

Catalytic wet oxidation of the sodium salts of citric, lactic, malic and tartaric acids in highly alkaline, high ionic strength solution

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The catalytic wet oxidation (WO) of four low molecular weight sodium salts of hydroxy carboxylic acids that can be found in alumina industry process water has been investigated using a representative synthetic solution. The most active catalyst (CuO) catalysed the WO of the compounds studied predominantly via a homogenous complexation based reaction mechanism.

KEY WORDS: catalytic wet oxidation; alkaline; Bayer process; hydroxy carboxylic acids

1. Introduction

The removal of organic pollutants from industrial process waters and wastewaters is important as it can enable recycling and hence conservation of water, while removal of organic pollutants from industrial wastewaters that are discharged into the environment is also important as it can reduce the environmental impacts of these waters.

There are a number of processes available for removing organic pollutants from industrial process waters and wastewaters. Of the many processes available one process that has received considerable interest recently is catalytic wet oxidation (CWO). The CWO process removes organic pollutants via complete oxidation to carbon dioxide and water using air or oxygen in the presence of a catalyst. The main advantages of this process over a number of other water treatment processes are that it is very clean (no harmful chemicals are required and harmless products are produced) and it can be used to treat complex and toxic waters containing a wide range of organic compounds. The main drawback of the CWO process however is that high temperatures and/or long residence times are sometimes required to achieve complete oxidation of some organic compounds, such as acetic and propionic acids, that are formed from partial oxidation of high molecular weight compounds. This drawback can however be potentially overcome through the use of the right catalyst.

Although there have been a number of studies conducted on CWO [1–14] there is still a lack of information on catalytic mechanisms that occur during CWO of various organic compounds, particularly catalytic mechanisms in alkaline solution. In this study the catalytic wet oxidation of the sodium salts of four hydroxy carboxylic acids (citric, lactic, malic and tartaric) has been investigated in an alkaline solution simulating that encountered in the alumina refining

industry. Removal of organic pollutants from alumina refining process water (Bayer liquor) is of great interest as organic pollutants significantly hinder the productivity of the alumina refining process. Alumina producers worldwide suffer productivity losses well in excess of US\$100M per year due to organic contaminants. The sodium salts of hydroxy carboxylic acids such as sodium lactate and tartrate in particular have been shown to have a detrimental effect on the quantity and/or quality of alumina [15–17] produced. Removal of organic pollutants will also reduce the environmental impacts of this process water when it is discharged.

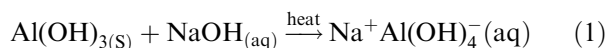
2. Experimental

The highly alkaline solution simulating that encountered in alumina refining is hereafter referred to as synthetic Bayer liquor. The method for preparing 2.4 L batches of 4.4 M NaOH synthetic Bayer liquor was as follows: NaOH (422.40 g) was dissolved in ~1 L milli-Q water in a 2 L plastic beaker. Once dissolution of the NaOH was complete, Al(OH)₃ (366.95 g), was added slowly whilst heating (~100°C) and stirring. In a separate beaker, Na₂CO₃ (101.76 g), was dissolved in ~500 mL of hot milli-Q water and then added to the sodium aluminate solution (heating and stirring continuously). NaCl (48.00 g), Na₂SO₄ (60.00 g), Na₃PO₄ (0.88 g) and silicic acid (2.56 g) were then dissolved as much as possible in ~500 mL hot milli-Q water in a separate beaker before being added to the sodium aluminate solution containing Na₂CO₃. The resulting synthetic liquor was then allowed to heat and stir continuously for ~1 h to ensure complete dissolution of all components. The synthetic Bayer liquor was then filtered (vacuum) while hot (~80 °C) through a Whatman No. 1 filter paper. Any solids remaining (inorganic salts) on the filter paper after filtration were dissolved using hot milli-Q water. The filtered synthetic Bayer liquor was then made up to 2.4 L with hot milli-Q water and separated immediately into four equal portions.

