

Aerobic Oxidation of *para*-Xylene in Sub- and Supercritical Water. Part 2: The Discovery of Better Catalysts

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SUPPLEMENTARY DATA

Experimental section

The scheme of the oxidation rig is shown in Figure S1. All the experiments were conducted using tubular continuous flow reactors. The continuous oxidation was carried out in supercritical water (SCW) using aqueous solutions as catalysts. The conditions are those optimized and previously reported by us for the oxidation of *p*-xylene to terephthalic acid,ⁱ except the catalyst concentration that is ¼ of this value to make sure it is “unsaturated”. Concentration of *p*-xylene is relatively diluted (0.5% organic w/w). An aqueous solution of H₂O₂ of 2% vol. was used as the source of O₂. That solution is driven via a reciprocating pump, which allows for accurate control of the O₂:substrate ratio. The H₂O₂ solution was pumped into the system and decomposed in a coiled pre-heater under the required experimental conditions to generate a homogeneous mixture of O₂ and SCW. The residence time in the pre-heater was long enough to achieve total decomposition of H₂O₂. The volumetric flow rate through the rig was 12 mL/min. The water/H₂O₂ flowrate was 8 mL/min; the catalyst flowrate was 4 mL/min and the organic flowrate was 0.06 mL/min. Catalyst strength is typically 7.7 mM feed (2.6 mM in reactor). At the reactor outlet, the mixture was quenched with a solution of NaOH 1M to prevent precipitation of TA and to keep CO₂ in solution in the form of carbonate. Quench solution flowrate: 3.5 mL/min. All the chemicals were purchased from Aldrich Ltd and used without further purification.

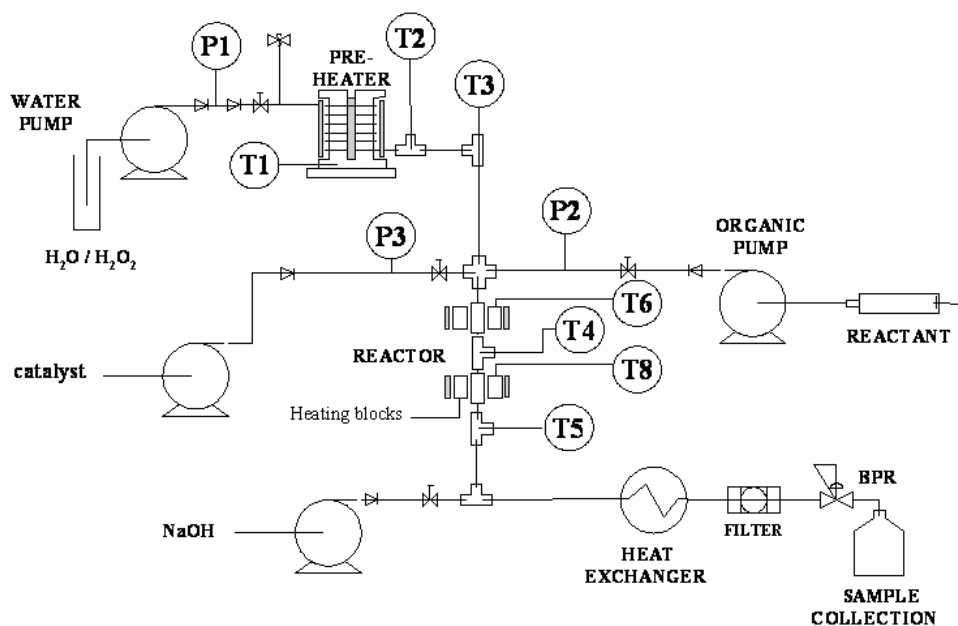


Figure S1. Configuration of the continuous aerobic oxidation reactor. P1-3 pressure transducers. T2-5: log temperatures. T1, T6 and T8: control temperatures.

The reactor was made of Hastelloy C276 pipe ¼ inch. external diameter and 0.46 cm inner diameter. The length of the reactor from the mixing to the quench point was 34 cm. At a total flowrate of 12 g/min and the density of pure waterⁱⁱ, a residence time of 5.8 seconds was calculated for 380 °C and 19.2 s for 330 °C.

Figure S2 shows a detail of the mixing point of the reactor. All the reactants and solvent are mixed at a ¼ inch mixing cross on the top. The catalyst and organic were delivered from the sides by 1/16 inch hastelloy alloy pipes of 0.57 mm inner diameter. Catalyst and organic pipes protrude into the body of the cross piece, $l_1 = 3\text{cm}$. If not stated, this is the typical configuration for the experiments. Some

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experiments in this paper were done using slightly different geometries that are described in the text. Experiments done with different reactor configuration may not be comparable.

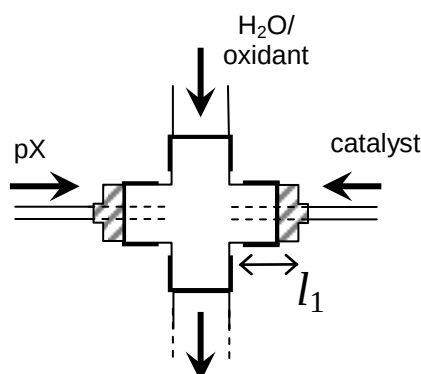


Figure S2. Detail of the mixing point.

CAUTION: This type of oxidation is potentially extremely hazardous, and must be approached with care and a thorough safety assessment must be made. The apparatus is regularly hydrostatically pressure tested. Before every run, water was pumped at 230 bar and room temperature at the desired flowrates. It was then heated. Once the operating temperature had been reached, the pumps for the reactants were started. Typically, an experiment was run for 40 minutes. The products were collected for sequential periods of 5 min and analysed.

Analysis of the products was done by HPLC. A Waters Xterra reverse phase C18 column, maintained at 37 °C, was used (flow rate 0.7 mL/min, run time 15 min; UV detection at 230 nm). Solvents acetonitrile (ACN) and $\text{CH}_3\text{CO}_2\text{Na}/\text{CH}_3\text{CO}_2\text{H}$ buffer were used. The method was as follows: isocratic method (16.7% ACN) for the first 4 minutes; 4-8 min, gradient method (16.7 to 40% ACN); back to isocratic method (16.7% ACN) for the last 7 minutes. The stock buffer solution was prepared by dissolving 15 g $\text{CH}_3\text{CO}_2\text{Na}$ anhydrous in 250 mL de-ionised water, before adding $\text{CH}_3\text{CO}_2\text{H}$ (50% v/v, 100 mL). The pH was adjusted to 3.9 with 5% $\text{CH}_3\text{CO}_2\text{H}$, before diluting to 500 mL. The dilute buffer was prepared by diluting 30 mL of the stock buffer solution to 500 mL with de-ionised water.

