the major conclusions from this work are:

1. At a concentration of 2.6 mM, $CuBr_2$ is a significantly better catalyst than $MnBr_2$ in terms of high TA yield and low burn, even though Cu is a poor catalyst in acetic acid.[23]
2. If the $Br^-$ concentration is kept constant, some of the $CuBr_2$ can be substituted by HBr or $NH_4Br$ to give Cu/H/Br and $Cu/NH_4/Br$ catalysts which have higher activity than $CuBr_2$ alone. We have found that both HBr and $NH_4Br$ are synergistic with $CuBr_2$.
3. There is a strong synergy between Cu and Co even though $CoBr_2$ alone is a poor catalyst in SCW.
4. The synergy of Cu and Co is not unique and several other metals, *e.g.* $Ni^{2+}$, also enhance the performance of $CuBr_2$ in SCW (see Tables S8 and S10).
5. The best Cu/Co/Br catalyst so far performs better in terms of TA selectivity and burn in sub-critical water at 330 °C than in SCW at 380 °C at the same catalyst loading and flowrates.

Mechanistically, the aerobic oxidation of pX is a complex multi-step process with potentially competing pathways at several points. Despite this complexity, it is possible to present a plausible rationalisation which could explain how these conclusions arise.

The basis of this rationalisation is that the mechanism of the reaction in SCW is similar to that in acetic acid. This seems to be a reasonable assumption because the sequence of intermediates is the same[1,7,8] and the TA selectivity and yield are favoured by increasing the concentration of catalyst.[6–8] In addition, the relative yields of TA and the reaction intermediates give an idea of the facility which the reactions 1 to 5 in Scheme 1 take place. In both acetic acid and SCW, we generally observe higher concentrations of TA and PTA than for the rest of compounds, indicating that the "difficult step" of the sequence is the activation of the methyl group, *i.e.* reactions 1, 1a, 3, 3a. Very small amounts of 4HMBA are usually detected, suggesting that the sequence goes mainly through reactions 1 and 3 rather than through 1a and 3a.

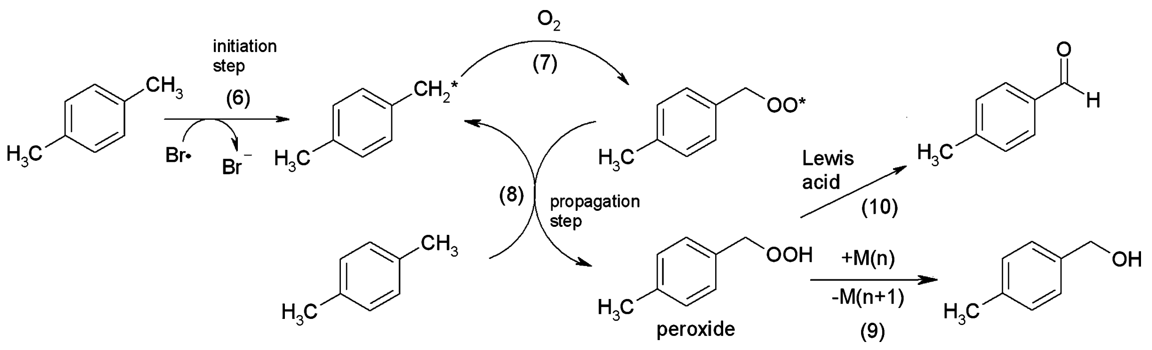
In acetic acid, the oxidation of pX to TA proceeds through a catalyst-modified free radical chain mechanism. The reaction is initiated by a oxidized bromide specie, $Br^•$ (reaction 6, Scheme 2). The propagation step is the rapid reaction of the benzylic radical with molecular oxygen followed by the hydrogen atom abstraction of the methyl group with the peroxy radical (reaction 8). The metal can react with the hydroperoxide in two different ways: either by a redox reaction to form a benzylic alcohol (reaction 9) or acting as a Lewis acid to generate the aldehyde by dehydration (reaction 10), thereby by-passing reaction 9 and the formation of the alcohol.[39–41] Very low amount of such alcohols are usually found, so reaction 10 dominates reaction 9 in Scheme 2. The aldehyde is then oxidized to the acid following a set of analogous reactions but in addition the peroxyacid thus formed rapidly oxidizes the catalyst metals.[27] Finally, the oxidized metal is reduced by reacting with $Br^-$ to restart the catalytic cycle.

