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Platinum catalysed wet oxidation of phenol in a stirred slurry reactor

The role of oxygen and phenol loads on reaction pathways

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Abstract

The catalytic wet oxidation of phenol was studied in a slurry phase continuous stirred tank reactor (CSTR) using platinum on graphite support as a catalyst. The investigation was carried out in the temperature range 120–180 °C and at total pressure of 1.8 MPa, while the phenol feed concentration was varied between 5 and 70 mol/m^3, and oxygen partial pressures between 0.01 and 0.8 MPa. It was found that both the oxygen load and the stoichiometric oxygen excess determine the extent of oxygen coverage on the platinum surface, which influences the reaction pathways and selectivity to CO_2 and H_2O. A fully oxidised platinum surface resulted into catalyst deactivation (over-oxidation), which favoured the formation of *p*-benzoquinone and polymeric products. Whereas free platinum surface was vulnerable to poisoning by carbonaceous compounds, a fully reduced platinum surface favoured the formation of acetic and succinic acids which are difficult to oxidise. A reaction scheme for platinum catalysed phenol oxidation in liquid phase is proposed.

Keywords: Catalytic wet oxidation; Phenol oxidation; Platinum/graphite; Wastewater treatment; Reaction network

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1. Introduction

The application of noble metal catalysts for liquid phase oxidation provides a potential for treatment of wastewaters containing organic pollutants. In addition to their high activity, noble metal catalysts have the advantage over the supported oxides of transition metals like copper oxide, manganese oxides, etc., that no dissolution of the active component into the liquid, even in hot acidic environment, takes place [1,2]. Other possible catalyst deactivation mechanisms that are reported to occur in commercial catalytic reactors include: deactivation by reduction of the support surface (sintering), deactivation by deposition of carbonaceous material on the catalyst surface (coking or fouling), and deactivation by irreversible adsorption on active sites by poisoning molecules (poisoning) [1,3,4]. Platinum catalysts have been reported to be effective during catalytic liquid phase oxidation of alcohols [5], formic acid [6], and ammonia [7]. The main drawback for platinum metal catalysts is their rapid deactivation in the liquid phase. Deactivation mechanisms reported for platinum metal catalysts

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Nomenclature

CSTR	continuous stirred tank reactor
CWO	catalytic wet oxidation
GC	gas chromatography
HPLC	high performance liquid chromatography
O_2-First	reactor start-up with oxygen first followed by oxygen
O_2-Ph-Sim	simultaneous feed of oxygen and phenol at start of reaction
Ph	phenol
Ph-First	reactor start-up with phenol first followed by phenol
Pt	platinum
SCWO	supercritical water oxidation
S.E.	stoichiometric oxygen excess (%)

include over-oxidation and elution of the catalyst (leaching) as described by Mallat and Baiker [8]. The deactivation by over-oxidation has been explained as a result of an increase of the catalyst potential [5,9]. There is, however, limited information on the platinum activity during wet oxidation of phenolic wastewater and its influence on the reaction pathways and selectivity to end products.

Different reaction networks for liquid phase phenol oxidation have been reported in literature [2,10–12]. The reaction pathways were derived through the identification of reaction intermediates and end products. The formation of a variety of partial oxidation and polymerisation products during wet oxidation has in most cases involved oxidation, decarboxylation, dehydration, and rearrangement of the molecules or combination of these steps.

In both catalysed and non-catalysed phenol oxidation, the ultimate partial oxidation compounds reported are low molecular mass mono- and dibasic acids such as glyoxylic, oxalic, propionic, acetic, and formic acid. Devlin and Harris [12] proposed a reaction pathway for non-catalysed phenol oxidation in aqueous solution by molecular oxygen at 413–498 K and oxygen pressures up to 20.7 MPa, in which unsaturated acids, viz. maleic acid and acrylic acid, were the main intermediates. The intermediate ring compounds, catechol, hydroquinone, and benzoquinones were not observed under conditions of excess oxygen. Dimers such as 2-phenoxy-phenol, 4-phenoxy-phenol, 2,2-biphenol, dibenzofuran, 2-dibenzofuranol, and dibenzo-1,4-dioxin were identified during supercritical water oxidation (SCWO) of phenol [10].

Phenol reaction networks in SCWO have been recently reviewed [10], in which the formation of dimers and other intermediates like single-ring compounds (e.g. hydroquinone), ring-opening products (e.g. maleic acid, glyoxylic acid, acetic acid, and other organic acids), and gases (e.g. CO, CO_2) are reported. Some of these partial oxidation products and intermediates, especially the dimers, are relatively more toxic than phenol.

The reaction intermediates reported on phenol oxidation catalysed by supported metal oxides, like copper, zinc, and manganese and other metal catalysts, are similar to those of non-catalysed phenol oxidation [13–17]. The formation of polymeric products in liquid phase has been reported in different studies [11,18]. Pintar and Levec [11] reported that polymers were formed by the reaction between glyoxale and phenol, and polymerisation of the C-2 aldehyde (glyoxale). The homogeneous polymerisation was related to catalyst deactivation. Polymerisation reactions might be suppressed by use of reactors with high solid-to-liquid ratio such as a trickle-bed reactor [17].

Hamoudi et al. [14,19] reported that the use of noble metal containing catalyst (such as platinum on alumina) generated lesser build-ups of deposits of polymeric products, which cause catalyst deactivation via physical blockage of active sites. They further suggested that platinum very likely catalyses the C–C bond rupture within organic molecules, while simultaneously it prevents polymerisation of the reactive intermediate radicals that are formed in the course of catalytic wet oxidation (CWO). The role of oxygen and phenol loads on the platinum catalyst is not well explained yet in literature. While the operation window for platinum catalysed phenol oxidation, where loss of catalyst activity is avoided, has recently been reported [20], the reaction pathways for phenol oxidation over platinum catalyst are also not clearly reported in literature.

The purpose of this work is to identify the most likely pathways for platinum catalysed phenol oxidation in the liquid phase. The influence of reactant concentrations on phenol conversion to CO_2 and H_2O, and the role and reactivity of phenol oxidation intermediates and end products have been investigated. Moreover, a reaction pathway is proposed.

2. Experimental

The liquid phase oxidation of phenol by oxygen was investigated using a commercially available catalyst, graphite supported platinum (5 wt.% Pt/G, Johnson Matthey JM287). The average graphite particle size was 7 μm and 95% of the particles were smaller than 15 μm, as confirmed by particle size measurement (Coulter LS 130 apparatus). Other catalyst specifications include: metal surface area of 2.58 $m^2 g^{-1}$, metal dispersion 20.6%, and BET surface area of 15 $m^2 g^{-1}$.