The analysis for phenols and benzene was not done because they are present only in very small amounts. Phenols are present in very small amounts because they are oxidized much more rapidly than pX. Benzene is present in very small amounts because it would require the consecutive decarboxylation of terephthalic acid to benzoic acid and then benzoic acid to benzene.

CO_3^{2-} concentration was measured by titration of the sample with HCl 0.2N. The difference between the first two titres was used to calculate the carbonate concentration. The first titre accounts for the excess OH^- and the second for the protonation of CO_3^{2-} to HCO_3^- . At the beginning of the project, the titrations were performed manually using a burette and a pH meter. Later, an autotitrator METROHM (785 DMP titrino) was used. A test confirmed that the difference between the two methods was within the experimental error.

Results

Table S1 shows the results for some configurations trying V, Ti, and W alone and with other sources of bromide. Very low TA yields are obtained in most of the cases. Ti and V are poor catalysts even when Br is added. In entries 1 to 3 CO_2 yield is not calculated because it may be coming from the ligand of Ti and hence, be meaningless. W itself is also poor catalyst, in combination with Cu, Co and Br, it does not enhance the catalyst performance.

Table S1. Experiments using V, Ti and W based catalysts.

entry	catalyst	[catalyst]/ 2.6 mM	Br:metals mol/mol	Yield, mol %			Selectivity					
				CO_2	TA	burn	TA	PTA	4-CBA	HMBA	pTOL	BA
1 ^{a,b}	Ti	1.0	-	-	4.0	-	24.2	27.2	20.9	2.9	22.0	2.9
2 ^{a,b}	Ti/H/Br	1.0/2.0	2.0	-	5	-	15.7	49.1	10.8	2.4	19.7	2.3
3 ^{a,b,c}	Ti/H/Br	1.0/2.0	2.0	-	5	-	13.0	43.0	10.7	1.8	30.0	1.4
3 ^{d,e}	V	1.0	-	5	3.9	1.28	31.8	16.9	41.3	3.6	2.3	4.1
4 ^{b,d}	V	1.0	-	8	3.7	2.16	22.7	27.0	21.9	1.9	24.6	1.9
5 ^{b,d}	V/Br	1.0/1.0	1.0	35	4.4	7.95	16.1	47.9	9.8	1.6	22.5	2.1
6 ^{b,d}	V/Br	1.0/2.0	2.0	21	4.9	4.29	16.6	53.7	6.8	1.9	18.9	2.0
7 ^e	W	1	-	7	4.2	1.67	49.3	13.8	4.6	19.3	12.7	0.0
8 ^f	Cu/W/Br	0.1/0.9/2	2.0	29	33.3	0.87	61.3	23.3	5.0	0.0	0.9	9.6
9 ^f	Cu/Co/ Br/W	0.1/0.9/ 3/0.2	2.5	24	61	0.39	93.3	0.0	0.0	0.0	0.4	6.3

^a Ti is introduced as Titanium(IV) bis(ammonium lactate) dihydroxide. ^b Premixer configuration used. ^c Temperature is 330 °C. ^d V is introduced as NH_4VO_3 and Br as NH_4Br . ^e W introduced as Na_2WO_4 . ^f Catalyst is a mixture of $\text{CuBr}_2 + \text{CoBr}_2 + \text{Na}_2\text{WO}_4 + \text{HBr}$

Table S2 shows the effect of adding HBr and NaBr to MnBr₂. Entry 3 show that an equimolecular amount of HBr lowered the activity of the catalyst. If the amount of HBr is four times higher, (entry 2) TA yield and selectivity is higher. However no synergic effect occurs because TA yield and selectivity of H/Br(8/8) itself are 19 and 68% respectively.ⁱⁱⁱ A modest improvement is observed when adding a mixture of HBr and NaBr (entry 4) even though Br concentration is high. That suggests NaBr is a poor bromide source.

Table S2. Effect of HBr in the catalytic activity of MnBr₂ catalyst

entry	catalyst	[catalyst]/ 2.6 mM	Br:metals mol/mol	Yield, mol %			Selectivity					
				CO ₂	TA	burn	TA	PTA	4-CBA	HMBA	pTOL	BA
1 ^a	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
2	Mn/H/Br ^b	1/8/10	10.0	25.2	46.9	0.54	96.2	0.3	0.1	0.0	0.5	3.0
3 ^a	Mn/H/Br ^b	1/1/3	3.0	14.2	22.7	0.63	39.8	45.2	8.2	3.0	0	3.7
4	Mn/H/Br ^c	1/3/8	8.0	25.5	36.7	0.69	58.8	30.4	5.5	1.9	0.0	3.5

^a Reference iii. ^b Addition of MnBr₂ + HBr. ^c Addition of MnBr₂ + HBr + NaBr (proportion 1:3:3)

A study has been done in order to evaluate HBr, NH₄Br and alkaline and alkaline earth bromide salts as sources of bromide with copper. The results are gathered in Table S3. Attempts to substitute Br by other halogens are shown in Table S4

Table S3. Effect of different sources of bromide added to CuBr₂

entry	catalyst	[catalyst]/ 2.6 mM	Br:metals mol/mol	Yield, mol %			Selectivity					
				CO ₂	TA	burn	TA	PTA	4-CBA	HMBA	pTOL	BA
1	Cu/Br	0.15/0.3	2.0	17.5	12.2	1.43	21.6	58.4	10.2	1.6	1.0	7.2
2	H/Br	2/2	-	29.7	8.0	3.71	30.8	52.2	7.1	2.0	0.6	7.2
3	Cu/H/Br	0.15/1.7/2	13.3	19.9	53.9	0.37	90.8	1.4	0.2	0.0	0.0	7.6
4	Cu/H/Br	0.15/2.7/3	20.0	20.1	55.9	0.36	94.5	0.0	0.0	0.0	0.0	5.5
5	Cu/Br (CuBr ₂ + NaBr)	0.15/2	13.3	17.7	32.6	0.54	49.6	33.7	5.8	1.5	0.0	9.3
6	Cu/Br (CuBr ₂ + KBr)	0.15/2	13.3	28.0	21.0	1.33	57.0	21.0	8.5	2.2	0.0	11.3
7	Cu/Br (CuBr ₂ + CaBr ₂)	0.15/2	13.3	25.5	45.4	0.56	81.0	4.4	1.2	0.0	0.7	12.7
8	NH ₄ /Br	1.7	-	35.2	13.4	2.63	38.2	43.9	4.7	3.5	0.0	9.8
9	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	0.0	7.9
10	BrO ₃ ⁻	2	-	16.6	5.4	3.07	31.0	33.1	25.0	4.9	3.6	2.3

