

Oxidative Degradation of Phenol using *in situ* Generated Hydrogen Peroxide Combined with Fenton's Process

Supported palladium-iron catalysts for the removal of model contaminants from wastewater

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Oxidative destruction of organic compounds in water streams could significantly reduce environmental effects associated with discharging waste. We report the development of a process to oxidise phenol in aqueous solutions, a model for waste stream contaminants, using Fenton's reactions combined with *in situ* synthesised hydrogen peroxide (H_2O_2). Bifunctional palladium-iron supported catalysts, where Pd is responsible for H_2O_2 synthesis while Fe ensures the production of reactive oxygen species required for the degradation of phenol to less toxic species is reported. A comparison is made between *in situ* generated and commercial H_2O_2 and the effect of phenol degradation products on catalyst stability is explored.

Introduction

Phenolic compounds are present in waste streams produced by a variety of industries; including petrochemical, pharmaceutical, plastics and resin

manufacturing (1, 2). Due to their high toxicity to both humans and aquatic life, even at concentrations as low as 2 mg l^{-1} (3), it is essential to remove phenolic compounds from these waste streams before discharge to the mains water system or the wider environment. One approach to destroy the contaminants is through oxidative degradation to less toxic compounds or total mineralisation to carbon dioxide (CO_2). Fenton's reaction, the catalytic formation of hydroxyl and hydroperoxy radicals by the disproportionation of hydrogen peroxide, can be considered one of the most efficient catalytic systems for degradation of organic pollutants in wastewater streams at low to moderate concentrations (4–9). Comparison of different oxidation processes for phenol degradation by Esplugas *et al.* reports the efficacy of Fenton's reagent over approaches including photocatalytic approaches and ozonation (10). There are a number of advantages associated with the use of Fenton's reactions to treat wastewater streams, such as its simplicity (being operated at room temperature and at atmospheric pressure) and its lack of toxicity, with H_2O_2 degrading to environmentally benign species such as H_2O and O_2 .

A range of catalytically active iron species have been utilised as Fenton's reagents, these can consist of metal salts (Fe(II) (11, 12) or Fe(III) (13)), metal oxides (Fe_2O_3 , Fe_3O_4) (14) and zero-valent iron (Fe(0)) (15, 16). A range of heterogeneous iron based catalysts have also been reported, including Fe-doped zeolites (Fe-zeolite-Y (17), Fe-ZSM5 (18) and Fe-beta (18)) Fe_2O_3 intercalated between layered clays such as laponite (19, 20)

and bentonite (21) as well as Fe containing SBA-15 (22) and other Fe containing catalysts (22–25).

It is currently accepted that the oxidation of phenol follows the mechanism proposed by Devlin and Harris (26), where phenol is first decomposed into aromatic compounds, such as catechol and hydroquinone. These initial products in turn undergo oxidation to produce carboxylic acids, such as oxalic, acetic and formic acids, the intermediates formed in the production of these acids often have greater toxicity than phenol itself (27). However, catalyst deactivation, especially due to metal leaching of Fe into aqueous solution, presents new challenges including the need for removal of ferrous or ferric contaminants from the waste stream, in addition to the continual replenishment of the heterogeneous catalyst. Besides iron, a range of other transition metals with multiple redox states such as cobalt (28, 29), copper (30–32), manganese (33) and ruthenium (34) can all decompose H_2O_2 into $\bullet\text{OH}$ radical species through Fenton-like pathways. However, due to economic and environmental concerns iron is still often the preferred choice for the process.