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The composition (table 1) of synthetic Bayer liquors was confirmed using a variety of analytical methods. Although the amount of sodium hydroxide used to prepare synthetic Bayer liquors was the amount required to give a concentration of 4.4 M the actual “free” hydroxide ion concentration in the synthetic Bayer liquors used was significantly lower. This is due to the reaction between sodium hydroxide and aluminium hydroxide (reaction 1) to produce the sodium aluminate ion.



The following organic compounds were used without further purification; citric acid, $\text{HO}_2\text{CCOH}(\text{CH}_2\text{CO}_2\text{H})_2$ (AR, Sigma); lactic acid, $\text{CH}_3\text{COHCO}_2\text{H}$ (BDH Chemicals); D-L-malic acid, $\text{HO}_2\text{CCHOHCH}_2\text{CO}_2\text{H}$ (99.0%, BDH Chemicals); (+/-) tartaric acid, $\text{HO}_2\text{C}(\text{CHOH})_2\text{CO}_2\text{H}$ (99.5%, May and Baker), succinic acid, $\text{HO}_2\text{C}(\text{CH}_2)_2\text{CO}_2\text{H}$ (99.0 + %, BDH Chemicals).

The transition metal oxides used in CWO experiments were as follows: copper(II) oxide, CuO, (99.0 + %, Aldrich); iron(III) oxide, Fe_2O_3 (95%, BDH Chemicals); cobalt(II/III) oxide, Co_3O_4 (pro analysi, Merck); manganese(IV) oxide, MnO_2 (LR, Ajax); and nickel(III) oxide, Ni_2O_3 (extra pure, Merck).

All reactions were conducted in a 1.2 L inonel autoclave (Parr Instruments Co, IL, USA). The autoclave was equipped with a magnetically driven stirrer (consisting of two six blade impellers), and fittings for gas addition and sample removal. The autoclave set-up also included a Parr 4843 controller to allow temperature and stirrer speed to be maintained at predetermined values. Pressure readings were also obtained using the controller via a pressure transducer directly attached to the autoclave assembly.

All autoclave reactions were conducted as follows: 600 mL of synthetic Bayer liquor was added to the reaction vessel, followed by the organic compound(s) to be studied. All organic compounds used were added in their acid form though it can be readily assumed these were quickly converted to their sodium salt form in synthetic Bayer liquor based on the $\text{p}K_a$ values of the organics studied and the pH of synthetic Bayer liquor ($\text{pH} \geq 14$). The reaction vessel was then sealed and evacuated to -65 kPa to remove oxygen in the head-space area, to minimise the possibility of oxygen induced

Table 1
Composition of synthetic Bayer liquor

Compound	Concentration (g/L)
Al	100.0 (expressed as Al_2O_3) (1.96 M)
NaOH	176.0 (4.40 M)
Na_2CO_3	42.4 (0.40 M)
Na_2SO_4	25.0 (0.18 M)
NaCl	20.0 (0.34 M)
Na_3PO_4	0.37 (0.002 M)
Si	0.82 (expressed as SiO_2) (0.014 M)

oxidation before reaching the set point temperature. The reaction solution was then stirred and heated until reaching the desired set point temperature. The time at reaching the set point temperature was designated time zero. Once the desired temperature was reached oxygen (Linde, minimum purity of 99.5%) was added at the partial pressure required (500 kPa). The oxygen partial pressure used was shown by preliminary tests to be sufficient for the organic concentrations used in this study [18]. The partial pressure of oxygen was maintained at the required amount throughout the course of the reaction. Samples were removed at pre-determined times throughout the course of the reaction.

Sodium hydroxide, sodium carbonate and aluminium concentrations were measured using an automated potentiometric titration system. Total organic carbon concentrations were measured using an OI-analytical total organic carbon (TOC) Analyser. Gas chromatography was used for identification and quantitation of the following organic compounds (as their methyl esters): acetic, formic, lactic, malic, fumaric, malonic and oxalic. The overall oxidation of the sodium salts of citric and tartaric acid was determined based on the products identified. Sodium chloride and sodium sulphate were analysed using capillary electrophoresis. Phosphorous and transition metal concentrations were analysed using ICP-AES.