CuBr₂ at low concentration gives low TA yields and selectivities (entry 1). Different Br-containing compounds are added to keep the Br concentration at 5.2 mM. HBr catalytic activity is low at concentrations of 5.2 mM, as seen in entry 2. However, when it is added to CuBr₂ (entry 3), the TA selectivity and yield are improved substantially. The TA selectivity is even better than when CuBr₂ is used alone, showing clearly that not much copper is needed, but a sufficient amount of bromine instead. Increasing the amount of HBr added results in a slightly better TA yield and selectivity as shown in entry 4. Non-redox salts such as NaBr, KBr and CaBr as a source of bromine gave worse results than for HBr. Alkaline salts are not a good source of bromide, however, NaBr and KBr differ even though they are very similar compounds. CaBr₂ however gives a fairly good TA selectivity and yield.

NH₄Br was also evaluated and to our surprise it behaves very differently from NaBr or KBr. If this salt is evaluated by itself and even though the concentration is slightly lower than in entry 2, the TA selectivity and yield are better (entry 8). Used as a source of bromide with CuBr₂ (entry 9), the results are comparable (even slightly better) to those obtained when using HBr. KBrO₃ has also been tried as a bromine species giving worse results than HBr and NH₄Br.

Table S4. Effect of substituting Br by other halogens on the catalytic activity of Cu-based catalysts.

entry	catalyst	[catalyst]/ 2.6 mM	Br:metals mol/mol	Yield, mol %			Selectivity					
				CO ₂	TA	burn	TA	PTA	4-CBA	HMBA	pTOL	BA
1	Cu/Br	1/2	2.0	25	55.6	0.45	86.4	5.9	1.2	0.0	0.0	6.5
2	Cu/Br/Cl	1/1/1	1.0	24.4	27.3	0.89	46.1	35.6	7.9	1.5	0.0	8.8
3	Cu/H/Br	0.15/1.7/2	13.3	19.9	53.9	0.37	90.8	1.4	0.2	0.0	0.0	7.6
4	Cu/H/Cl ^a	0.15/2/2	0	4.3	4.0	1.08	25.8	24.8	40.1	2.1	5.3	2.0
5	Cu/Co/Br	0.15/0.85/2	2.0	15.3	61.7	0.25	92.1	0.0	0.0	0.0	0.0	7.9
6	Cu/Co/I/Br	0.15/0.85/ 1.7/0.3	0.3	21	5.5	3.82	13.6	55.6	14.6	1.3	14.2	0.7
7	Cu/Co/I/Br	0.15/0.85/ 1.0/1.0	1.0	27	32.6	0.83	54.6	31.0	9.7	0.0	1.0	3.7

^a Addition of Cu(AcO)₂ + HCl

As shown in table S4, attempts to reduce or remove the bromide from the reaction result in a dramatic decrease of performance. Substituting half of the CuBr₂ by CuCl₂ reduces TA yield and selectivity by nearly half its value (entry 2). The yield of the intermediates, and especially PTA increases as does the CO₂ generated. Removing the bromide completely results in very low TA yield and selectivity.

Addition of iodide results in an even larger decrease in TA yield and selectivity. If we compare entry 6 to entry 1, table S3, I appears to be a catalytic poison.

Some runs using *N*-hydroxyphthalimide (NHPI) as reaction initiator were also done but with very low TA yields. Results are gathered in Table S5.

Table S5. Catalytic activity of combinations using NHPI as initiator

entry	catalyst	[catalyst]/ 2.6 mM	Yield, mol %		Selectivity					
			CO ₂	TA	TA	PTA	4-CBA	HMBA	pTOL	BA
1	NHPI	<1	18	5	42.0	28.0	10.0	9.8	3.7	6.5
2 ^a	Cu/NHPI	0.1/0.2	7	5	54.4	20.9	8.5	10.4	3.2	2.7
3 ^a	Cu/Co/NHPI	0.1/0.9/2.0	24	3	33.2	35.2	6.1	3.7	5.6	16.3
4 ^b	Cu/Co/Br/NHPI	0.1/0.9/0.2/1.8	25	3	26.2	50.5	5.3	3.6	5.2	9.2

^a Cu and Co are added as Co(AcO)₂; ^b Addition of Cu(AcO)₂ + CuBr₂

In table S6 formulations with Cu and two or more metals are shown. All combinations including Mn, Co, and Ni were tried as well as a combination of all the metals. Substituting part of the Co by Ni has a slight beneficial effect in TA yield, although burn is higher. Due to the complexity of these combinations, it is difficult to obtain definitive conclusions. However entry 5 is interesting because even though the Cu concentration is less than half that in the rest of the configurations, it has a high performance. CO₂ yield however has not been reduced when compared to the Cu/Co/Br configuration (entry 1). ScCl₃ strongly deactivates the catalyst. Entries 7 to 9 should be compared to entry 6. Notice that on substituting part of the Co by Zn, the burn is decreased. Compare entries 10 and 6.