The experiments were conducted in a continuous stirred tank reactor (CSTR), a 500 ml autoclave (Autoclave Engineers, Zipperclave Hastelloy) that is equipped with a gas dispersion impeller. During reaction, the reactor was kept at constant temperature within ±0.3 K, in a wide range of temperatures, by a heating element around the reactor. The pressure in the reactor was kept constant by using a backpressure regulator. During the experiments the flow rates of the phenol feed solution and the gas entering the reactor were kept constant. Details of the experimental set-up and reactor start-up procedures are reported elsewhere [20]. The reactor operating conditions are given in Table 1.

In each experiment, the progress of the reaction and the catalytic activity were monitored by measurement of the reactor effluent composition as a function of time. The liquid samples were analysed by an on-line HPLC for residual phenol and intermediate reaction products. Phenol and other aromatic compounds were analysed in a 300 mm × 4.6 mm ID Lichroma SS column, packed with a Benson type of cation-exchange resin (Ca^{2+}) using a UV detector, while carboxylic acids were analysed in a 300 mm × 8 mm ID RSpak KC-811 column using a refractometer detector (Waters R401). The composition of the outlet gas was determined by using an O_2 sensor and on-line GC. Nitrogen gas was used as a standard while helium was used as carrier gas.

For all experimental data, the overall carbon balance and the oxygen balance were verified after every experiment; they were within 95–100%, which was considered analytically acceptable.

Table 1
Reactor operating conditions

	Standard	Range
Temperature (°C)	150	120–180
Total pressure (MPa)	1.8	1.5–2.0
Oxygen partial pressure (MPa)	0.5	0.01–0.8
Oxygen flow rate (ml/min)	40	0–80
Nitrogen flow rate (ml/min)	90	10–120
Phenol concentration (mol/m^3)	20	5–70
Liquid flow rate (ml/min)	10	5–20
Liquid reactor volume (ml)	350	350
Catalyst amount (kg_{cat}/ml^3)	6	1–30
pH	Uncontrolled	2–8
Stirrer speed (rpm)	1200	350–1800

3. Results and discussion

3.1. Influence of reactor temperature

The influence of reaction temperature on phenol oxidation and selectivity of intermediates was determined at temperatures between 120 and 180 °C at standard conditions as shown in Table 1. It was found that at temperatures above 150 °C, phenol conversion to CO_2 and H_2O of 99% and higher was attained, while at 135 and 120 °C, lower phenol conversions were obtained. Neither *p*-benzoquinone nor maleic acid were detected in the liquid samples obtained at 165 and 180 °C. At the lower temperatures, the residual phenol concentration increased gradually over time while a decline in the activity of the platinum catalyst was observed.

The liquid effluent obtained at 120 °C was characterised by a brownish colour and showed the formation of *p*-benzoquinone, maleic acid, and insoluble (polymeric) products. Unless otherwise mentioned, all other experiments reported were carried out at 150 °C.

3.2. Influence of reactant concentration

To determine the effect of the reactant concentrations on the reaction mechanism and pathway, the ratio of the molar flow rate of the reactants, expressed as percentage stoichiometric oxygen excess (S.E.) to phenol, was varied. The experiments were carried out at a constant phenol feed concentration of 0.02 mol/l

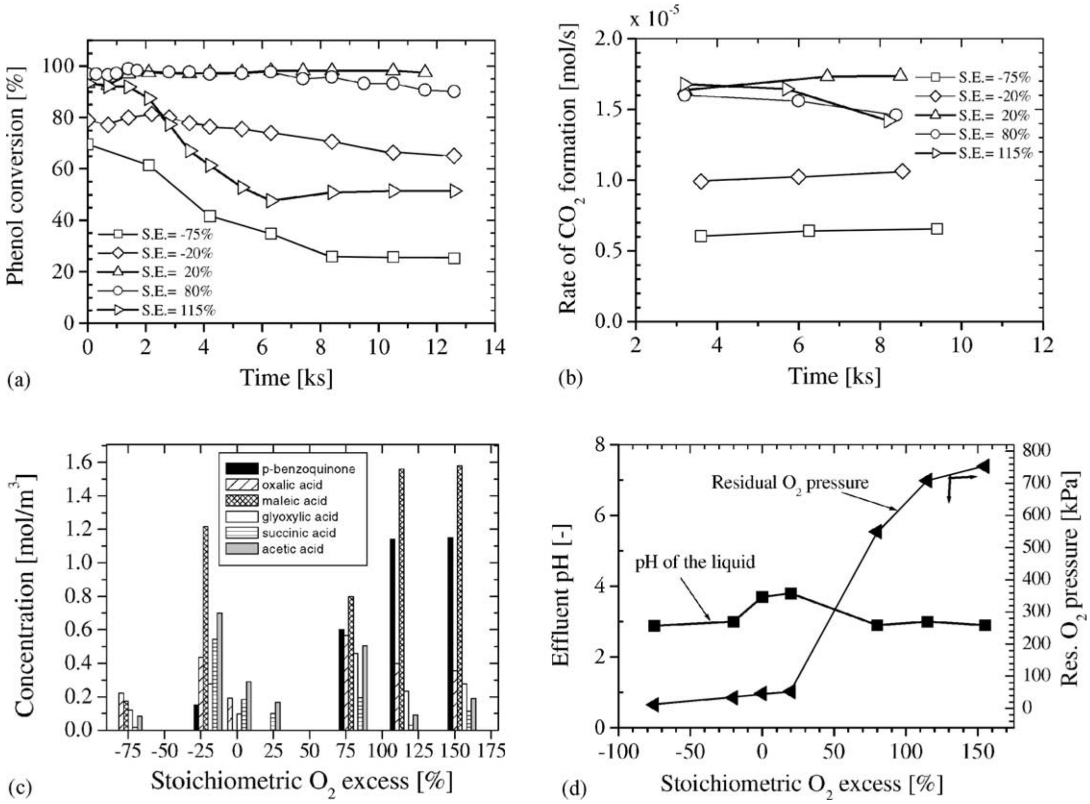


Fig. 1. Influence of oxygen load on phenol oxidation at standard conditions (Table 1) using the O_2-Ph-Sim start-up method: (a) phenol conversion; (b) CO_2 formation; (c) concentration of intermediates; (d) residual oxygen partial pressure and effluent pH.

while the oxygen partial pressures were varied between 10 and 800 kPa. A start-up method where phenol and oxygen are fed simultaneously to the reactor was used [20].