3. Results and discussion

The ability of several transition metal oxides to catalyse the WO of the sodium salts of four hydroxy carboxylic acids (citric, lactic, malic and tartaric) present in the same high alkaline, high ionic strength solution was studied. The results of these tests (extent of overall oxidation and mineralization) and the reaction products identified are given in tables 2 and 3, respectively.

Of the transition metal oxides studied CuO was capable of both the highest extent of mineralization and overall oxidation (mineralization + partial oxidation).

Table 2
Catalyst screening results

Transition metal oxide	Overall oxidation (%) ^a	Mineralization (%)
None	33.6	14.9
CuO	61.0	21.0
Co_3O_4	34.8	13.2
Fe_2O_3	30.9	12.1
MnO_2	43.2	20.6
Ni_2O_3	32.5	11.9

Conditions: reaction time = 2 h; $T = 165^\circ\text{C}$; $P_{\text{O}_2} = 500$ kPa; 4.4 M NaOH synthetic Bayer liquor; MeO = 5g/L; [organics] = 1.87 g/L organic carbon each of sodium citrate, lactate, malate and tartrate.

^aOverall oxidation = Mineralization + partial oxidation (to salts of low molecular weight acids).

Table 3
Reaction products

Transition metal oxide	Reaction products (g organic carbon/L)				
	Sodium formate	Sodium acetate	Sodium oxalate	Sodium malonate	Sodium carbonate
None	0.14 (5.6)	0.73 (29.2)	0.50 (20.0)	0.01 (0.4)	1.12 (44.8)
CuO	0.19 (4.2)	0.59 (12.9)	2.17 (47.5)	0.02 (0.4)	1.60 (35.0)
Co ₃ O ₄	0.39 (14.9)	0.65 (24.8)	0.63 (24.0)	0.02 (0.8)	0.93 (35.5)
Fe ₂ O ₃	0.18 (8.0)	0.68 (30.4)	0.49 (21.9)	0.01 (0.4)	0.88 (39.3)
MnO ₂	0.52 (16.0)	0.77 (23.8)	0.31 (9.6)	0.08 (2.5)	1.56 (48.1)
Ni ₂ O ₃	0.43 (17.6)	0.80 (32.7)	0.42 (17.1)	0.00 (0.0)	0.80 (32.7)

Conditions: reaction time = 2 h; $T = 165^{\circ}\text{C}$; $P_{\text{O}_2} = 500 \text{ kPa}$; 4.4 M NaOH synthetic Bayer liquor; MeO = 5 g/L; [organics] = 1.87 g/L organic carbon each of sodium citrate, lactate, malate and tartrate.

% Proportion in parentheses.

The order of activity in terms of mineralization was $\text{CuO} > \text{MnO}_2 > \text{no catalyst} > \text{Co}_3\text{O}_4 > \text{Fe}_2\text{O}_3 \cong \text{Ni}_2\text{O}_3$, while the order of activity in terms of overall oxidation was $\text{CuO} > \text{MnO}_2 > \text{Co}_3\text{O}_4 > \text{no catalyst} > \text{Ni}_2\text{O}_3 > \text{Fe}_2\text{O}_3$. The higher activity of CuO was assumed to be most likely predominantly due to the higher solubility of this oxide in highly alkaline solution compared to the other oxides studied. This assumption was based on the results of previous studies using the same transition metal oxides in the same solution containing different organic compounds [18]. The negative activity observed for nickel(III) and iron(III) oxides, which are both extremely insoluble in highly alkaline solution, was most likely due to these compounds scavenging free radical intermediates and therefore hindering auto-oxidation, and therefore overall oxidation. This has been reported by Lee and Kim [19] to occur during CWO of maleic acid in the presence of alumina.