Table S6. Catalytic activity using CuBr₂ plus combinations of several metallic bromides.

entry	catalyst	[catalyst]/ 2.6 mM	Yield, mol %			Selectivity					
			CO ₂	TA	burn	TA	PTA	4-CBA	HMBA	pTOL	BA
1	Cu/Co/Br	0.15/0.85/2	15.3	61.7	0.25	92.1	0.0	0.0	0.0	0.0	7.9
2	Cu/Co/Ni/Br	0.14/0.57/0.28/2	22.3	65.2	0.34	92.3	0.3	0.6	0.0	0.0	6.9
3	Cu/Co/Mn/Br	0.15/0.12/0.72/2	20.0	55.6	0.36	91.1	0.3	0.0	0.0	0.0	8.6
4	Cu/Ni/Mn/Br	0.14/0.28/0.57/2	25.9	63.7	0.41	90.5	1.2	0.7	0.0	0.0	7.6
5	Cu/Co/Ni/ Mn/Br	0.06/0.26/ 0.13/0.53/2	21.9	63.0	0.35	91.9	0.2	0.7	0.0	0.0	7.2
6	Cu/Co/Br	0.1/0.9/2	21.5	64.9	0.33	91.6	0.1	0.7	0.0	0.0	7.8
7 ^a	Cu/Sc/NH ₄ /Br	0.15/0.85/1.7/2.0	23.0	39.5	0.58	68.3	15.2	5.6	0.0	0.0	10.9
8 ^b	Cu/Co/Fe/Br	0.1/0.9/0.2/2	23.4	61.0	0.38	92.9	0.0	0.0	0.0	0.0	7.1
9	Cu/Co/La/Br	0.1/0.9/0.1/2.3	18.0	64.4	0.28	87.7	7.4	1.6	0.0	0.0	7.4
10	Cu/Co/Zn/Br	0.1/0.45/0.45/2.0	17.9	63.8	0.28	89.3	0.0	0.2	0.7	0.0	9.7

Br:metals is 2 in every entry; ^aSc introduced as ScCl₃, ^bCo(PhCOO)₂ was used to keep a Br concentration of 2.

In Table S7 some combinations where Fe plays the role of Cu are shown. Comparing entry 3 to entry 2 and entry 9 in Table 1 shows that a synergistic effect between FeBr₃ and CoBr₂ seems to occur. Nevertheless, this combination does not give better results than FeBr₃ alone or than the combination Cu/Co/Br. Comparison between entries 3 and 4 shows a high sensitivity of the results to Br concentration. Iron in the form of ferrocene (bis(cyclopentadienyl)iron) has been also tried alone (entries 5 and 6) and with HBr (entry 7). TA yields are low: however, in the latter case selectivities are unusually high. Finally, entry 8 shows that NH₄Br does not have the same positive effect on Fe that it does on Cu.

Table S7. Catalytic activity of some Fe-based combinations

entry	catalyst	[catalyst]/ 2.6 mM	Br:metals mol/mol	Yield, mol %			Selectivity					
				CO ₂	TA	burn	TA	PTA	4-CBA	HMBA	pTOL	BA
1	Fe/Br	1.0/3.0	3.0	20	39	0.51	75.3	9.9	3.2	0.0	4.8	6.8
2	Fe/Br	0.2/0.6	3.0	24	22	1.09	45.3	29.4	9.7	4.5	2.8	8.3
3	Fe/Co/Br	0.1/0.9/2.1	2.1	22	36	0.61	66.9	15.0	6.5	4.3	1.1	6.2
4	Fe/Co/Br ^a	0.1/0.9/2.0	2.0	29	22	1.32	41.1	31.8	9.4	4.3	8.4	5.1
5	Fe ^b	0.2	-	9	3.8	2.37	29.8	17.1	23.2	2.4	25.6	1.9
6	Fe ^b	1.0	-	17	3.6	4.72	29.8	16.8	23.8	8.0	20.3	1.3
7	Fe/Br ^b	1.0/3.0	3.0	-	18.4	-	90.2	1.0	0.0	0.0	0.0	8.8
8	Fe/NH ₄ /Br	0.15/1.70/2.15	2.15	29	10	2.90	26.3	37.3	5.1	2.9	23.6	5.0

^a Addition of Cu(AcO)₂ + HBr. ^bFe is introduced as ferrocene (bis(cyclopentadienyl)iron)

Table S8 gives other non-Cu containing combinations of metals. None of them is as good as Cu-based formulations. These results again point out the high activity of Cu as catalyst. Notice in entry 1 how a combination of Fe and Co gives the best results in this table with a

TA selectivity of 67 % and a yield of 36 %, Followed by two Mn-containing configurations (entries 5 and 6). Notice that the activity of the metallic bromides shown in Table 1 is Fe>Mn>others.

Table S8. Catalytic activity using different combinations of non-Cu metallic bromides.

entry	catalyst	[catalyst]/2.6 mM	Br:metals mol/mol	Yield, mol %			Selectivity					
				CO ₂	TA	burn	TA	PTA	4-CBA	HMBA	pTOL	BA
1	Fe/Co/Br	0.1/0.9/2.1	2.1	21.6	35.8	0.60	66.9	15.0	6.5	4.3	1.1	6.2
2	Fe/Zn/Br	0.15/0.85/2.15	2.15	26.9	6.9	3.90	21.7	41.2	9.8	3.7	20.3	3.3
3	Co/Fe/Zn/Br	0.45/0.1/0.45/2.1	2.1	21.7	10.7	2.03	26.1	36.8	12.0	3.0	19.0	3.1
4	Ni/Co/Br	0.33/0.66/2	2.0	18.6	7.8	2.38	20.6	56.2	15.0	3.3	2.6	2.3
5	Ni/Mn/Br	0.33/0.66/2	2.0	24.5	33.2	0.74	51.9	34.8	6.7	0.0	0.0	6.6
6	Ni/Co/ Mn/Br	0.14/0.28/0.57/2	2.0	17.4	21.1	0.82	35.5	51.7	8.6	0.2	0.8	3.3
7	Co/Ni/ Ce/Br	0.22/0.11/0.44/2	2.0	23.6	8.0	2.95	23.4	59.5	10.8	0.3	3.2	2.7
8	Co/Ce/Br	0.25/0.5/2	2.0	26.5	10.5	2.52	27.1	56.4	9.7	0.3	2.5	4.0

^a Addition of Cu(AcO)₂ + HBr

La and Eu behave similarly to Co. They are poor catalysts alone but in combination with Cu, their performance is significantly improved. Notice that, as Zn, La only has one oxidation state. Details of the experiments using catalysts with La and Eu are gathered in Table S9.