Fig. 1 shows the typical results on phenol conversion at different S.E. The oxygen load has two opposing effects on the reaction rate (Fig. 1(a) and (b)). At sub-stoichiometric amount of oxygen (S.E. $< 0\%$), increasing the oxygen partial pressure, which means the dissolved oxygen concentration, enhanced the oxidation rate of phenol. Above the stoichiometric oxygen amount, the reaction rate is enhanced up to a certain point at which the oxygen concentration started to inhibit the phenol oxidation rate. The inhibitory effect observed at S.E. above 80% can be explained by the loss of activity of the platinum catalyst as a result of over-oxidation. This negative effect of a high oxygen concentration on the activity of platinum catalyst was also observed during alcohol oxidation [5,8] and ammonia oxidation [7].

It can be seen in Fig. 1(c) and (d) that when insufficient oxygen is fed, the reaction is dominated by the formation of low molecular weight carboxylic acids, while within the residual oxygen pressure range of 20–40 kPa, neither *p*-benzoquinone nor maleic acid were detected in the colourless liquid effluent. The pH of 3.8 is within the range for water saturated with CO_2, indicating that mainly CO_2 was present in the liquid. At high residual oxygen partial pressure, which means high oxygen concentration at the catalyst surface, both *p*-benzoquinone and maleic acid were detected in high concentrations in the brownish coloured liquid effluent. These results suggest that the extent of oxygen coverage on the platinum surface influences the reaction network and selectivity to reaction products.

4. Reaction intermediates and pathways

The reaction intermediates and products identified during the oxidation of phenol are listed in Table 2. Reactor start-up methods, at which particular end products and intermediates are found, are also given in the table. These include intermediate ring compounds, and unsaturated and saturated carboxylic acids. Although these reaction products are similar to those reported in literature [11,12,15], their evolution and stability during the catalytic reaction depend on whether the reaction is carried out within or outside the operation window (viz. oxygen and phenol loads) [20].

To properly elucidate the phenol oxidation reaction network, the fate of these compounds, namely oxalic, acetic, glyoxylic, malonic, succinic, and maleic acid, were investigated at similar experimental conditions. In addition, muconic acid, catechol, hydroquinone, and benzoquinone solutions were oxidised at the same conditions.

4.1. Oxidation of oxalic acid and glyoxylic acid

The oxidation of oxalic acid solution using Pt/graphite gave complete conversion to CO_2 and H_2O. Formic acid was not observed in the liquid effluent. The pH of 4.6 and the residual oxygen pressure of 300 kPa remained constant during the oxidation period indicating a high potential of the platinum surface.

The oxidation pathway of oxalic acid on platinum surface requires a high oxidation potential to split the C–C bond of the saturated acid. This is an exceptional case when compared to other platinum catalysed reactions in which the oxidation mechanism involves dehydrogenation of the C–H bond as the first step [8]. These results are in accordance to Markusse et al. [5], who reported that oxalic acid was easily oxidised at the oxidised platinum surface while it was difficult at a reduced platinum surface.

When oxidation of 0.02 mol/l glyoxylic acid solution was undertaken, full conversion with 100% selectivity to CO_2 was attained. The pH of 4.3 and the residual oxygen partial pressure of 290 kPa remained constant. Neither formic acid nor oxalic acid was detected in the liquid effluent. However, this result does not exclude the possibility that oxalic acid and formic acid might be formed as intermediates especially at a reduced platinum surface. This is because at similar conditions formic acid was completely converted to CO_2 and H_2O.

In Fig. 2, a profile of phenol oxidation before and after replacing the feed solution with a solution containing 0.02 mol/l phenol, 0.01 mol/l oxalic acid, and 0.01 mol/l glyoxylic acid, is presented. A decline in phenol conversion from 92 to 86% before and after injection of the compounds was observed. In this case,

Table 2
Reaction intermediates and products during phenol oxidation [20][a]

Compound	Formula	High P_{O_2} (S.E. $>$ 80%)			Low P_{O_2} (0% $<$ S.E. $<$ 80%)		
		A	B	C	A	B	C
Phenol	C_6H_5OH						
p-Benzoquinone	$C_6H_4O_2$	++	++	++	+(0)	+(0)	–
Maleic acid	*Cis*-$HO_2C–CH{=}CH–CO_2H$	++	++	++	+(0)	+(0)	–
Fumaric acid	*Trans*-$HO_2C–CH{=}CH–CO_2H$	+	+	+	–	–	–
Succinic acid	$HO_2C–(CH_2)_2–CO_2H$	+	+	+	+	+	+
Malonic acid	$HO_2C–CH_2–CO_2H$	–	–	–	+	+	+
Acetic acid	$CH_3–CO_2H$	+	+	+	+	+	+
Glyoxylic acid	$CHOCO_2H$	++	++	+	+(0)	+(0)	–
Oxalic acid	$HO_2C–CO_2H$	++	++	+	+(0)	+(0)	–
Insoluble compounds	Not identified	++	++	+	–	–	–
Carbon dioxide	CO_2	++	++	++	+++	+++	+++

[a] S.E.: the stoichiometric oxygen excess to phenol. Start-up procedures—A (O_2-First): start with oxygen feed followed by phenol; B (Ph-First): start with phenol feed followed by oxygen; C (O_2-Ph-Sim): feeding of both oxygen and phenol at the start of the reaction. Selectivity: +++: highest; ++: high; +: low; (0): high only at the start of reaction; –: not identified.

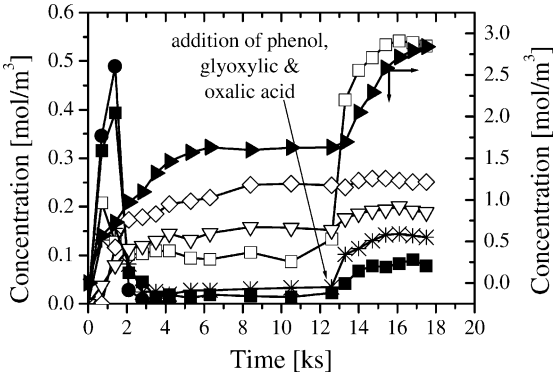


Fig. 2. In situ oxidation of solution containing 0.02 mol/l phenol, 0.01 mol/l oxalic acid, and 0.01 mol/l glyoxylic acid using O_2-First start-up method at standard conditions (Table 1): phenol (▶), *p*-benzoquinone (●), oxalic acid (□), maleic acid (■), glyoxylic acid (✳), succinic acid (▽), acetic acid (◇).