The same main reaction products (sodium formate, sodium acetate, sodium oxalate and sodium carbonate) were identified in CWO tests using each of the different transition metal oxides (table 2) and in the uncatalysed system. The proportions of the aforementioned products

were also very similar in each case except for the CuO catalysed system where a significantly higher proportion of sodium oxalate and lower proportion of sodium acetate were produced. This result indicates that a significantly different mechanism occurred in this system compared to the uncatalysed system, which is not typical in WO/CWO systems. In most cases similar reaction mechanisms usually occur for both uncatalysed and catalysed systems according to Debellefontaine et al. [20] as acetic acid/sodium acetate is usually formed as the major product in both systems.

As CuO was clearly the most active catalyst tested (in terms of overall oxidation) and the product distribution data obtained for this catalyst was significantly different than the uncatalysed system (and the other catalysed systems) it was decided to investigate the mechanism of this catalyst in detail. The possibility of CuO acting as a predominantly homogeneous catalyst (as mentioned earlier) was firstly investigated by determining the effect of CuO loading on the extent of overall oxidation. The results of these tests are presented in figures 1 and 2 respectively. From the data presented in figure 1 it can be seen that CuO loading has a significant effect on the extent of overall oxidation. The extent of overall oxidation increased significantly with increasing CuO loading up until the solubility limit, while a further increase in loading in excess of the solubility limit ($\sim 5\times$) had very little effect on the extent of overall oxidation. This result indicates that the activity of CuO is predominantly due to dissolved CuO (copper hydroxy species of the general form, $[\text{Cu(II)}_x(\text{OH})_y]^{2x-y}$). From figure 1 it can also be seen that a significant reduction in overall oxidation occurred when a CuO loading far in excess of the solubility limit ($\sim 15\times$) was used. This same trend has also been observed for CuO catalysed WO of actual Bayer liquor [21]. This was originally presumed to be due to quenching of free radicals by the large amount of insoluble CuO present. However inspection of the soluble copper data (figure 2) indicates that it was most likely due

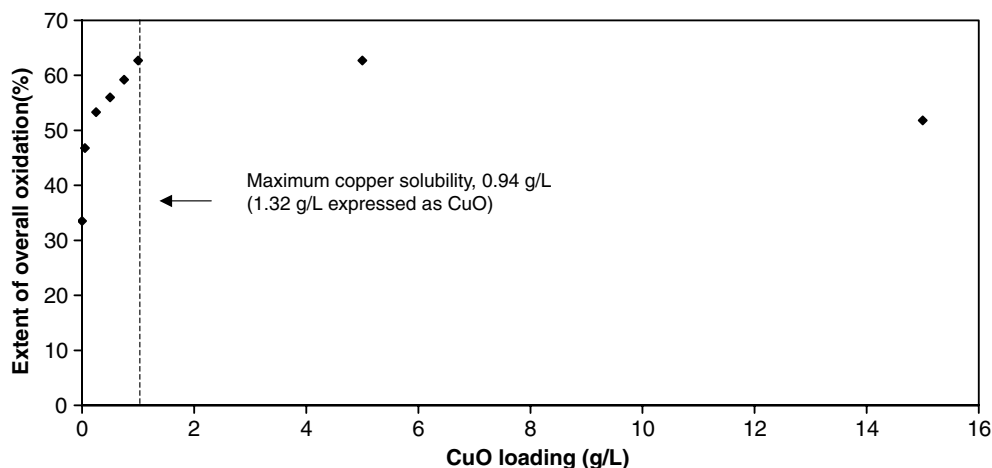


Figure 1. Effect of CuO loading on extent of overall oxidation.