Nevertheless, a number of drawbacks are associated with using commercial hydrogen peroxide for this process that remain to be solved, namely the costs associated with the anthraquinone process, the means by which H_2O_2 is produced industrially. Although this process can be considered highly efficient the requirement for the constant replacement of the anthraquinone and the energy costs associated with H_2O_2 concentration, transportation, storage and dilution at source prior to use has led to the investigation of alternative means of H_2O_2 production *in situ* for the application of wastewater treatment (35–38). A number of studies have investigated the efficacy of H_2O_2 generated *in situ* over Pd-Fe based catalysts utilising a range of hydrogen sources such as formic acid, hydroxylamine and hydrazine (35–38, 40). Herein we investigate the activity of Pd-Fe bimetallic catalysts supported on titania (TiO_2) and silica (SiO_2) for the degradation of phenol *via* the *in situ* synthesis of H_2O_2 from molecular H_2 and O_2 .

Experimental

Catalyst Preparation

In a typical preparation of Pd-Fe/ TiO_2 , the requisite amount of PdCl_2 aqueous solution (6 mg ml^{-1} Pd, 0.58 M HCl) and FeCl_3 aqueous solution (6 mg ml^{-1} Fe) were added to a 50 ml round

bottom flask. Water was then added to achieve a total solution volume of 16 ml. The solution was then heated to 60°C with 1000 rpm stirring and the required amount of support TiO_2 (P25 Degussa) was added. After complete addition of support the temperature was raised to 95°C with stirring (1000 rpm) for 16 h to allow complete evaporation of the water. The dried catalyst was then ground and reduced under flowing 5% H_2/Ar (500°C, 4 h, 10°C min^{-1}). An analogous preparation method was employed for Pd-gold, Pd-manganese and Pd-copper where $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (Strem Chemicals, 99.8%), $\text{Mn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ (Sigma-Aldrich, 99.99%) and $\text{Cu}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ (Sigma-Aldrich, 99.99%) were utilised as metal precursors.

Phenol Oxidation

Oxidation of Phenol *via in situ* Synthesis of Hydrogen Peroxide from Hydrogen and Oxygen

Phenol oxidation reactions were performed in a Parr stainless steel autoclave with a nominal volume of 50 ml and a maximum working pressure of 14 MPa. In a typical test the autoclave was charged with catalyst (0.01 g, 1 g l^{-1}) and phenol (1000 ppm in H_2O , total mass 8.5 g). The charged autoclave was then purged three times with 5% H_2/CO_2 (0.7 MPa) before filling with 5% H_2/CO_2 to a pressure of 2.9 MPa, followed by the addition of 25% O_2/CO_2 (1.1 MPa). The reactor was then heated to 30°C followed by stirring (1200 rpm) of the reaction mixture for typically 2 h. After 2 h the reaction solution was collected and filtered, followed by analysis by high performance liquid chromatography (HPLC) fitted with an Agilent Poroshell 120 SB-C18 column.

Oxidation of Phenol Using Preformed Hydrogen Peroxide

Phenol oxidation reactions were performed in a Parr stainless steel autoclave with a nominal volume of 50 ml and a maximum working pressure of 14 MPa. In a typical test the autoclave was charged with catalyst (0.01 g, 1 g l^{-1}) and phenol (1000 ppm in H_2O , total mass 8.5 g) and either stabilised hydrogen peroxide (50 wt% in H_2O stabilised, Fluka™) or unstabilised hydrogen peroxide (30 wt% in H_2O , ACROS). The charged autoclave was then purged three times with 25% O_2/CO_2 (0.7 MPa) before filling with 25% O_2/CO_2 (4 MPa). The reactor was then heated to 30°C followed by stirring (1200 rpm) for typically 2 h.

After 2 h the reaction solution was collected and filtered, followed by analysis by HPLC fitted with Agilent Poroshell 120 SB-C18 column.

Characterisation

X-ray photoelectron spectroscopy (XPS) analyses were made on a Kratos Axis Ultra DLD spectrometer. Samples were mounted using double-sided adhesive tape and binding energies were referenced to the C 1s binding energy of adventitious carbon contamination that was taken to be 284.7 eV. Monochromatic Al K_{α} radiation was used for all measurements; an analyser pass energy of 160 eV was used for survey scans while 40 eV was employed for detailed regional scans. The intensities of the Pd 3d and Fe 2p features were used to derive metal loadings. Microwave plasma atomic emission spectroscopy (MP-AES) analysis of post reaction solutions were carried out using an Agilent 4100 MP-AES. Samples were investigated for the presence of Pd and Fe using multiple wavelength calibrations for each individual element.