When $CoBr_2$ is used by itself as a catalyst, it acts by linking the redox pair Co(III)/Co(II) with Br(0)/$Br^-$. The same mechanism has been proposed for the SCW process with Mn playing the same role in SCW as Co does in acetic acid, see Scheme 3.

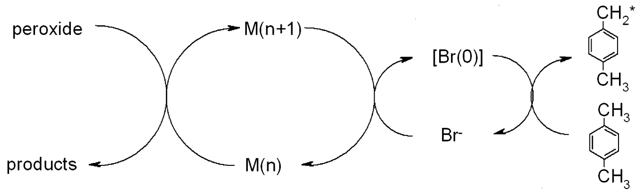
### Why is $CuBr_2$ an active catalyst in SCW?

Presumably, $CuBr_2$ acts as a catalyst in SCW *via* a similar mechanism to Scheme 3. This is slightly surprising because Cu does not have a higher consecutive oxidation state in aqueous solution at ambient temperatures. However, its redox behaviour will change at the temperature is increased. The redox behaviour of the different metals in aqueous solution can be represented in *E*–pH diagrams (Pourbaix diagrams) that show the thermodynamically stable chemical form of the metal at different redox potential and pH. Such diagrams have been available for many years for metals in water at room and moderate temperatures.[43]

More limited studies have been carried out at high temperatures. Beverskog and Puigdomenech reported *E*–pH diagrams for Cu, Fe, Ni, Zn at temperatures up to 300 °C.[44–47] Fig. 7



**Scheme 2** Reaction mechanism of the catalyzed oxidation of pX to TA in acetic acid.



**Scheme 3** Suggested redox cascade for metal bromide catalyzed oxidation of pX in water.[42]

shows that at increasing temperature, an increasingly broad region of stability for $Cu^+$ appears. Indeed, the potential for the pair $Cu^+/Cu^{2+}$ increases with temperature up to 0.5 V at 300 °C. Furthermore, the existence of $Cu^+$ in presence of $Br^-$ has been experimentally observed by EXAFS structural studies at 325 °C.[48] At this temperature $Cu^{2+}$ was found to be a highly oxidizing species, since it was able to oxidize Pt(0) from the spectroscopic cell. Thus Cu(II) in SCW would have a sufficiently high redox potential to oxidize bromide and even pX itself. In addition, due to its stability in high temperature water, Cu(I) would remain in the solution thus being oxidized by the peroxide to close the redox cycle.

### Why are HBr and $NH_4Br$ effective in partial replacement of $CuBr_2$ in the catalyst?

Scheme 3 shows that the metal and $Br^-$ play different roles in the catalytic cycle and there is no *a priori* reason why the 1 : 2 ratio defined by the formula $CuBr_2$ should be the optimal ratio for highest activity. Additional experiments showed that addition of several different bromide sources enhanced the activity of $CuBr_2$ but that HBr and $NH_4Br$ were particularly effective (see Table S3 in the ESI†).