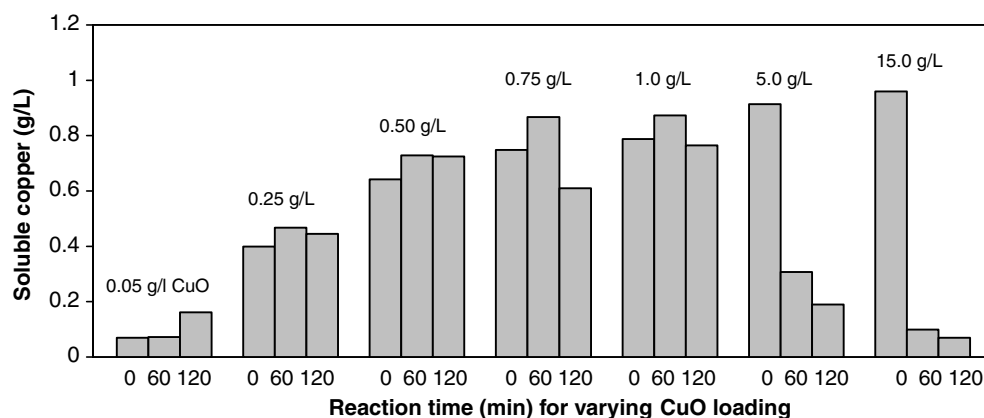


Figure 2. Effect of CuO loading on soluble copper levels.

to the fact that the level of soluble copper in this test dropped dramatically within the first hour. The reason for this dramatic drop in soluble copper at high CuO loading is not clear. A possible explanation could involve the excess undissolved CuO acting as a seed for the copper species produced after interaction with the starting organic compounds/intermediate species/oxygen.

The ability of CuO to catalyse the WO of the sodium salts of each of the hydroxy carboxylic acids individually was also tested to study the CuO catalytic reaction mechanism in more detail. The results of these tests (extent of overall oxidation, mineralization and reaction products) are given in tables 4 and 5, respectively.

A significant amount of sodium fumarate was detected at time zero in the sodium malate test. As this was produced from dehydration (and not oxidation) of sodium malate this was not taken into account when calculating the overall oxidation of sodium malate. A small amount of thermal oxidative degradation also occurred during the heat up period in the sodium citrate and tartrate tests, indicating that these compounds can

undergo oxidative degradation in the presence of copper and the absence of oxygen. As this amount was however relatively small (< 5% overall oxidation) and the main goal of this study was the investigation of CuO catalysed WO in the presence of oxygen this was not investigated further.

The order of catalytic activity in terms of mineralization for each of the individual compounds was sodium malate > lactate > tartrate > citrate, while the order in terms of overall oxidation was sodium tartrate > lactate > malate > citrate. As the chemical structures of the compounds tested were very similar (refer to table 4) it was decided to investigate the different extents of overall catalytic oxidation. One hypothesis that was considered for explaining the order of overall catalytic oxidation observed involved the degree of complexation of soluble copper with each of the respective compounds. The level of soluble copper at time zero in the sodium tartrate test was significantly higher than that in the other tests (which was expected due to the well-known formation of copper-tartrate

Table 4
CuO catalysed WO of individual compounds

Organic compound	Extent of overall oxidation (%)		Activity (CuO catalysed – uncatalysed)
	Uncatalysed	CuO catalysed	
Sodium citrate NaO ₂ CCOH(CH ₂ CO ₂ Na) ₂	50.3 (12.0)	59.8 (14.4)	9.5 (2.4)
Sodium lactate CH ₃ COHCO ₂ Na	8.6 (4.3)	43.0 (10.2)	34.4 (5.9)
Sodium malate NaO ₂ CCHOHCH ₂ CO ₂ Na	5.6 (2.2)	32.2 (12.8)	26.6 (10.6)
Sodium tartrate NaO ₂ C(CHOH) ₂ CO ₂ Na	51.0 (12.8)	90.1 (17.6)	39.1 (4.8)

Conditions: reaction time = 2 h; $T = 165\text{ }^{\circ}\text{C}$; $P_{\text{O}_2} = 500\text{ kPa}$; 4.4 M NaOH synthetic Bayer liquor; CuO = 5 g/L; [organic] = 1.87 g/L organic carbon. Extent of mineralization in parentheses.