Table S9. Catalytic activity for combinations containing La or Eu.

entry	catalyst	[catalyst]/2.6 mM	T / °C	Yield, mol %			Selectivity					
				CO ₂	TA	burn	TA	PTA	4-CBA	HMBA	pTOL	BA
1	La/Br	0.66/2	380	13.3	2.5	5.32	12.3	61.7	11.2	2.5	9.6	2.7
2	Eu/Br	1/3	380	22.7	4.8	4.73	13.4	48.9	14.9	2.7	17.0	3.1
3	Eu/Br	1/3	330	8.9	0.8	11.13	3.6	28.6	8.8	0.9	58.1	0.0
4	Cu/Co/Br	0.1/0.9/2.0	380	18.8	65.9	0.29	92.5	0.0	0.0	0.0	0.0	7.5
5	Cu/Co/Br	0.1/0.9/2.0	330	15.9	66.9	0.24	83.6	6.9	5.8	0.0	0.0	3.7
6	Cu/La/Br	0.1/0.6/2.0	380	22.7	52.0	0.44	90.0	2.3	0.0	0.0	0.0	7.7
7	Cu/La/Br	0.1/0.9/2.9	380	23.4	57.5	0.41	90.8	0.0	0.0	0.0	0.0	9.2
8	Cu/Eu/Br	0.1/0.9/2.9	380	21.6	56.2	0.38	90.4	0.0	0.0	0.0	0.0	9.6
9	Cu/La/Br	0.1/0.9/2.9	330	23.6	57.0	0.41	92.0	2.3	1.8	0.0	0.0	3.9
10	Cu/Eu/Br	0.1/0.9/2.9	330	18.8	63.9	0.29	89.9	3.3	2.2	0.0	0.0	4.6

Strong synergic effects are very often observed in pX oxidation in acetic acid. In this paper, when combining CuBr₂ and other metallic or non-metallic bromides, an enhancement of the activity is observed, showing synergic effects as well. We define ‘synergy factor’ as $SF_{X'/X''} = Y_{X'/X''} / (Y_{X'} + Y_{X''})$ where $Y_{X'}$ and $Y_{X''}$ are the TA yield for two different catalysts and $Y_{X'/X''}$ is the TA yield when the catalysts are combined at the same concentrations. Table S10 shows some synergic factors calculated for the combination of CuBr₂ and other species.

Table S10. Synergy factors of various catalysts with Cu/Br. C2 is the catalyst added to C1 = Cu/Br(0.15/0.3).

Entry	C2	[C2] / mM	SF _{C1/C2}
1	Co/Br	0.85/1.7	3.3
2	Mn/Br	0.85/1.7	1.1
3	Ni/Br	0.85/1.7	3.5
4	Zn/Br	0.85/1.7	3.3
6	Co/Ni/Br	0.57/0.28/1.7	3.3
7	H/Br	1.7/1.7	2.7
8	NH ₄ Br	1.7	2.1

TA yields for C1 are taken from Table S3, entry 1. TA yields for C2 in entries 1 to 4 and 7 to 9 are taken from table 1 and S3, neglecting the small difference in concentrations. For entry 6 TA yield for C2 is taken from table S8.

As can be seen on Table S10, when small amounts of copper(II) bromide are added to Co, Mn, Ni and Zn bromide catalysts the rate of reaction is faster than the individual Cu/Br and Co/Br, Mn/Br, Ni/Br and Zn/Br catalysts. There is also a synergy between Cu/Br and H/Br and NH₄/Br catalysts see entries 7 and 8. Interestingly, in supercritical water, Cu now has the same characteristics as Co in acetic acid i.e. small amounts added to various other elements or mixtures of elements make it a much more active catalyst system.

We evaluated some alcohols and aldehydes as cooxidants with Cu-containing catalysts. The results are shown in Table S11. 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 did react. Similarly the use of other co-oxidants such as phenol, isopropanol, methanol or toluene does not improve TA yield or selectivity.

Table S11. Co-oxidation of p-xylene with selected substrates at 380 °C.

entry	Catalyst ([catalyst]/ 2.57,mM)	Co-oxidant, other	Yield, mol %		Selectivity					
			CO ₂ *	TA	TA	PTA	4-CBA	HMBA	pTOL	BA
	none	none	14.3	0.6	8.4	73.3	4.7	1.8	9.9	1.9
	Cu (0.1)	benzaldehyde;19mM	7.9	0.5	13.9	47.3	14.0	0.0	22.2	2.7
	Cu/Br	none	17.6	12.2	21.6	58.4	10.2	1.6	1.0	7.2
	(0.1/0.2)	benzaldehyde;19mM	17.7	8.5	14.6	46.7	9.5	0.4	1.5	27.4
	Cu/Co/Br	none	21.9	66.4	92.0	0.0	0.5	0.0	0.0	7.6
	(0.1/0.9/2.0)	phenol; 31mM	39	55.8	87.1	0.3	1.0	0.7	0	10.7
		isopropanol; 54mM	23.4	49.2	70.6	16.8	4.1	0.0	0.0	8.5
		methanol; 19mM	24.9	50.8	68.8	19.0	5.5	0.0	0.0	6.7
		methanol; 16mM	25.7	59.8	88.5	1.3	1.3	1.2	0.1	7.7
		benzaldehyde; 19mM	25.1	59.5	74.5	0.0	1.0	0.0	0.0	24.5

* Calculated without taking into account the correction of eqn 2. Notice that part of this CO₂ can come from total oxidation of the co-oxidant

Table S12 show the effect of concentration for the Cu/Co/Br catalyst. Even when the Cu concentration is as low as 0.18 mM, The catalyst is able to achieve a TA yield of 60%. However, four times more catalyst only increases the TA yield to 65.1%, indicating that it is close to saturation.

Table S12 effect of concentration for the Cu/Co/Br catalyst at 380 °C

entry	[catalyst]/2.6 mM	Yield, mol %			Selectivity					
		CO ₂	TA	burn	TA	PTA	4-CBA	HMBA	pTOL	BA
1	0.07/0.42/1	15.9	60.0	0.27	88.5	1.0	0.3	0.0	0.0	10.2
2	0.15/0.85/2	15.3	61.7	0.25	92.1	0.0	0.0	0.0	0.0	7.9
3	0.3/1.7/4	15.4	65.1	0.24	95.5	0.0	0.0	0.0	0.0	4.5

In Table S13, the raw data of the optimization of Cu:Co ratio are shown. They are the original data for Figure 4. Notice that burn is minimum for the entry with maximum TA yield. The combination Cu/Mn/Br, shown in entries 11 and 12 appears to follow a similar trend.