In acetic acid, there is little difference in Co/Br catalyzed oxidation when using NaBr or $NH_4Br$ as source of bromide.[49] Since $NH_4Br$ and NaBr, at ambient conditions, are simple bromide salts, one might expect their catalytic activity also to be similar in SCW. Instead we find that NaBr is a very inferior catalyst to $NH_4Br$ when combined with $CuBr_2$. When Cu/Br and $NH_4Br$ or HBr are added together they are not acting independently, *i.e.* there is a synergistic interaction. $NH_4Br$ has a similar catalytic effect to HBr both when used alone or in combination with copper. In ambient water, the ammonium cation is a weak acid: $NH_4^+Br^- \rightleftharpoons NH_3 + HBr$; $K_a = 1.8 \times 10^{-5}$. In SCW the equilibrium could be quite different. Due to the low dielectric constant, some of the non-ionic acids such as HCl and

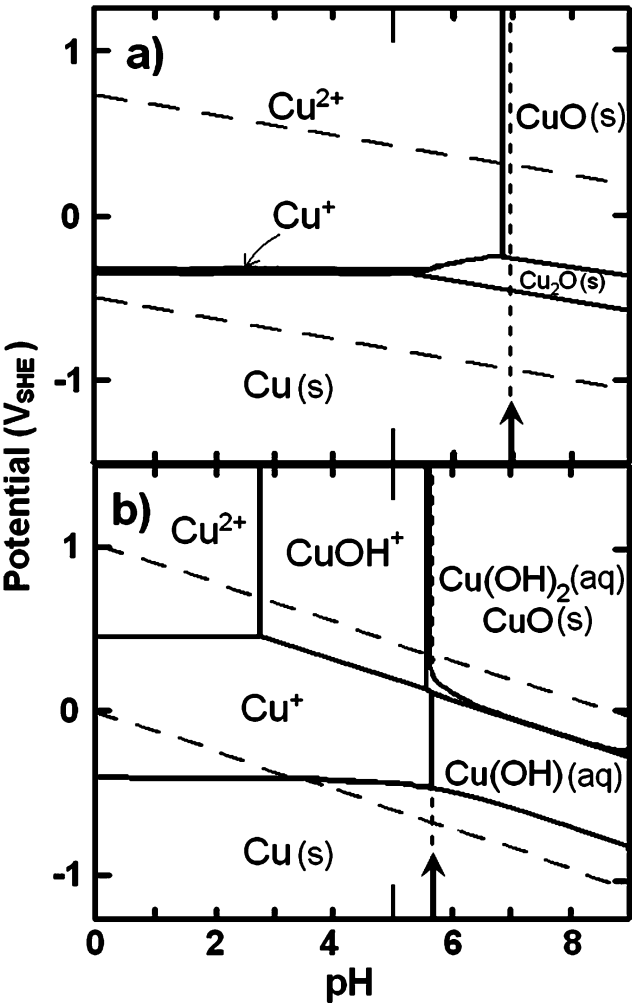


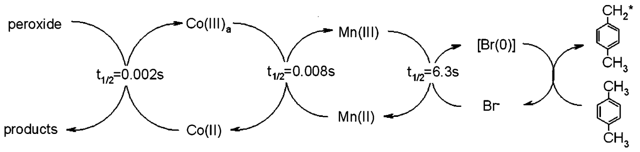
**Fig. 7** *E*–pH diagrams for copper in water at (a) 25 °C and (b) 300 °C. Note the greatly enlarged coexistence area for $Cu^+$ at 300 °C. We believe that the existence of Cu(I) in solution is a key factor in making Cu a highly active catalyst for the oxidation of pX. The arrows indicates the value of neutral pH. The dashed sloped lines are the stability limits of water under these conditions. The diagrams have been redrawn from reference 44, which also includes data at higher pH. Reproduced by permission of ECS – The Electrochemical Society.

$NH_4OH$ become weaker, *i.e.* less dissociated;[50] that would cause the equilibrium to be displaced towards $NH_3$ + HBr and hence there would be an increase in the amount of HBr in the medium.

The lower activity of Cu/NH$_4$/Br catalyst at 330 °C may be due to a shift in this equilibrium at different temperature. The NH$_3$ might also coordinate with either Cu(I) or Cu(II) and change their catalytic behaviour.