Table 5
Reaction products for CuO catalysed WO of individual compounds

Organic	Reaction products (g organic carbon/L)			
	Sodium oxalate	Sodium carbonate	Sodium acetate	Sodium formate
Sodium citrate	0.35 (0.22)	0.27 (0.23)	0.42 (0.47)	0.03 (0.04)
Sodium lactate	0.37 (0.04)	0.19 (0.09)	0.10 (0.05)	0.06 (0.00)
Sodium malate	0.23 (0.03)	0.24 (0.04)	0.10 (0.03)	0.02 (0.00)
Sodium tartrate	1.08 (0.37)	0.33 (0.23)	0.02 (0.23)	0.05 (0.08)

Conditions: reaction time = 2 h; $T = 165\text{ }^{\circ}\text{C}$; $P_{\text{O}_2} = 500\text{ kPa}$; 4.4 M NaOH synthetic Bayer liquor; CuO = 5 g/L; [organic] = 1.87 g/L organic carbon. Uncatalysed results in parentheses.

complexes in alkaline solution), while the extent of overall catalytic oxidation of this compound was also highest. The levels of soluble copper in the tests with the salts of the other three hydroxy carboxylic acids, which were slightly higher than that observed in organic free synthetic Bayer liquor, were very similar and hence the degree of copper complexation of these compounds could not be easily compared under the reaction conditions used. To investigate the extent of copper complexation with each of these compounds more closely, tests were conducted using higher initial organic concentrations. The soluble copper data from these tests are presented in figure 3. From figure 3 it can be seen that the level of soluble copper in each test is significantly different at the beginning of the test indicating the different extent at which each of these compounds complex with copper under the reaction conditions used.

The order of the overall oxidation of the compounds studied correlated well with the order of the amount of soluble copper present at the beginning of each test (figure 4), indicating that CuO catalysed WO of these compounds could involve a complexation based catalytic reaction mechanism. This type of reaction mechanism was previously reported to possibly occur

during copper catalysed WO of actual Bayer liquor based on a visual observation [22]. Complexation based catalytic reaction mechanisms are rarely reported as CWO reaction mechanisms. The majority of mechanisms reported, as homogeneous CWO reaction mechanisms, are usually free radical based such as the well-known reaction mechanism involving catalytic decomposition of alkyl hydroperoxide intermediates [23]. Hence it was decided to investigate the possibility of a free radical based reaction mechanism occurring in conjunction with a complexation based reaction mechanism during CuO catalysed WO of the sodium salts of citric, lactic, malic and tartaric acids.

The occurrence of co-oxidation (oxidation of an organic compound by free radical intermediates produced from another compound undergoing oxidation in the same solution) was used to investigate the possibility of free radical reactions occurring in CuO catalysed WO of the sodium salts of citric, lactic, malic and tartaric acids. This method has been used previously under similar reaction conditions to study the WO and CWO of low molecular weight mono and dicarboxylic acids [24–25]. Sodium succinate was used as a co-oxidisable organic compound as it does not undergo appreciable (>2%) overall oxidation under the condi-

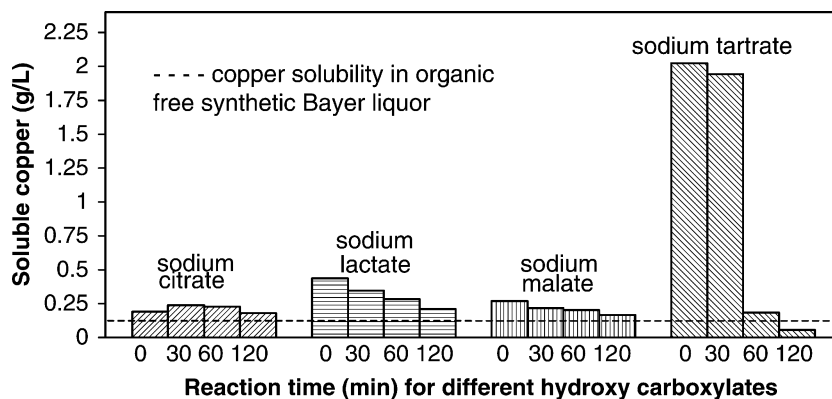


Figure 3. Soluble copper during CuO catalysed WO of individual compounds.