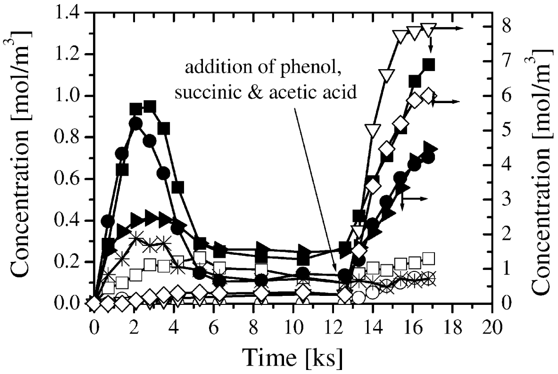


Fig. 3. In situ oxidation of solution containing 0.02 mol/l phenol, 0.01 mol/l acetic acid and 0.01 mol/l succinic acid using O_2-First start-up method at standard conditions (Table 1): phenol (▶), *p*-benzoquinone (●), oxalic acid (□), maleic acid (■), glyoxylic acid (✳), succinic acid (▽), acetic acid (◇).

changes before and after injection were observed in the residual partial pressure of oxygen, dropping from 50 to 30 kPa, while the pH also changed from 3.7 to 3.4. The decline in conversion was attributed to the limited amount of oxygen for competing oxidation reactions of phenol, glyoxylic, and oxalic acid. The additional formation of succinic acid, which could be due to transfer hydrogenation, and of oxalic acid due to its limited breakdown at a reduced platinum surface, supports this argument. It can further be noted that the absence of polymeric products suggests that glyoxylic acid is not a polymer precursor as suggested by others [11].

4.2. Oxidation of acetic acid and succinic acid

The oxidation of 0.014 mol/l acetic acid solution was carried out at standard conditions (Table 1). There were no intermediate products detected in the liquid and the pH remained at 3.4. The residual oxygen pressure was the same as the initial value of 350 kPa, which indicates that acetic acid is stable at these experimental conditions. These observations suggest that acetic acid is an end product during platinum catalysed phenol oxidation at 150 °C rather than an intermediate. The results are in agreement with those in literature whereby acetic acid is reported to be stable even above 200 °C [21,22].

The oxidation of 0.02 mol/l succinic acid solution showed that succinic acid did also not react at standard conditions. Both the pH (3.0) and the residual oxygen partial pressure remained constant. This suggests that succinic acid is also an end product rather than an intermediate product.

In Fig. 3 the profile of the co-oxidation of 0.01 mol/l acetic and 0.01 mol/l succinic acid in the presence of 0.02 mol/l phenol is shown. While very little acetic acid conversion could not be excluded, the results clearly indicated that succinic acid did not react. The decline of phenol conversion after injection of these acids could be attributed either to inhibition of its reaction due to competitive adsorption or by the drop in pH from 3.4 to 2.8 caused by the unconverted acids, which could influence the oxidation potential of the platinum surface, causing the residual partial pressure of oxygen to increase from 80 to 220 kPa. The evolution of benzoquinone and maleic acid seem to result from phenol oxidation on platinum at a higher potential. The results confirmed that both succinic and acetic acid are end products during phenol oxidation.

4.3. Oxidation of malonic acid

Fig. 4(a) shows the oxidation of malonic acid where conversion above 84% is achieved at 150 °C and it increases to above 90% conversion at 170 °C.

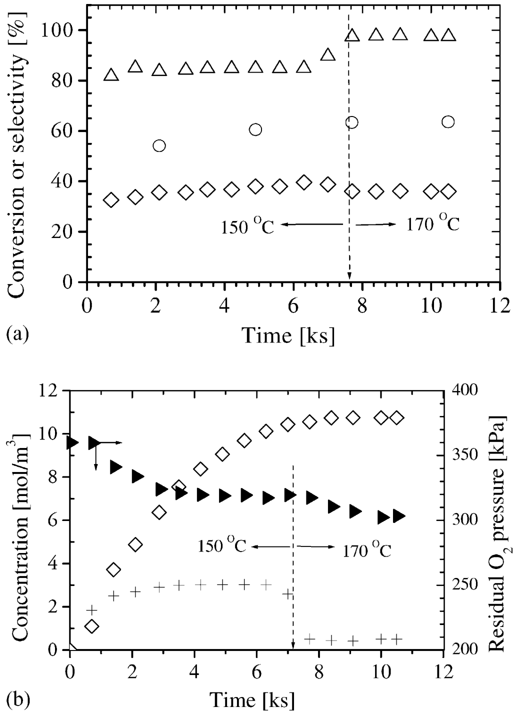


Fig. 4. Oxidation of 0.02 mol/l malonic acid using the O_2-Ph-Sim start-up method at standard conditions (Table 1): (a) malonic acid conversion (△), selectivity to CO_2 (○) and acetic acid (◇); (b) concentration of malonic acid (+), and acetic acid (◇) and residual oxygen partial pressure (▶).

The main end products were acetic acid and CO_2 as shown in Fig. 4(a) and (b) with their respective selectivities of 38 and 62%. Although malonic acid conversion increased at high temperature, the selectivity to acetic acid remained the same while the liquid effluent pH changed from 3.6 to 2.8, indicating the increase of acetic acid formation. The residual oxygen partial pressure of 320 kPa shows that little amount of oxygen is consumed during the reaction.

The results suggest that two parallel reaction routes for malonic acid exist, namely direct oxidation to CO_2 and H_2O, and decarboxylation to CO_2 and acetic acid. Decarboxylation of malonic acid is reported to be the main reaction [23,24], while the contribution of direct oxidation is scarcely considered. Taking into account the feed concentration of 20 mol/m^3 of malonic acid, the relative contributions of the two reactions were determined whereby 60% of malonic acid reacted via decarboxylation while 40% by direct oxidation. However, decarboxylation of malonic acid produces acetic acid, which is difficulty to oxidise even at 170 °C. The stability of acetic acid formed from decarboxylation of malonic acid was also observed in other studies, even at 240 °C [21].

4.4. *Oxidation of maleic acid*

Maleic acid, which appeared at almost all conditions, though sometimes in trace amounts, is an important compound in understanding the phenol reaction network. Fig. 5(a) and (b) shows the profile of 0.01 mol/l maleic acid oxidation in which a steady state conversion of 80% was achieved while selectivity to CO_2 was 91% at residual oxygen partial pressure of 300 kPa. The reaction intermediates detected in the liquid samples with pH of 2.7 are succinic, acetic, and fumaric acid.

It can be inferred from these observations that maleic acid reacts catalytically to CO_2, probably through glyoxylic and oxalic acid, which are very reactive at the test conditions. The appearance of fumaric acid could be due to the *cis*–*trans*-isomerisation of maleic acid. While the formation of succinic acid is explained by transfer hydrogenation, the formation of acetic acid could be due to bond cleavage followed by transfer hydrogenation.