### Why does CoBr$_2$ enhance the activity of CuBr$_2$ in SCW?

The discovery of the synergy between Co and Mn gave scientific explanation to the superior activity of this combination in the development of the acetic acid process.[28] This combination of two metals enables the oxidation to proceed through a set of linked redox reactions thus lowering the activation energy very substantially, Scheme 4.[15,23,51]



**Scheme 4** Redox cascade for the Co/Mn/Br catalyzed oxidation of pX in acetic acid.[51]

The experiments summarised in Table 2 and in Table S10 show that CuBr$_2$ also experiences a synergistic enhancement of its activity with a range of metal bromides, particularly Co but also Fe, Ni and Zn. It is possible that some of these metals acted *via* linked redox cycles similar to those in Scheme 4. However, this clearly cannot apply to all metals because Zn, for example, is not redox active.

There is, however, a second role for a metal catalyst, namely as a Lewis acid to promote the conversion of the peroxide intermediate to the aldehyde, reaction 10 in Scheme 2. Increasing the rate of this transformation will necessarily decrease the extent of the competing generation of OH$^\bullet$ which is formed by the thermal dissociation of the peroxide. The hydroxyl radical is highly energetic, with a redox potential of 2.9 V and unselective. It attacks the aromatic ring and hence destroys the aromatic moiety.[22]

Metals such as Zr, Fe, V, Ti, Hf *etc.* activate Co and Co/Mn catalyst in oxidation of methylaromatics in acetic acid.[39,40] The intermediates observed suggest that they favour reaction 10 and there is a correlation between the degree of activation and Lewis acidity.[40] The same may be true for synergies with CuBr$_2$ in SCW. If we take $Z/r^2$ as a measure of Lewis acidity, where $Z$ is the formal charge of the cation and $r$ its ionic radius,[52] there is a reasonably good correlation between $Z^2/r$ of a particular metal and the TA yield and selectivity when that metal is added to CuBr$_2$, see Fig. 8. Particularly encouraging is the fact that there is monotonic increase in TA yield in the presence of the non-transition metals which can only act as Lewis acids *i.e.* Zn(II) > Ca(II) > Na(I) > K(I).

However, the correlation in Fig. 8 is only positive up to a maximum at $Z^2/r \leq 6.2$ (Co) and negative for higher values. This suggests two opposing effects related to Lewis acidity. Thus, as already explained, a Lewis acid can catalyze the dehydration of the peroxide (Scheme 2, reaction 10) but a too strong Lewis acid may have its activity limited by hydrolysis and eventual precipitation of the metal oxide, $MBr_x + yH_2O \rightarrow MBr_{x-y}(OH)_y + yHBr$. Indeed, it is known in acetic acid that Zr, which is a very strong Lewis acid, in a Co/Mn/Zr/Br catalyst does hydrolyze and precipitate during oxidation.[33] And as mentioned before this is likely to happen in water.

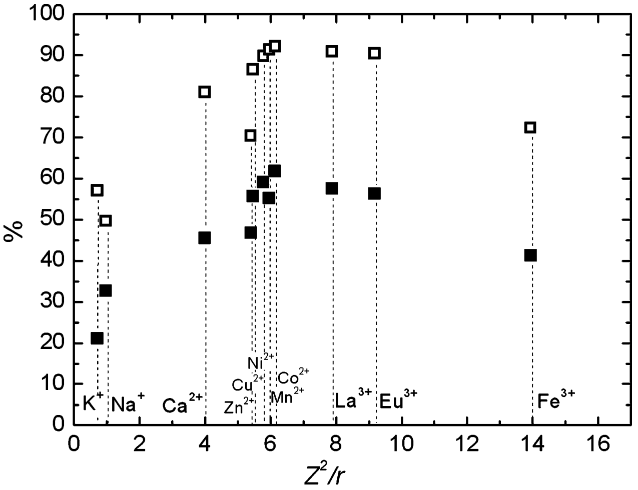


**Fig. 8** Correlation between (■) TA yield and (☐) TA selectivity with Lewis acidity of M in the catalyst Cu/M/Br. Fe$^{3+}$ is shown rather than Fe$^{2+}$ because our experiments used FeBr$_3$ as catalyst.