Results and Discussion

Our initial investigations into removing phenol by utilising *in situ* H_2O_2 production combined with Fenton's chemistry examined the activity of bimetallic Pd based catalysts for the degradation of phenol, *via* the *in situ* generation of H_2O_2 . In our choice of catalyst combinations we utilised Pd as the H_2O_2 generating species and varied the second metal to metals that have known activity as Fenton type catalysts. We compare these catalysts to a well-established catalyst used for the direct synthesis of H_2O_2 , 2.5% Pd-2.5% Au/TiO₂ (41, 42).

Figure 1 shows the extent of phenol conversion over time utilising bimetallic catalysts that contain the H_2O_2 degradation component in the presence of 1000 ppm phenol. Over the reaction period, phenol conversion was limited (less than 5%) for all Pd-X/TiO₂ catalysts other than Pd-Fe/TiO₂, which demonstrated a significant conversion of phenol (78%) after a reaction time of 2 h despite both Mn (33, 43) and Cu (44, 45) being studied as Fenton-like catalysts in their own right. Post reaction investigations of the reaction medium by MP-AES revealed a significant amount of Fe leaching from the catalyst support, with 38% Fe leached after 120 min. Building on these initial findings we investigated the role of both Pd and Fe in the degradation of phenol (**Figure 2**). It was determined

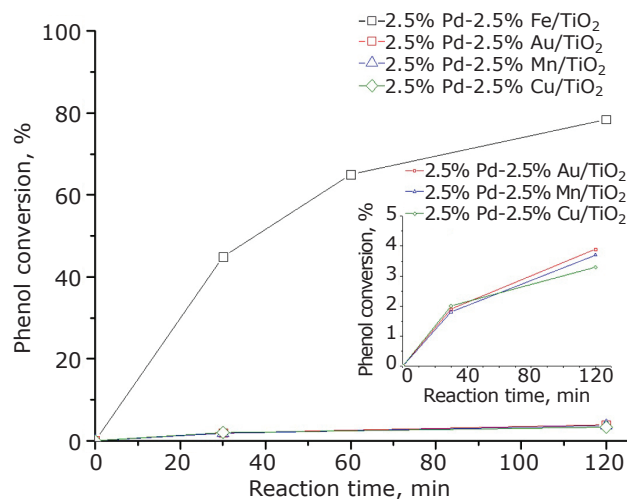


Fig. 1. The activity of 2.5% Pd-2.5% X/TiO₂ catalysts towards the oxidation of phenol, *via* the *in situ* synthesis of H_2O_2 from H_2 and O_2 , where X = Fe, Mn, Cu or Au. Reaction conditions: catalyst (0.01 g, 1 g l⁻¹), phenol (1000 ppm, 8.5 g), 5% H_2/CO_2 (420 psi), 25% O_2/CO_2 (160 psi), 30°C, 2 h, 1200 rpm