Fig. 5(c) shows the influence of maleic acid on phenol oxidation, when a solution containing 0.02 mol/l of maleic acid and 0.02 mol/l phenol was oxidised. While phenol conversion dropped from 82 to 70% during 4.2 ks (double liquid residence time), the concentration of maleic acid increased with time with slight increase in the concentration of glyoxylic acid followed by oxalic acid. Fumaric acid, the isomer of maleic acid, was also formed in relatively low concentration. The decline of phenol conversion could be due to either coverage of the active catalyst sites by organic species or a lower pH.

The results suggest that glyoxylic acid is formed from maleic acid by carbon–carbon cleavage and oxidation, and that glyoxylic acid possibly reacts sequentially to CO_2 through oxalic acid. The appearance of oxalic acid could be explained by the decrease in oxidation potential of the platinum surface as a result of the lower pH, which decreased from 3.4 (before) to 2.4 (after injection).

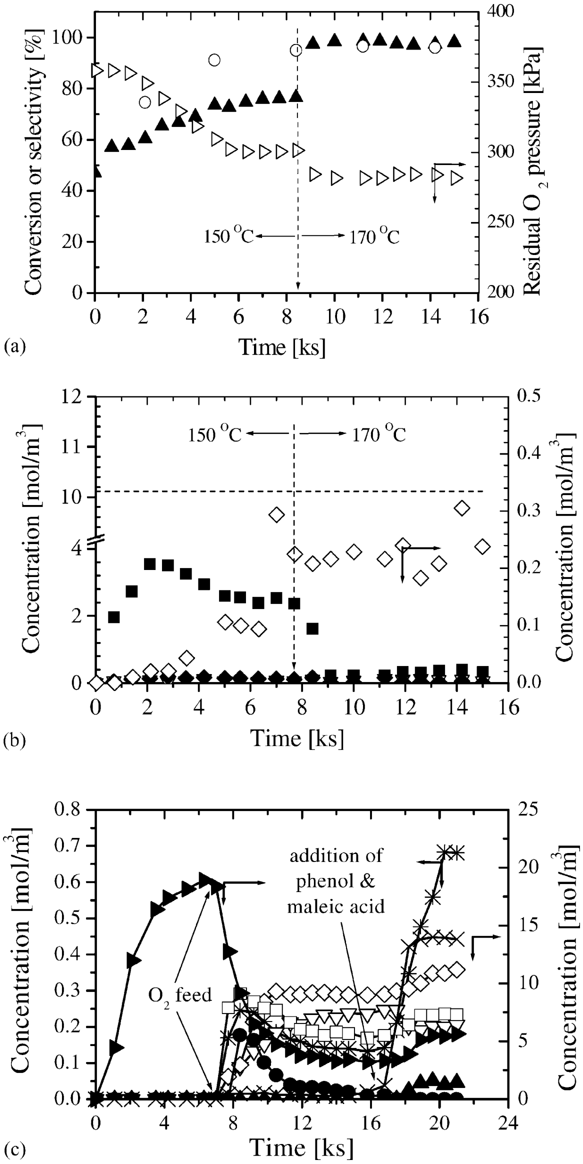


Fig. 5. Oxidation of maleic acid solution using O_2-Ph-Sim start-up method at standard conditions (Table 1): (a) maleic acid conversion (▷), selectivity to CO_2 (○), and residual oxygen partial pressure (▲); (b) concentration of intermediates; (c) oxidation of solution with 0.02 mol/l phenol and 0.02 mol/l maleic acid. Symbols for (b) and (c): phenol (▶), *p*-benzoquinone (●), oxalic acid (□), maleic acid (▲), glyoxylic acid (✳), succinic acid (▽), acetic acid (◇), and malonic acid (×).

4.5. Oxidation of hydroquinone

A 0.02 mol/l hydroquinone solution oxidised in the presence of Pt/graphite catalyst, easily reacted to form *p*-benzoquinone, and maleic acid with low concentrations of oxalic and acetic acid (Fig. 6(a)), while a selectivity to CO_2 of 76% was attained. Significant changes were observed after increasing the temperature to 170 °C in which conversion above 95% to CO_2 was attained and the pH of the effluent liquid increased to over 4.0 while the residual oxygen partial decreased (Fig. 6(b)). The brownish colour of the liquid effluent, which is a typical characteristic of *p*-benzoquinone also disappeared at the higher temperature. These observations are consistent with results obtained during phenol oxidation at oxygen S.E. above 80%, thus proving that *p*-benzoquinone is an intermediate product, which agrees with others [11,12,15,18].

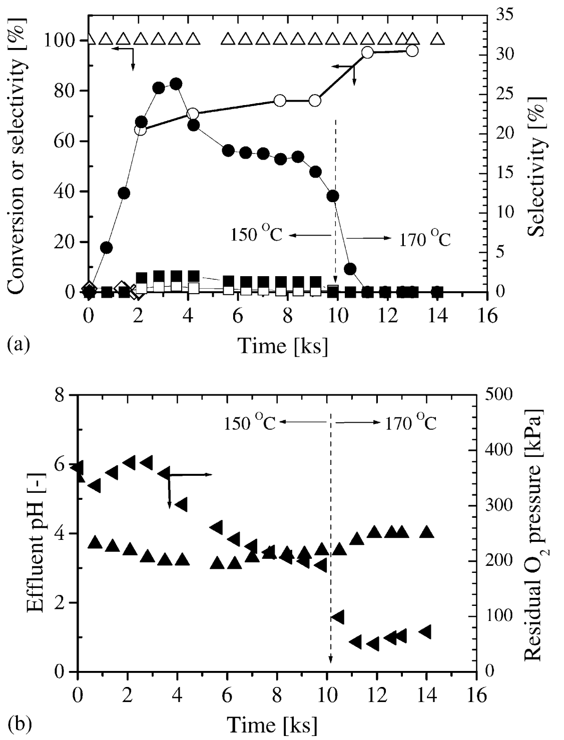


Fig. 6. Oxidation of a solution containing 0.02 mol/l hydroquinone using O_2-Ph-Sim start-up method at standard conditions (Table 1): (a) conversion of hydroquinone (△) and selectivity to: CO_2 (○), *p*-benzoquinone (●), oxalic acid (□), maleic acid (■), glyoxylic acid (✳), succinic acid (▽), acetic acid (◇), malonic acid (×); (b) residual oxygen partial pressure (◀) and liquid pH (▲).