Hydrolysis of metal salts and formation of metal oxide nanoparticles in SCW is a significant research area in its own right.[53–55] It is therefore quite interesting that Co$^{2+}$ salts are known to give rise to oxide particles in SCW much more readily than Cu$^{2+}$.[54] This agrees with some of the observations we have already made. Furthermore, we have noticed that Cu-based catalysts give rise to less fouling of the reactors by precipitation than MnBr$_2$. The presence of HBr, will lower the pH and further discourage precipitation.

### Why does Cu/Co/Br work better at 330 °C than 380 °C?

Generally the rate of a given reaction increases with temperature. However we have a complex set of reactions and a continuous process so it not easy to evaluate the effect of temperature in the reaction performance. Temperature can affect the process by (a) modifying the reaction rate; (b) changing undesirable side reactions such as decarboxylation, which deactivates the catalyst[3] or (c) changing the residence time as a consequence of variation of density with temperature.

The shape of the TA selectivity and yield *vs.* temperature in the Fig. 5 suggests the existence of opposing effects that are optimized at 330 °C. The large difference in TA selectivity and yield from 310 to 330 °C as well as the dramatic reduction of intermediates (see Table S14) clearly indicates an enhancement of the reaction rate with temperature. At higher temperatures, however, only the by-products (BA and CO$_2$) increase significantly; hence effect (b) is making the difference. The fact that few intermediates are seen at 330 or 380 °C also indicates that residence time is sufficient to complete the reaction.

In some cases temperature can have a major impact on the activity of a catalyst. The clearest example, as shown above is the Cu/NH$_4$/Br catalyst. A possible explanation is a shift in the equilibrium $NH_4^+Br^- \rightleftharpoons NH_3 + HBr$. That would be consistent with the fact that, in Table 3, further addition of NH$_4$Br does improve the performance of the Cu/Co/NH$_4$/Br catalyst at

330 °C while at 380 °C it does not. This also explains the shape of the curves in Fig. 6.

## Summary and Conclusions

A detailed study of the catalytic effect of different substances on the oxidation of pX to TA as catalyst has been carried out. $CuBr_2$ itself, or combined with other metallic bromides, has been shown to be the best in terms of TA selectivity, of TA yield and of burn. Low concentrations of copper are enough to give good performances provided that the overall amount of bromide is high enough. Br can be added in several different ways (as metallic bromide, HBr or $NH_4Br$), all giving high TA yields and selectivities.

The role of the different species in the reaction mechanism has been discussed: Cu is the most active redox catalyst, Mn and Fe are weaker redox catalysts. Many metallic bromides can activate $CuBr_2$ acting as redox metals, Lewis acids or sources of HBr by hydrolysis. There is a strong synergy between Cu and Co and probably the best composition identified so far is $Cu/Co/NH_4/Br$ because the concentrations of both metals are minimized, the TA yield is high and the burn is low.

Overall, this paper has described the discovery of new and substantially different catalysts for the aerobic oxidation of pX to TA in high temperature and supercritical water. Given this new direction, there is almost certainly opportunity for further improvement and optimization of this fascinating reaction.