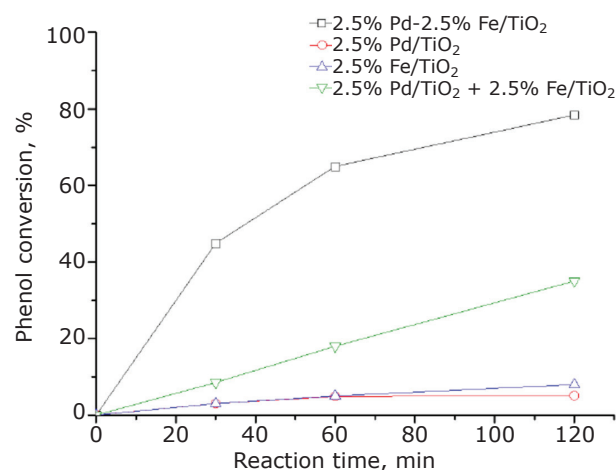


Fig. 2. The activity of Pd and Fe based catalysts towards the oxidation of phenol, *via* the *in situ* synthesis of H_2O_2 from H_2 and O_2 . Reaction conditions: catalyst (0.01 g, 1 g l⁻¹), phenol (1000 ppm, 8.5 g), 5% H_2/CO_2 (420 psi), 25% O_2/CO_2 (160 psi), 30°C, 2 h, 1200 rpm

that both monometallic Pd and Fe catalysts offer limited activity towards the degradation of phenol, 5% and 8% conversion respectively, indeed the extent of phenol conversion is comparable to that observed when no catalyst is present (Table S.1 in the Supplementary Information). This limited conversion can be related to the inactivity of Fe

to synthesise H_2O_2 . In comparison, Pd supported catalysts are well known for their activity towards the degradation of H_2O_2 to H_2O (46, 47), as such the production of reactive oxygen species ($\bullet\text{OOH}$ and $\bullet\text{OH}$) responsible for the degradation of phenol is limited.

A physical mixture of Pd/TiO₂ and Fe/TiO₂ catalysts resulted in a substantial improvement in phenol conversion to 35% compared to the monometallic Pd and Fe catalysts alone supporting the synergistic effect of having both components in the reaction. However, this was still far lower than the phenol conversion achieved when employing the bimetallic catalyst (78%) despite containing the same amount of each metal component. This demonstrates the need for either an alloyed Pd-Fe species or the requirement for both metals to be in close proximity, by being supported on the same support, to limit non-selective H_2O_2 decomposition during diffusion between sites responsible for H_2O_2 generation and degradation to reactive oxygen species, likely $\bullet\text{OOH}$ and $\bullet\text{OH}$. Georgi *et al.* (48) have reported accelerated rates of Fenton's reaction when heterogeneous Pd is utilised alongside homogeneous Fe, in the presence of H_2 , due to improved rates of Fe^{3+} reduction to Fe^{2+} and we suggest the increased rate of phenol conversion observed for the bimetallic Pd-Fe catalyst may be, at least in part, attributed to this enhancement in Fe reduction rate.

The effect of the Pd:Fe ratio on catalytic activity towards phenol conversion was investigated, with total Pd loading fixed at 2.5 wt% and varying the Fe content of the catalyst between 0.5–2.5 wt% (Figure 3). A correlation can be drawn between total Fe loading and activity towards phenol conversion, with the activity of the 2.5% Pd-2.5% Fe/TiO₂ catalyst approximately five times greater than that of the 2.5% Pd-0.5% Fe/TiO₂ catalysts.

Investigation of the post reaction solution by MP-AES revealed leaching of Fe in all Pd-Fe/TiO₂ catalysts, ranging from 6 ppm in the high Fe loaded samples to <1 ppm in low Fe loading samples (Figure S.1 in the Supplementary Information). The total Fe leaching was closely related to phenol conversion in all reactions with both low Fe loaded catalysts (2.5% Pd-1% Fe/TiO₂ and 2.5% Pd-0.5% Fe/TiO₂) showing minimal Fe leaching despite reasonable rates of phenol conversion (15% and 23% respectively). Investigation into the relationship between phenol conversion and Fe leaching reveals a close relationship between the two. Monitoring the extent of Fe leaching over the course of a reaction using the 2.5% Pd-2.5% Fe/TiO₂ catalyst reveals Fe content dramatically