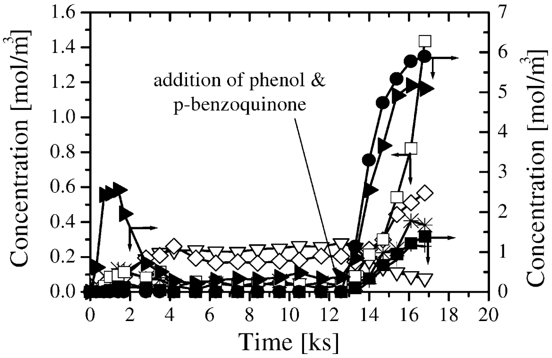


Fig. 7. Oxidation of a solution containing 0.02 mol/l phenol and 0.02 mol/l *p*-benzoquinone using O_2-Ph-Sim start-up method at standard conditions: phenol (▶), *p*-benzoquinone (●), oxalic acid (□), maleic acid (■), glyoxylic acid (✳), succinic acid (▽), acetic acid (◇), malonic acid (+).

The formation of *p*-benzoquinone and maleic acid seems to be sequential. Similarly, the formation of acetic acid seems to be sequential from maleic acid. In order to verify this hypothesis, a solution of 0.02 mol/l of phenol and 0.02 mol/l of *p*-benzoquinone was used as a feed after 12.6 ks of reaction. Fig. 7 shows the profile of oxidation intermediates before and after changing the feed solution in which a decline in phenol conversion from over 99 to 70% was observed. The colour of the liquid effluent changed from colourless to dark brownish, as the concentrations of *p*-benzoquinone, maleic acid, and oxalic acid increased. These changes were accompanied by the formation of insoluble compounds attributed to polymeric products. Whenever *p*-benzoquinone was formed insoluble compounds attributed to polymeric products were also formed, which most likely resulted in the loss of platinum catalyst activity.

4.6. Oxidation of catechol

During phenol oxidation experiments, catechol was not detected. When catechol was oxidised in a separate experiment, it was easily converted into oxidation products, mainly CO_2 (selectivity of 90%) as shown in Fig. 8. Intermediates formed in the oxidation, though in small amounts (selectivity <5% in total), were oxalic, acetic, succinic, and malonic acid. Fig. 8(b) shows the pH of the liquid effluent and the corresponding residual oxygen partial pressure. Neither *o*-benzoquinone nor maleic acid were detected in the yellowish coloured liquid effluent. However, the yellowish colour can be associated with the presence of unmeasurable traces of *o*-benzoquinone since catechol is colourless under oxygen-free environments.

The possible explanation of the absence of *o*-benzoquinone could be that *o*-benzoquinone produced by oxidation reacts rapidly under ring cleavage to end products. It is most likely that during ring cleavage the splitting of C-6 to form C-4 and C-2 compounds is favoured. However, the splitting of C-6 into C-3 compounds cannot be excluded since malonic acid is also formed, although in trace amount. The formation of succinic and acetic acid proves the idea that catechol is a strong reducer, thus reduced platinum favours transfer hydrogenation reaction in addition to oxidation.

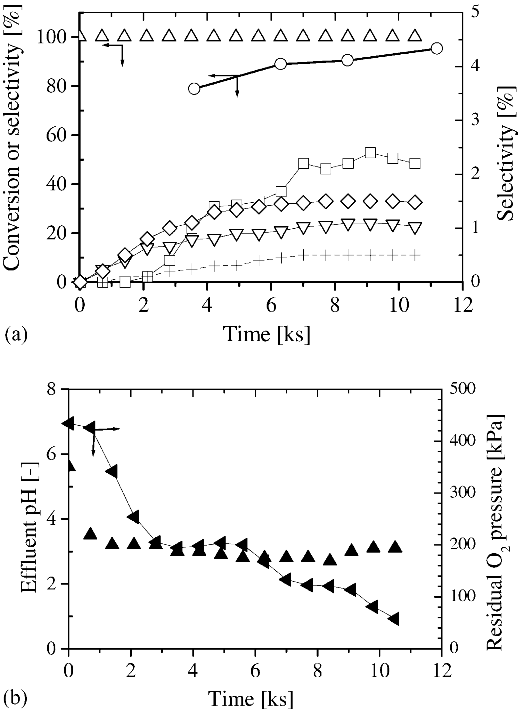


Fig. 8. Oxidation of 0.02 mol/l catechol using O_2-Ph-Sim start-up method at standard conditions: (a) conversion of catechol (△), and selectivity to: CO_2 (○), oxalic acid (□), malonic acid (+), succinic acid (▽), acetic acid (◇); (b) residual oxygen partial pressure (◀) and liquid pH (▲).

4.7. Oxidation of muconic acid

Although muconic acid was not detected in our experiments, it is generally considered as the intermediate compound during phenol oxidation to CO_2. Therefore, the reactivity and hence reaction intermediates during oxidation of muconic acid were investigated at standard conditions. Fig. 9(a) presents the reaction profile of muconic acid in which a steady state conversion of 94% and a selectivity to CO_2 of 65% were achieved. In Fig. 9(b) the concentrations of muconic acid, propanoic, succinic, acetic, and malonic acid are shown. Both maleic and oxalic acid were detected in trace amounts. At 170 °C, muconic acid was fully converted with selectivity to CO_2 over 90%. The corresponding changes in the residual oxygen partial pressure are depicted in Fig. 9(a). The formation of propanoic acid in relatively high concentration raises doubt on whether muconic acid is a reaction intermediate in the phenol oxidation. This is due to the reason that both propanoic acid, which seems to be stable at the test conditions, and muconic acid were never detected during our phenol oxidation experiments.