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## References

1 P. A. Hamley, T. Ilkenhans, J. M. Webster, E. García-Verdugo, E. Vernardou, M. J. Clarke, R. Auerbach, W. B. Thomas, K. Whiston and M. Poliakoff, *Green Chem.*, 2002, **4**, 235–238.
2 J. Fraga-Dubreuil, E. García-Verdugo, P. A. Hamley, E. M. Vaquero, L. M. Dudd, I. Pearson, D. Housley, W. Partenheimer, W. B. Thomas, K. Whiston and M. Poliakoff, *Green Chem.*, 2007, **9**, 1238–1245.
3 E. García-Verdugo, E. Vernardou, W. B. Thomas, K. Whiston, W. Partenheimer, P. A. Hamley and M. Poliakoff, *Adv. Synth. Catal.*, 2004, **346**, 307–316.
4 E. Garcia-Verdugo, J. Fraga-Dubreuil, P. A. Hamley, W. B. Thomas, K. Whiston and M. Poliakoff, *Green Chem.*, 2005, **7**, 294–300.
5 J. Fraga-Dubreuil, E. García-Verdugo, P. A. Hamley, E. Pérez, I. Pearson, W. B. Thomas, D. Housley, W. Partenheimer and M. Poliakoff, *Adv. Synth. Catal.*, 2009, **351**, 1866–1876.
6 R. L. Holliday, B. Y. M. Jong and J. W. Kolis, *J. Supercrit. Fluids*, 1998, **12**, 255–260.
7 P. E. Savage, J. B. Dunn and J. Yu, *Combust. Sci. Technol.*, 2006, **178**, 443–365.
8 J. B. Dunn and P. E. Savage, *Environ. Sci. Technol.*, 2005, **39**, 5427–5436.
9 J. B. Dunn and P. E. Savage, *Ind. Eng. Chem. Res.*, 2002, **41**, 4460–4465.
10 J. B. Dunn, D. I. Urquhart and P. E. Savage, *Adv. Synth. Catal.*, 2002, **344**, 385–394.
11 Y.-L. Kim, S. J. Chung, J.-D. Kim, J. S. Lim, Y.-W. Lee and S.-C. Yi, *React. Kinet. Catal. Lett.*, 2002, **77**, 35–43.
12 Y.-L. Kim, J.-D. Kim, J. S. Lim, Y.-W. Lee and S.-C. Yi, *Ind. Eng. Chem. Res.*, 2002, **41**, 5576–5583.
13 M. Osada and P. E. Savage, *AIChE J.*, 2009, **55**, 710–716.
14 J. B. Dunn and P. E. Savage, *Green Chem.*, 2003, **5**, 649–655.
15 W. Partenheimer and M. Poliakoff in *Handbook of Green Chemistry – Green Catalysis: Homogeneous Catalysis*, ed. P. T. Anastas and R. H. Crabtree, Wiley-VCH, Weinhein, 2009, vol 1, ch. 12, pp. 375–397.
16 H. Weingärtner and E. U. Franck, *Angew. Chem., Int. Ed.*, 2005, **44**, 2672–2692.
17 A. Kruse and E. Dinjus, *J. Supercrit. Fluids*, 2007, **39**, 362–380.
18 J. Fraga-Dubreuil and M. Poliakoff, *Pure Appl. Chem.*, 2006, **78**, 1971–1982.
19 P. E. Savage, *Chem. Rev.*, 1999, **99**, 603–621.
20 D. Bröll, C. Kaul, A. Krämer, P. Krammer, T. Richter, M. Jung, H. Vogel and P. Zehner, *Angew. Chem., Int. Ed.*, 1999, **38**, 2998–3014.
21 M. D. Bermejo and M. J. Cocero, *AIChE J.*, 2006, **52**, 3933–3951.
22 E. Pérez, J. Fraga-Dubreuil, L. Dudd, E. Garcia-Verdugo, P. A. Hamley, M. L. Thomas, C. Yan, W. B. Thomas, D. Housley, W. Partenheimer and M. Poliakoff, Selective aerobic oxidation of *para*-xylene in sub- and supercritical water. Part 1. Comparison with *ortho*-xylene and role of the catalyst, *Green Chem.*, DOI: 10.1039/c1gc15137a.