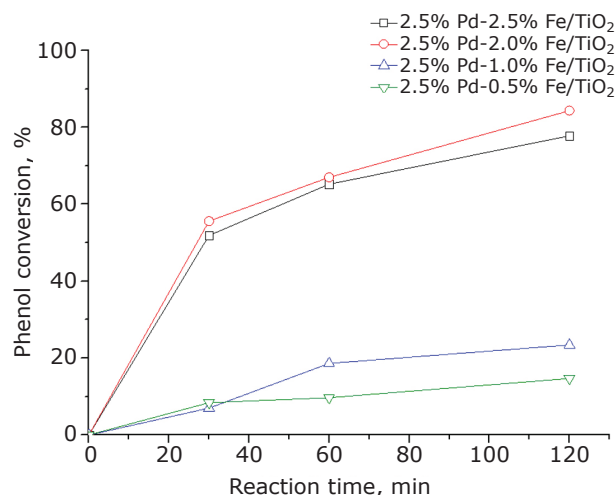


Fig. 3. The effect of total Fe content of bimetallic Pd-Fe/TiO₂ catalysts towards the oxidation of phenol, *via* the *in situ* synthesis of H_2O_2 from H_2 and O_2 . Reaction conditions: catalyst (0.01 g, 1 g l⁻¹), phenol (1000 ppm, 8.5 g), 5% H_2/CO_2 (420 psi), 25% O_2/CO_2 (160 psi), 30°C, 2 h, 1200 rpm

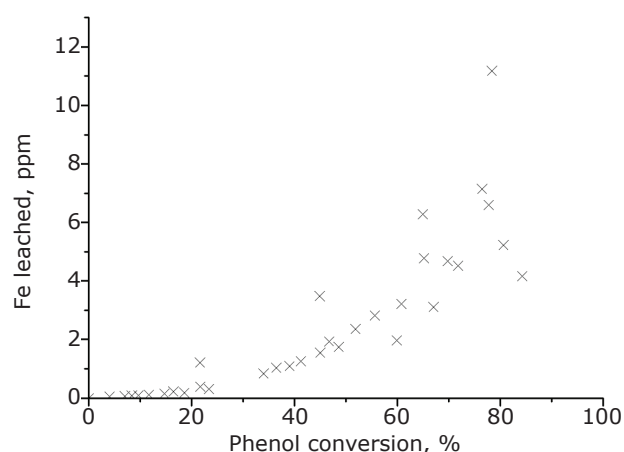


Fig. 4. The relationship between phenol conversion and leaching of Fe from 2.5% Pd-2.5% Fe/TiO₂. Reaction conditions: catalyst (0.01 g, 1 g l⁻¹), phenol (1000 ppm, 8.5 g), 5% H_2/CO_2 (420 psi), 25% O_2/CO_2 (160 psi), 30°C, 1200 rpm

increases as phenol conversion increases beyond 30% (Figure 4). This indicated that while conversion levels below 20% could be reached with minimal Fe leaching the generation of further oxidation products such as carboxylic acids or alcohols resulting from the degradation of phenol may have been responsible for accelerated leaching of Fe from the catalyst. It is well known that the

Table I XPS Analysis of 2.5% Pd-2.5% Fe/TiO₂ Treated with Catechol (1000 ppm) and Oxalic Acid (1000 ppm)

Element	Fresh catalyst, at%	Catechol treated, at%	Oxalic acid treated, at%
O 1s	31.0	37.6	36.6
C 1s	54.8	48.5	47.7
Ti 2p	9.7	10.8	13.3
Fe 2p	2.7	2.7	1.4
Pd 3d	0.8	0.5	0.3
Cl 2p	1.1	0	0

Fenton process is highly dependent on solution pH, with activity reduced at elevated pH due to the formation of inactive iron oxohydroxides (49) in addition to increased decomposition of H₂O₂ (50). We have previously reported the beneficial effect of the CO₂ diluent in promoting the stability of H₂O₂, through the formation of carbonic acid in solution. We report a decrease in reaction solution to pH 4 when a CO₂ rich atmosphere is utilised, which is comparable to the pH reported as optimal for the Fenton reaction (49, 51).