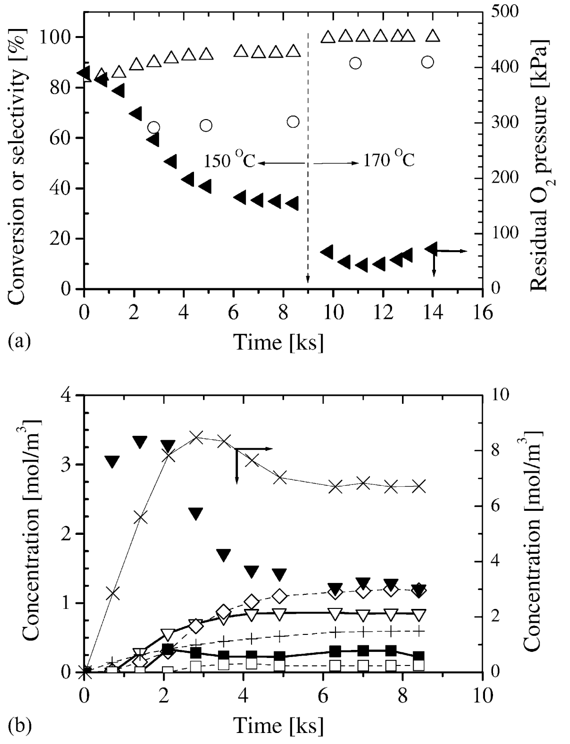
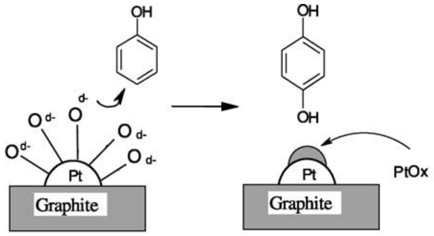


Fig. 9. Oxidation of 0.02 mol/l muconic acid solution using O_2-Ph-Sim start-up method at standard conditions: (a) muconic acid conversion (△), selectivity to CO_2 (○), and residual oxygen partial pressure (◀); (b) concentrations of muconic acid (▼), propanoic acid (×), oxalic acid (□), malonic acid (+), maleic acid (■), succinic acid (▽), and acetic acid (◇).

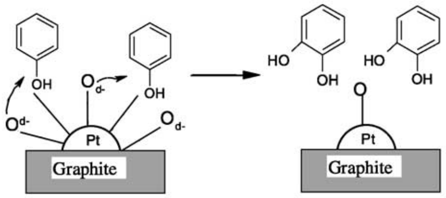
4.8. Mechanistic interpretation and reaction pathways

The oxidation of phenol in aqueous solution is very complex for both non-catalytic and catalytic systems. A proposal of a complete mechanism of platinum catalysed oxidation of phenol based on the evidence presented is not yet possible. However, the reaction intermediates and end products observed in this study (Table 2) provide a basis to postulate a preliminary reaction mechanism. During oxidation, phenol seems to react to either catechol or hydroquinone, which can react further to end products. The π-electrons of the phenol molecule are uniformly conjugated over the C-atoms and the O-atom, while for σ-bonds a dipole points towards the OH-group. Catalysts in the presence of oxygen can promote the formation of hydroxyl radicals, which can activate the phenol aromatic ring. This makes phenol become most reactive at the *para*-position especially for non-catalysed reactions in acidic environment. However, the reaction pathways and selectivity to CO_2 and H_2O seem to be controlled by the extent of oxygen coverage of the platinum surface.

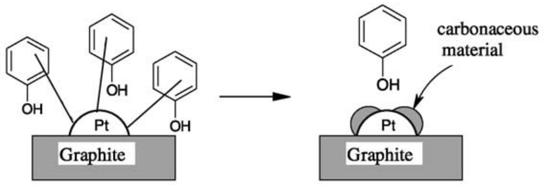
The results strongly suggest four possible situations (see Scheme 1), namely: fully oxidised, partly oxidised, free, and partly hydrogen covered platinum surfaces. When the oxidation takes place on a partly oxidised surface of platinum (Scheme 1(b)), phenol and oxygen adsorb simultaneously and react on the platinum surface. The high potential of the platinum surface orients the phenol molecule in such a way that dehydrogenation of the *ortho*-C–H can take place followed by hydration or hydroxylation to form catechol, which reacts further through unstable *o*-benzoquinone and ring cleavage compounds and finally to CO_2 and H_2O. It is well known that *o*-benzoquinone is fairly unstable and easily cleaved to form aliphatic compounds [25]. This mechanism can be maintained when the reaction is carried out within the proper operation window [20].



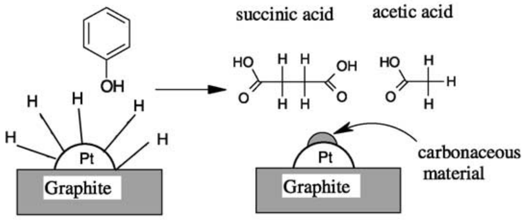
(a) Over-oxidized Pt surface. Steps: attack by OH radicals or oxygen insertion.



(b) Partly oxidized Pt surface. Steps: dehydrogenation, or hydroxylation.



(c) Free Pt surface. Steps: carbon deposition.



(d) Partly hydrogen covered Pt surface. Steps: ring cleavage and hydrogenation.

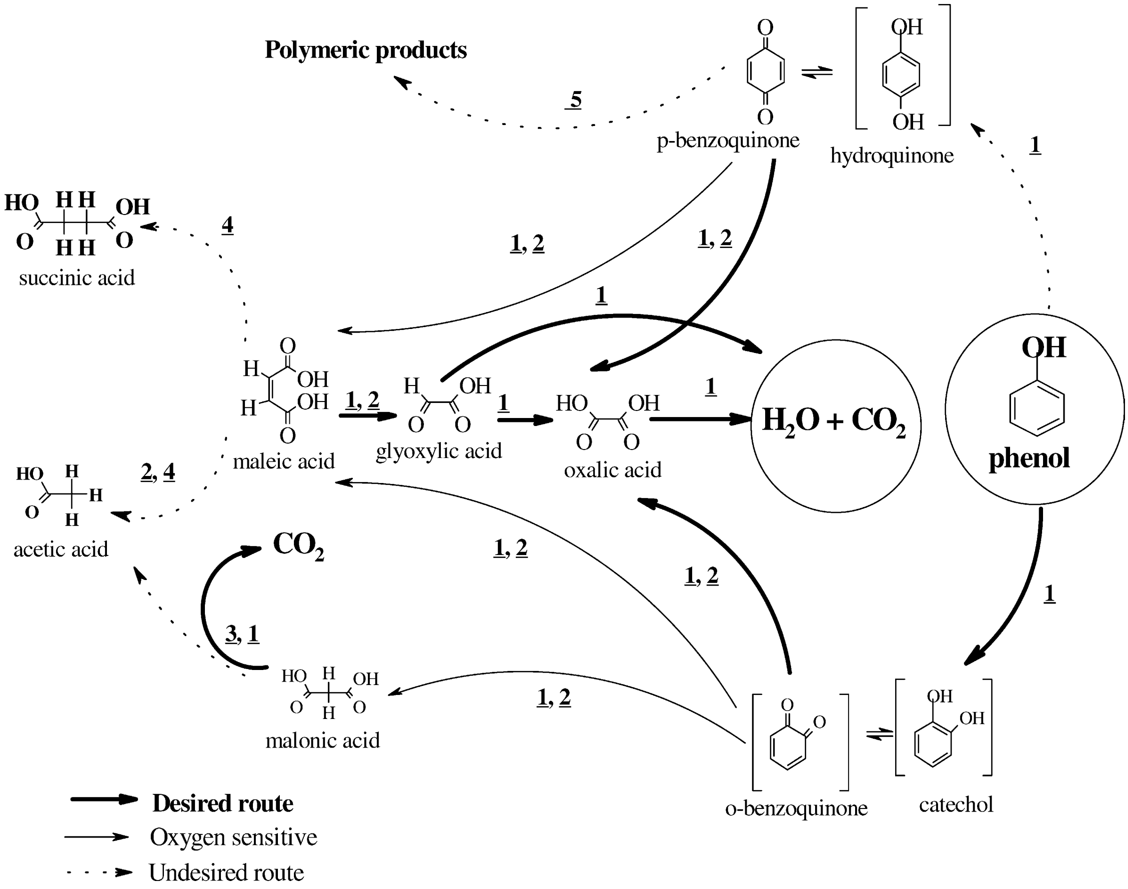
Scheme 1. Mechanisms of platinum catalysed phenol oxidation.