23 W. Partenheimer, *Catal. Today*, 1995, **23**, 69–158.
24 W. Partenheimer, *J. Mol. Catal.*, 1991, **67**, 35–46.
25 A. Saffer and R. S. Barker, *Chem Eng. Prog.*, 1968, **64**, 20.
26 US Patent 4 786 753, 1988.
27 R. K. Gipe and W. Partenheimer, *Stud. Surf. Sci. Catal.*, 1997, **110**, 1117–1127.
28 W. Partenheimer in *Catalysis of Organic Reactions*, ed. F. E. Herkes, Marcel Dekker Inc., New York, NY, 1998.
29 H. D. Holtz, *J. Org. Chem.*, 1972, **37**, 2069–2074.
30 H. D. Holtz, *Chem Commun.*, 1971, **19**, 1166.
31 F. Recupero and C. Punta, *Chem. Rev.*, 2007, **107**, 3800–3842.
32 N. V. Sidwick, *The chemical elements and their compounds*, Oxford-Clarendon Press, 1950, vol 1.
33 US patent 5 112 992, 1954.
34 US patent, 2 673 217, 1957.
35 W. Partenheimer and R. K. Gipe in *Catalytic Selective Oxidation*, ed S. T. Oyama and J. W. Hightower, American Chemical Society, 1993, pp. 81–88.
36 US Patent 5 183 933, 1993.
37 V. N. Aleksandrov, *Kinet. Katal.*, 1978, **19**, 1057–1060.
38 J. B. Dunn, M. L. burns, S. E. Hunter and P. E. Savage, *J. Supercrit. Fluids*, 2003, **27**, 263–274.
39 W. Partenheimer, *J. Mol. Catal. A: Chem.*, 2003, **206**, 105–119.
40 W. Partenheimer, *J. Mol. Catal. A: Chem.*, 2003, **206**, 131–144.
41 E. J. Y. Scott, *J. Phys. Chem.*, 1970, **74**, 1174–1182.
42 Y. Chen, J. L. Fulton and W. Partenheimer, *J. Am. Chem. Soc.*, 2005, **127**, 14085–14093.
43 M. Pourbaix, *Atlas of Electrochemical Equilibria in Aqueous Solutions*, Pergamon Press, 1966.
44 B. Beverskog and I. Puigdomenech, *J. Electrochem. Soc.*, 1997, **144**, 3476–3486.
45 B. Beverskog and I. Puigdomenech, *Corros. Sci.*, 1996, **38**, 2121–2135.
46 B. Beverskog and I. Puigdomenech, *Corros. Sci.*, 1997, **39**, 969–980.
47 B. Beverskog and I. Puigdomenech, *Corros. Sci.*, 1997, **39**, 107–114.
48 J. L. Fulton, M. M. Hoffman, J. G. Darab and B. J. Palmer, *J. Phys. Chem. A*, 2000, **104**, 11651–11663.
49 Y. Kamiya, T. Nakajima and K. Sakoda, *Bull. Chem. Soc. Jpn.*, 1966, **39**, 2211–2215.
50 K. P. Jonhston and J. B. Chlistunoff, *J. Supercrit. Fluids*, 1998, **12**, 155–164.
51 W. Partenheimer, in *Catalytic Selective Oxidation*, ed. S. T. Oyama and J. W. Hightower, American Chemical Society, 1993, ch. 7.
52 R. D. Shannon, *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.*, 1976, **32**, 751–767.
53 T. Adschiri, Y. Hakuta, K. Sue and K. Arai, *J. Nanopart. Res.*, 2001, **3**, 227–235.
54 K. Byrappa, T. Adschiri and Progr, *Prog. Cryst. Growth Charact. Mater.*, 2007, **53**, 117–166.
55 E. Lester, P. Blood, J. Denyer, D. Giddings, B. Azzopardi and M. Poliakoff, *J. Supercrit. Fluids*, 2006, **37**, 209–214.