XPS investigation of the surface concentration of Pd and Fe in 2.5% Pd-2.5% Fe/TiO₂ before and after treatment with the diol catechol and oxalic acid as examples of degradation products of phenol (1000 ppm), both of which we have detected as reaction intermediates by HPLC, can be seen in **Table I**. It was observed that for the catechol treated catalyst, the surface concentration of Fe was similar to that of the fresh. However, for the oxalic acid-treated catalyst, there was a decrease from 2.66 at% to 1.40 at%. In the case of Pd, there was a large loss in surface concentration for both the catechol and oxalic acid treated catalysts. When the catalyst was treated with catechol the surface concentration of Pd decreased from 0.82 at% to 0.47 at%, while the analogous treatment with oxalic acid Pd content is reported to decrease to 0.17 at%.

To better understand the role of the support and to identify if improved rates of phenol conversion could be achieved, a SiO₂ support with a significantly higher surface area than the TiO₂ was used to prepare an analogous 2.5% Pd-2.5% Fe/SiO₂ catalyst in an attempt to suppress Fe leaching. As can be seen in **Table II** the extent of phenol oxidation was much greater for the 2.5% Pd-2.5% Fe/SiO₂ catalyst (92%) compared to 2.5% Pd-2.5% Fe/TiO₂ (78%). Analysis of the post reaction medium by MP-AES revealed that total Fe leaching increased for the 2.5% Pd-2.5% Fe/SiO₂ catalyst in comparison to

Table II Comparison of Catalytic Activity of Pd-Fe Catalysts Towards Phenol Conversion

Catalyst	Phenol conversion, %	Fe leaching, ppm
2.5% Pd-2.5% Fe/TiO ₂ ^a	78	7
0.5% Pd-0.5% Fe/TiO ₂ ^a	22	1
0.5% Pd-0.5% Fe/TiO ₂ ^b	51	8
2.5% Pd-2.5% Fe/SiO ₂ ^a	92	11
0.5% Pd-0.5% Fe/SiO ₂ ^a	34	1
0.5% Pd-0.5% Fe/SiO ₂ ^b	99	12

Reaction conditions: phenol (1000 ppm, 8.5 g), 5% H₂/CO₂ (420 psi), 25% O₂/CO₂ (160 psi), 2 h, 30°C, 1200 rpm

^a Total catalyst loading 0.01 g (1 g l⁻¹)
^b Total catalyst loading 0.05 g (0.5 g l⁻¹)

the 2.5% Pd-2.5% Fe/TiO₂ catalyst. We ascribe this to an increase in the extent of phenol conversion and a greater concentration of further oxidation products such as oxalic acid which we have shown is capable of leaching Fe species from the catalyst by chelation to form Fe-oxalate.

In an attempt to increase the dispersion of metals active towards the direct synthesis of H₂O₂ as well as those sites responsible for the production of reactive oxygen species, total metal loading was decreased to 0.5% Pd-0.5% Fe/SiO₂, achieving 99% phenol conversion, under identical conditions. By normalising catalyst mass to ensure the total amount of metal utilised was identical to the 2.5% Pd-2.5% Fe/SiO₂ catalyst, total Fe leaching was observed to be similar to that of the 5% Pd-Fe/SiO₂ catalyst, at 12 ppm and 11 ppm respectively. This supports the hypothesis that phenol conversion and Fe leaching are closely linked in all cases. The excellent rates of phenol conversion observed led us to investigate the efficacy of the 0.5% Pd-0.5% Fe/SiO₂ catalyst at shorter reaction times, as seen in **Figure 5**. We report very high rates of phenol conversion over 60 minutes, 96%, significantly higher than that of the standard 2.5% Pd-2.5% Fe/TiO₂ discussed above, with a phenol conversion of 65% over this time scale, despite five times greater metal content.