Table S13 Variation of the M'/M'' ratio with a Cu/Co/Br and Cu/Mn/Br catalysts during oxidation of p-xylene at 380 °C.

entry	catalyst	[catalyst]/2.6 mM	Yield, mol %			Selectivity					
			CO ₂	TA	burn	TA	PTA	4-CBA	HMB A	pTOL	BA
1	Co/Br	1/2	16.5	8.8	1.88	21.8	56.2	13.9	3.0	2.5	2.6
2	Cu/Co/Br	0.01/0.99/2	23.9	55.1	0.43	87.6	3.0	1.0	0.0	0.0	8.4
3	Cu/Co/Br	0.03/0.97/2	23.9	56.8	0.42	88.3	2.5	1.1	0.0	0.0	8.1
4	Cu/Co/Br	0.05/0.95/2	21.9	64.2	0.34	91.5	0.3	0.8	0.0	0.0	7.4
5	Cu/Co/Br	0.1/0.9/2	21.5	64.9	0.33	91.6	0.1	0.7	0.0	0.0	7.8
6	Cu/Co/Br	0.15/0.85/2	25.2	61.7	0.41	92.1	0.0	0.0	0.0	0.0	7.9
7	Cu/Co/Br	0.33/0.66/2	25.7	51.6	0.50	89.7	1.9	0.0	0.0	0.0	8.4
8	Cu/Co/Br	0.5/0.5/2	26.3	50.4	0.52	88.4	1.7	0.4	0.0	0.2	9.3
9	Cu/Co/Br	0.66/0.33/2	17.9	50.7	0.35	85.3	5.8	0.3	0.0	0.2	8.4
10	Cu/Br	1/2	27.6	52.6	0.52	84.6	7.2	1.3	0.0	0.0	6.9
11	Cu/Mn/Br	0.15/0.85/2	23.5	55.2	0.43	91.3	0.6	0.0	0.0	0.0	8.1
12	Cu/Mn/Br	0.85/0.15/2	26.1	50.7	0.51	83.3	8.2	1.3	0.1	0.0	7.1

Br/metals=2.0 mol/mol. [metals]=2.6 mM.

In Table S14, the effect of temperature is shown. Entries 1 to 4 show the original data for Figure 5. At 330 °C, TA yield is maximum while the amount of the intermediates is kept low. The by-products yield (CO₂ and BA) increase with temperature so burn is also minimum at 330 °C. The rest of the entries show a comparison between some selected catalysts at 330 and 380 °C. In general, yields for

Cu-containing catalysts are always higher at 330°C with correspondingly lower yields of CO₂ and BA. However, if NH₄Br is added to increase Br:metals ratio, the opposite effect is observed. Further confirmation can be found in Table S15. Inspection of that table reveals that this tendency is inverted at a certain Cu:NH₄ ratio. There are some exceptions to this rule: if Br concentration is higher than normal (entries 9, 10. See also Table 3 and S17) and for the formulation Cu/Co/Ni/NH₄/Br (entries 13 and 14). As expected, less active catalysts usually show better activity at the highest temperature. CO₂ and BA yields are always lower at 330 than at 380°C.

Table S14 Effect of reaction temperature for some selected catalysts.

en- try	catalyst	[catalyst]/2.6 mM	Br: Metals	T / °C	Yield, mol %			Selectivity					
					CO ₂	TA	burn	TA	PTA	4- CBA	HMBA	pTO L	BA
1	Cu/Co/Br	0.1/0.9/2.0	2.0	310	16	42.0	0.38	51.2	30.7	15.7	0.0	0.3	2.2
2				330	19	68.0	0.28	92.9	2.3	0.0	0.0	0.0	4.8
3				350	21	65.0	0.32	93.3	0.0	0.0	0.0	0.2	6.5
4				375	27	49.0	0.55	84.3	0.0	1.4	0	2	12.3
5	Cu/NH ₄ /Br	0.15/1.85/2.0	6.7	380	23.5	55.9	0.42	90.8	0.4	0.0	0.0	0.0	8.8
6				330	21.0	43.7	0.48	64.3	19.4	12.2	0.0	0.0	4.2
7	Cu/Co/NH ₄ /Br	0.15/0.43/0.85/2.0	3.4	380	17.9	66.8	0.27	93.1	0.0	0.0	0.0	0.0	6.9
8				330	17.0	64.9	0.26	85.2	6.0	5.1	0.0	0.0	3.7
9		0.15/0.43/1.85/3.0	5.2	380	23.3	60.1	0.39	91.6	0.0	0.0	0.0	0.0	8.4
10				330	17.8	70.5	0.25	91.6	1.7	2.5	0.0	0.0	4.2
11	Eu/Br	1/3	3.0	380	22.7	4.8	4.73	13.4	48.9	14.9	2.7	17.0	3.1
12				330	8.9	0.8	11.1	3.6	28.6	8.8	0.9	58.1	0.0
13	Cu/Co/Ni/NH ₄ /Br	0.1/0.3/0.15/0.9/2	3.6	380	22	61.2	0.36	91.3	0.0	0.0	0.0	0.0	8.7
14				330	19	62.8	0.30	80.5	8.6	6.8	0.0	0.0	4.2
15 ^a	Fe/Zn/Br	0.15/0.58/2.15	2.9	380	26	7	3.70	21.7	41.2	9.8	3.7	20.3	3.3
16 ^a				330	17	5	3.39	14.1	34.1	8.1	2.1	40.7	1.0
17 ^a	Co/Fe/Zn/Br	0.1/0.45/0.45/2.1	2.1	380	22	11	1.99	26.1	36.8	12.0	3.0	19.0	3.1
18 ^a				330	8	3	2.67	13.3	31.6	8.8	2.4	43.9	0.0

^a Reactor configuration: premixer

In table S15, the effect of varying CoBr₂ and NH₄Br ratio at 380 and 330 °C in the Cu/Co/NH₄/Br catalyst is shown. These are the original data presented in Figure 6.