A fully oxidised platinum surface results in a change in the selectivity of the reaction, and favours the formation of *p*-benzoquinone as simplified in Scheme 1(a). Under such reaction conditions, rapid loss of catalyst activity ascribed to 'over-oxidation' has been observed although it was temporary and could be reversed at reducing conditions. When the platinum surface is fully covered with oxygen (PtO_x), it is possible that the reaction proceeds under the free radical mechanism resulting into oxygen insertion at the *para*-position of the phenol molecule to form *p*-benzoquinone. The formation of *p*-benzoquinone when high oxygen loads are employed (Fig. 1) confirms this mechanism. We observed further that a prolonged operation with a fully oxidised platinum surface favoured the formation of polymeric products, which resulted into permanent deactivation of the catalyst (fouling). Analogous findings have been obtained during electrochemical oxidation of aqueous phenol [26].

While a free platinum surface was vulnerable to poisoning by carbonaceous compounds (Scheme 1(c)), a partly hydrogen covered platinum surface favoured the formation of acetic and succinic acid which are difficult to oxidise (Scheme 1(d)). The possible source of hydrogen in this case is phenol dehydrogenation. Also mixed situations are likely to occur during the reaction.

The mechanism of platinum catalysed oxidation of phenol, which is favoured in the presence of oxygen at the platinum active sites, seems to involve splitting of the C–H bonds. Therefore, the first role of oxygen is to raise the oxidation potential of the platinum necessary for releasing of a proton from the C–H bond ready for oxidation. At low oxidation potential, platinum active sites are vulnerable to poisoning by carbonaceous matter. The second role of oxygen is possibly protection of the platinum surface from irreversible poisoning by carbonaceous matter.

We suggest that there exist two catalytic routes for phenol oxidation. Scheme 2 presents the corresponding reaction network derived from the observed intermediate and end products. One route, which was clearly identified during the reaction start-up with ‘oxidative’ method (oxygen first fed into the reactor followed by phenol), shows that phenol reacts through hydroquinone to *p*-benzoquinone, which reacts further to maleic acid (C-4) and carboxylic acid



Scheme 2. Proposed reaction scheme in this work for liquid phenol oxidation catalysed with graphite supported platinum catalyst. Reaction steps include: (1) oxidation; (2) C–C bond cleavage; (3) decarboxylation; (4) transfer hydrogenation; (5) molecular coupling or polymerisation.

(C-2), and finally to the end products. However, once *p*-benzoquinone is formed, molecular coupling or polymerisation is likely to occur. This reaction route is favoured when there is a relatively high oxygen load on the platinum surface.

At S.E. close to 0% the platinum catalysed reaction goes through catechol, *o*-benzoquinone and ring-opening compounds (the second route), and finally to CO_2 and H_2O. The most favourable reaction seems to be the splitting of the C-6 ring into C-4 (e.g. maleic acid) and C-2 (e.g. glyoxylic or oxalic acid) which reacts further to end products.

The desired reaction pathway for platinum catalysed phenol oxidation is indicated by the bold arrows in Scheme 2. The explanation of this mechanism is not obvious, however it is logical to speculate that at S.E. within 0–80%, the platinum surface is at a relatively low oxidation potential, such that dehydrogenation and afterwards hydroxylation of the phenol molecule is favoured at the *ortho*-C–H bond to form catechol, a very reactive intermediate to carbon dioxide. As proposed earlier, catechol is a strong reducer on platinum, therefore the presence of oxygen on the platinum surface is of great importance to prevent transfer hydrogenation reaction to stable succinic and acetic acid.

5. Conclusions

It has been shown that the activity of the Pt/graphite catalyst and hence the selectivity of the oxidation products are influenced by the degree of oxygen coverage of the platinum surface. Four situations can be postulated from the extent of oxygen coverage, namely: over-oxidised, partly oxidised, free, and reduced platinum surfaces. Full conversion of phenol to CO_2 and H_2O is mostly favoured on a partly oxidised platinum surface. The first role of oxygen is to raise the oxidation potential of the platinum necessary for releasing of a proton from the C–H bond ready for oxidation. At low oxidation potential, platinum active sites are vulnerable to poisoning by carbonaceous matter. The second role of oxygen is the protection of the platinum surface from irreversible poisoning by carbonaceous matter.

The reaction pathways for platinum catalysed oxidation of phenol are reported in this work (Scheme 2). At low S.E., phenol is fully oxidised to CO_2 via catechol and *o*-benzoquinone. The most favourable reaction seems to be the splitting of the C-6 ring into C-4 and C-2 compounds which react to end products. Similarly, at higher S.E., phenol reacts through hydroquinone, which forms *p*-benzoquinone. It is clearly observed that *p*-benzoquinone is responsible for polymer formation. In addition, it has the potential to cause deactivation of the platinum catalyst by blocking of active sites leading to over-oxidation of the residual platinum sites.

It was found that glyoxylic acid is not a polymer precursor. Furthermore, it appears that both maleic and oxalic acid might be formed through parallel reaction of *p*-benzoquinone or *o*-benzoquinone by carbon–carbon cleavage and oxidation.

While malonic acid is formed from catechol by ring cleavage and oxidation, it reacts by direct oxidation (40%) to form CO_2 and by decarboxylation (60%) to form acetic acid and CO_2. The formation of propanoic acid in relatively high concentration, which remains stable at the test conditions, excludes muconic acid as an intermediate during phenol oxidation since both propanoic and muconic acid were never detected during phenol oxidation.

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