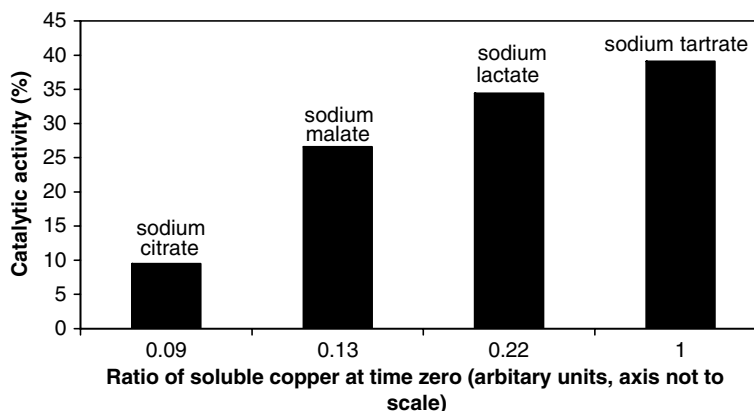


Figure 4. Correlation between catalytic activity and extent of complexation with copper for individual compounds.

tions used in this study and is not formed as a product from the CWO of the compounds studied. Sodium succinate was also selected because it can be co-oxidised by organic free radical intermediates under the same conditions used in this study [24–25].

The effect of sodium citrate, lactate, malate and tartrate undergoing CuO catalysed WO in the same solution as sodium succinate is given in Table 6. Each of the compounds was capable of co-oxidising sodium succinate, therefore free-radical intermediates are formed during CuO catalysed WO of the sodium salts of citric, lactic, malic and tartaric acids in highly alkaline solution. The actual extent of co-oxidation that was achieved by the aforementioned compounds (3.6–13.2%) was however quite low when compared to that achieved by sodium malonate (co-oxidation of ~45%) [25] using similar reaction conditions. This suggests that these compounds either do not produce a large number of free radical intermediates capable of co-oxidising sodium succinate or a relatively low number of free radicals in general are produced during CuO catalysed WO of these compounds and therefore the reaction mechanism involves predominantly ionic reactions.

A *proposed* general mechanism for CuO catalysed WO of the sodium salts of citric, lactic, malic and tartaric acids in highly alkaline solution are given in Reaction Schemes A and B. It is proposed that CuO catalysed WO of these compounds occurred predominantly via a complexation reaction mechanism based on the results obtained in this study (Reaction Scheme A). The first step in this proposed catalytic reaction mechanism involves dissolution of CuO. The second step involves complexation between dissolved CuO and the organic compounds studied. An attempt was made to investigate the different types of copper complexes formed with sodium citrate, lactate, malate and tartrate in the highly alkaline solution used in this study using FTIR-ATR (Fourier transform infrared-attenuated total reflectance) spectroscopy, as there was no literature available on copper complexes of these compounds under solution conditions similar to those used in this study. This attempt was however unsuccessful due to copper hydroxide precipitating on the ATR crystal

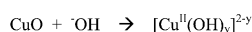
Table 6
Co-oxidation of sodium succinate by hydroxy carboxylates

Compound	Overall oxidation (co-oxidation) of sodium succinate (%)	
	Uncatalysed	CuO catalysed
Sodium citrate	9.1	13.2
Sodium lactate	<2	3.6
Sodium malate	<2	6.7
Sodium tartrate	<2	4.0

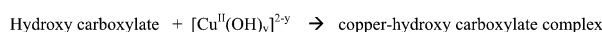
Conditions: reaction time = 2 h; $T = 165\text{ }^{\circ}\text{C}$; $P_{\text{O}_2} = 500\text{ kPa}$; 4.4 M NaOH synthetic Bayer liquor; CuO = 5 g/L; [succinate] = 1.87 g/L organic carbon; hydroxy carboxylate:succinate molar ratio = 5:1.