Table S15. Effect of varying CoBr₂ and NH₄Br in the Cu/Co/NH₄/Br catalyst

entry	[catalyst]/2.6 mM	T / °C	Yield, mol %			Selectivity					
			TA	CO ₂	burn	TA	PTA	4-CBA	HMBA	pTOL	BA
1	0.15/0/1.7/2.0	380	55.9	23.5	0.42	90.8	0.4	0.0	0.0	0.0	8.8
2	0.15/0.21/1.28/2.0	380	63.9	18.8	0.29	92.6	0.0	0.0	0.0	0.0	7.4
3	0.15/0.43/0.85/2.0	380	66.8	17.9	0.27	93.1	0.0	0.0	0.0	0.0	6.9
4	0.15/0.64/0.43/2.0	380	65.0	16.7	0.26	92.9	0.0	0.0	0.0	0.0	7.1
5	0.15/0.85/0/2.0	380	62.8	17.5	0.28	93.3	0.0	0.0	0.0	0.0	6.7
6	0.15/0/1.7/2.0	330	43.7	21.0	0.48	64.3	19.4	12.2	0.0	0.0	4.2
7	0.15/0.21/1.28/2.0	330	62.3	19.0	0.30	81.0	8.6	6.7	0.0	0.0	3.7
8	0.15/0.43/0.85/2.0	330	64.9	17.0	0.26	85.2	6.0	5.1	0.0	0.0	3.7
9	0.15/0.64/0.43/2.0	330	64.4	15.9	0.25	89.0	4.0	2.8	0.0	0.0	4.2
10	0.15/0.85/0/2.0	330	68.5	15.9	0.23	90.1	2.8	3.2	0.0	0.0	4.0

Table S16 show further experiments varying Cu:Co ratio in Cu/Co/NH₄/Br catalyst. The best TA yields are in entries 1 and 5. They correspond to Cu concentration of 2.6 mM×0.15. Lower Cu concentrations lead to lower TA yield and selectivity. Table S17 shows some entries of table 3 expanded.

Table S16 Effect of varying Cu:Co ratio in the Cu/Co/NH₄/Br catalyst

entry	catalyst	[catalyst]/2.6 mM	Br:metals mol/mol	Yield, mol %			Selectivity					
				CO ₂	TA	burn	TA	PTA	4-CBA	HMBA	pTOL	BA
1	Cu/NH ₄ /Br	0.15/1.70/2.00	13.3	24.8	54.3	0.46	89.7	0.5	0.0	0.0	0.0	9.8
2	Cu/Co/NH ₄ /Br	0.02/0.13/1.7/2.0	13.3	23.9	30.9	0.77	65.9	21.5	2.3	0.0	0.0	10.3
3	Cu/Co/NH ₄ /Br	0.075/0.075/1.7/2.0	13.3	21.9	50.6	0.43	78.6	8.4	3.3	0.0	0.0	9.7

4	Cu/Co/NH ₄ /Br	0.12/0.03/1.7/2.0	13.3	23.8	51.8	0.46	77.7	9.6	2.5	0.0	0.3	9.9
5	Cu/Co/NH ₄ /Br	0.15/0.15/1.4/2.0	6.67	20.5	57.9	0.35	88.6	1.5	0.0	0.0	0.0	9.9

Reactor configuration: both pX and catalyst pipes did not protrude in the mixing cross.

Table S17. Extension of table 3

entry	catalyst	[catalyst]/2.6 mM	T / °C	Yield, mol %			Selectivity					
				TA	CO ₂	burn	TA	PTA	4-CBA	HMBA	pTOL	BA
1	Cu/Co/NH ₄ /Br	1.0/2.0	380	36.1	18.1	0.50	51.3	34.9	6.3	1.4	0.0	6.0
2		1/1/3	380	22.7	14.2	0.30	39.8	45.2	8.2	3.0	0	3.7
3		1/8/10	380	46.9	25.2	0.54	96.2	0.3	0.1	0.0	0.5	3.0
4		0.15/0.43/0.85/2.0	380	66.8	17.9	0.27	93.1	0.0	0.0	0.0	0.0	6.9
5		0.15/0.43/1.85/3.0	380	60.1	23.3	0.39	91.6	0.0	0.0	0.0	0.0	8.4
6		0.15/0.43/2.85/4.0	380	63.0	23.6	0.37	92.4	0.0	0.0	0.0	0.0	7.6
7		0.15/0.43/0.85/2.0	330	64.9	17.0	0.26	85.2	6.0	5.1	0.0	0.0	3.7
8		0.15/0.43/1.85/3.0	330	70.5	17.8	0.25	91.6	1.7	2.5	0.0	0.0	4.2
9		0.15/0.43/2.85/4.0	330	70.2	17.4	0.25	92.6	1.2	2.2	0.0	0.0	4.0

Additional experiments

Catalysis using metallic copper

1.1 g of copper in shape of a 23 cm wire was coiled and placed into the reactor and a usual run was carried out passing HBr, CoBr₂ and CuBr₂ + CoBr₂ (Cu/Co/Br = 0.15/0.85/2.0) through catalysts pipe. Results for the three runs were very similar (TA selectivity: 88-89 %; TA yield: 55-57 %; CO₂ yield: 23-25%). The running time was 45-60 min because it took longer than usual to reach steady state. A longer experiment was run after that (3 hours) using HBr. At its end, the downstream was quenched with water and the amount of metals and bromine was analysed by X-ray fluorescence (XRF). The resulting solution had ~70 ppm of Cu and ~200 ppm of Br and also ~35 ppm of cobalt, probably recovered from a previous experiment. The copper turning had a black layer of CuO and it had lost 42% its weight. This shows evidence that the reaction was catalysed by Cu(II) formed in-situ by dissolution of copper metal by HBr.

Table S18. pX oxidation using metallic copper as heterogeneous catalyst.

entry	catalyst	[catalyst]/2.6 mM	Yield, mol %			Selectivity					
			CO ₂	TA	burn	TA	PTA	4-CBA	HMBA	pTOL	BA
1	Co/Br	1/2	22.0	55.5	0.40	88.0	0.8	0.8	0.0	0.0	10.4
2	Cu/Co/Br	0.15/0.85/2	23.9	55.3	0.43	88.5	0.7	0.9	0.0	0.0	9.9
3	H/Br	2/2	23.6	57.2	0.41	89.2	1.3	0.9	0.0	0.0	8.7

In entry 1, similar results to those when using HBr are obtained. There is also possibility of reaction catalyzed by Cu leaching. Evidence of heterogeneous catalysis could not be found.

Study of the sample colour

It can be seen that different colours in the samples can be obtained depending on the M/Br catalysts used (see Figure S3), from colourless to deep brown. The most common colour is pale yellow. HPLC Analysis of a series of pX SCWO samples was performed to determine if the concentration of minor components can be correlated with the sample colours (colour species). Results can be found in Table S19.

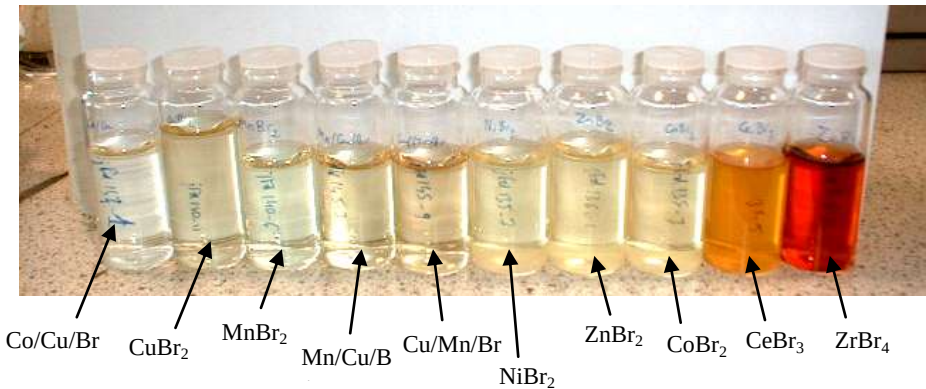


Figure S3. Photograph showing the colours typically observed in the liquid emerging from the back pressure regulator when different catalyst mixtures are used; see also Table S19.

Table S19. LC analysis of Cu-catalysed reactions

Catalyst make-up [cat]*0.007736M	0.1/0.45/2 Cu/Co/Br	0.0022/0.997/2 Cu/Co/Br	0.01/0.99/2 Cu/Co/Br	0.025/0.975/2 Cu/Co/Br	0.1/0.9/2 Cu/Co/Br	Cu/Ni/Co/Mn	0.05/0.95/2 Cu/Co/Br
Sample colour Colour intensities (by eye) 1 = colourless, 7 = Very dark yellow.	Intensity 3 – Very pale yellow	Intensity 6 – Dark yellow	Intensity 7 – Very dark yellow	Intensity 5 – Mid yellow	1 – colourless	2 – faint colour	4 – Pale yellow
4HMBA	nd	101	10	12	<2.5	<2.5	4
TA	3633	725	2947	3120	3827	3428	3395
4CBA	3	266	17	20	<2.5	4	8
Isopropanol	4	<2.5	8	8	6	6	7
2-BrTA	14	8	6	9	18	17	9
Orthophthalic acid	9	15	3	3	<2.5	<2.5	<2.5
BA	190	41	197	192	243	199	204
1,2,3-benzene tricarboxylic acid	<2.5	<2.5	<2.5	<2.5	<2.5	<2.5	<2.5
trimellitic acid	6	<2.5	9	9	5	6	7
biphenyltricarboxylic acid	5	<2.5	5	5	8	7	6
PTA	<2.5	1131	97	75	<2.5	<2.5	<2.5
4,4'-diphenic acid	<2.5	<2.5	<2.5	<2.5	<2.5	<2.5	<2.5
2,6-dicarboxybenzophenone	<2.5	<2.5	<2.5	<2.5	<2.5	<2.5	<2.5
Fluorenone	<2.5	<2.5	<2.5	<2.5	<2.5	<2.5	<2.5
2,6 Anthraquinone	3	<2.5	<2.5	<2.5	<2.5	<2.5	<2.5
2,7 Anthraquinone	nd	nd	nd	nd	<2.5	nd	nd
Fluorene	nd	nd	nd	nd	nd	nd	nd
Anthracene	nd	nd	nd	nd	nd	nd	nd

All concentrations in ppm. nd = not detected.

There is no obvious correlation between sample colour intensity and the concentration of the colour species. Almost no colour species have been detected by LC in most of the samples. However, the intensity of the colour observed by eye seems to correlate with the concentration of Cu/Co used or the nature of the M/Br salt. Dynamic Light Scattering (DLS) was performed on a series of coloured samples, from intensively coloured to colourless.

There is a possibility that the different colour is given by nanoparticles present in suspension. For that reason, the particle size distribution of the collected solutions was measured. Nanoparticles were detected in all the samples in Table S19 except in Cu/Co/Br (0.1/0.9/2.0). The size distribution, Z-Average and Mean intensity were not calculated because the concentration was too low to give a reasonable measurement (the nanoparticles are too far from each other and the light can not scatter properly. A bad correlation is obtained). Two additional samples highly coloured were analysed and results are presented in Table S20.

Table S20. Results obtained by DLS.

Catalyst make-up	Ce/Co/Br 0.25/0.5/2	Ni/Ce/Co/Br 0.1/0.2/0.4/2
Sample colour Colour intensities (by eye) 1=colourless, 7= very dark yellow.	8 – Orange	10 – Orange brown
Size distribution (nm)	32.7–220	91.3-459
Z-Average (nm)	77.4	178.5
Mean intensity %	13.5	16.3

According to these results, metal oxide nanoparticles are present in most of the samples. For the pale yellow ones, there are some particles but only a very small amount. The best sample (colourless sample) does not give any signal. As the solution becomes more intensely coloured, the size distribution of the particles becomes greater. This suggests that more particles could go through the filters and give more coloured samples. In the hydrothermal synthesis of nanoparticles, lower M/Br concentrations lead to smaller particles and in lower yields. Also, metal salts such as Zr, Ce, Co give easily nanoparticles in SCW in presence of oxygen, and moreover in presence

of NaOH. It is also noteworthy that in basic conditions nanoparticulate solution can appear “homogeneous” and can particularly be stable in basic conditions for quite long time without agglomerating and settling down. Those which give highly coloured samples are obtained with M/Br that are more prone to decomposition in SCW.

In conclusion, colour in the samples does not appear to be due to coloured organic compounds. The variation of the colours is probably due to the ability of the metal oxide “nanoparticles” to form from M/Br catalyst decomposition in the reactor and it is dependent on particle size (Table S20)

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