(which caused significant damage to the surface of the crystal). Hence, as information on the exact types of copper organic complexes that form could not be obtained these copper complexes have been depicted in a general form in the proposed mechanism. The next step in the proposed catalytic reaction mechanism, following formation of copper–organic complexes, involves direct thermal oxidative degradation of the copper–organic complexes (Reaction Scheme A, 3a) and/or reaction between oxygen (or an active species of oxygen) with the copper–organic complexes (Reaction Scheme A, 3b).

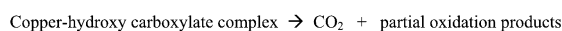
1. Dissolution of CuO



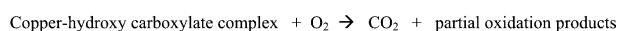
2. Complex formation



3a. Thermal degradation of copper complex



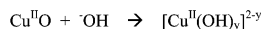
3b. Oxygen induced oxidation of copper complex



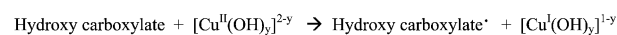
Reaction Scheme A. Complexation based mechanism (predominant mechanism).

A free radical based reaction mechanism is also proposed to occur during CuO catalysed WO of sodium citrate, lactate, malate and tartrate (Reaction Scheme B). This mechanism however is proposed to be the minor reaction mechanism. Some possible reactions that could lead to the formation of free radical intermediates are given in Reaction Scheme B. Free radical intermediates could also form via reactions 3a and 3b in the complexation based reaction mechanism (Reaction Scheme A).

1. Dissolution of CuO

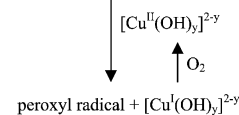
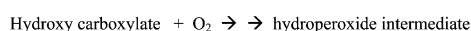


2a. Generation of free radical intermediates via direct pathway



O_2

2b. Generation of free radical intermediates via indirect pathway



Reaction Scheme B. Free radical based mechanism (minor mechanism).

Uncatalysed WO of sodium citrate, lactate, malate and tartrate is also proposed to occur simultaneously during copper catalysed WO. Based on the product distribution data obtained for the uncatalysed and copper catalysed tests for each of the compounds studied (table 5) it is proposed that very little uncatalysed WO occurred for sodium tartrate in the presence of copper, as very little sodium acetate formed in the CuO catalysed test compared to the uncatalysed test. This is also supported by the high extent of complexation between copper and tartrate under the reaction conditions used.

Although soluble copper (from CuO) is an active catalyst for removing the sodium salts of citric, lactic, malic and tartaric acids in highly alkaline solution via low temperature CWO, the removal and recovery of this catalyst, its cost and potential environmental effects all need to be considered when evaluating its potential use. A process for removing soluble copper from Bayer liquor has been reported in the literature [22]. This process involves co-crystallization of copper ions with either boehmite (hydrothermally in an autoclave) or with bayerite (under atmospheric conditions). The copper containing aluminium hydroxide can then be re-dissolved in Bayer liquor at high temperature releasing the active copper. The potential environmental effects of copper would most likely be minimal at an alumina refinery as only a small percentage (<10%) of the total plant flow would be treated and hence any copper that is not removed would be diluted considerably. Also there is very little aqueous waste run-off from alumina refineries (due to the cyclic nature of the Bayer process) and the waste that is produced is sent to controlled residue areas, where potential leaching into groundwater for example is highly unlikely.

4. Conclusions

CuO catalyses the WO of the sodium salts of citric, lactic, malic and tartaric acids in highly alkaline solution. This occurs predominantly via a homogeneous reaction mechanism with the active species most likely soluble copper hydroxy species formed from partial dissolution of CuO. These copper hydroxy species catalyse the WO of the aforementioned compounds predominantly via a complexation based reaction mechanism. Free radical reactions also occur during CuO catalysed WO of these compounds.

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