Evaluation of the catalytic activity of Pd-Fe/SiO₂ toward phenol degradation using pre-formed, commercial, H₂O₂ compared to that observed when utilising H₂O₂ produced *in situ* can be seen in **Table III**. It is observed that phenol conversion is limited in the presence of preformed H₂O₂ and O₂ (6%), and H₂ (81%), which Georgi *et al.* have

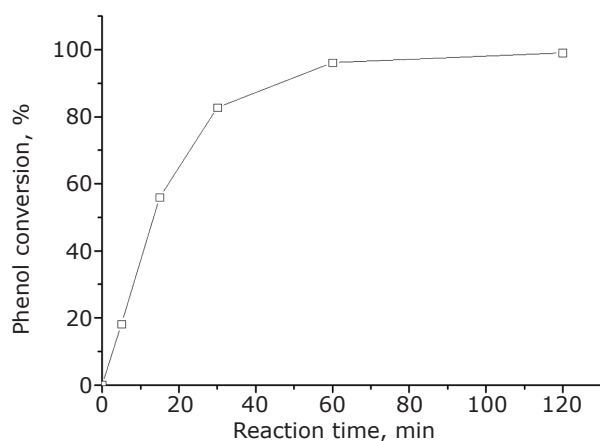


Fig. 5. Time on line profile of phenol conversion for 0.5% Pd-0.5% Fe/SiO₂ catalyst. Reaction conditions: catalyst (0.05 g, 0.5 g l⁻¹), phenol (1000 ppm, 8.5 g), 5% H₂/CO₂ (420 psi), 25% O₂/CO₂ (160 psi), 30°C, 1200 rpm

Table III Comparison of Catalytic Activity of H₂O₂ Generated *in situ* from H₂ and O₂ and Commercial H₂O₂ using 2.5% Pd-2.5% Fe/SiO₂

Reaction conditions	Phenol conversion, %
5% H ₂ /CO ₂ + 25% O ₂ /CO ₂ ^a	92
0.5 wt% H ₂ O ₂ (preformed) + 25% O ₂ /CO ₂ ^b	6
0.5 wt% H ₂ O ₂ (preformed) + 5% H ₂ /CO ₂ ^b	81

Reaction conditions

^a Catalyst (0.01 g, 1 g l⁻¹), phenol (1000 ppm, 8.5 g), 5% H₂/CO₂ (420 psi), 25% O₂/CO₂ (160 psi), 30°C, 1200 rpm

^b Catalyst (0.01 g, 1 g l⁻¹), phenol (1000 ppm, 8.5 g), 25% O₂/CO₂ (580 psi), 30°C, 1200 rpm

previously accredited to an enhancement in the Fe redox cycle (48). However, the utilisation of H₂O₂ synthesised from molecular H₂ and O₂ resulted in an enhanced phenol conversion, beyond that seen with commercially available H₂O₂ (96%). We ascribe the dramatic enhancement in catalytic activity to the absence of compounds such as phosphoric acid and acetanilide, known to be utilised as H₂O₂ stabilising agents (52), and the generation of a greater flux of reactive oxygen species responsible for phenol degradation.

In order to establish the key species required for the oxidation of phenol a number of hot filtration experiments were performed (Table S.2 in the Supplementary Information). From these experiments a number of conclusions can be

drawn, namely that *in situ* generation of H₂O₂ is required to achieve any activity in the phenol oxidation reaction. The extent of phenol conversion was far greater when H₂O₂ was generated from H₂ and O₂ compared to the use of preformed H₂O₂, possibly due to the presence of stabilising agents found in commercial H₂O₂ (52) or self-termination of radical species when all the H₂O₂ is added at the beginning of the reaction. In addition it is observed that homogeneous Fe species present in the solution can catalyse the degradation of phenol but only in the presence of a heterogeneous Pd catalyst, although the catalyst activity was far less than when the 0.5% Pd-0.5% Fe/SiO₂ catalyst was employed for the reaction, suggesting that while there is a homogeneous reaction occurring with the leached Fe species there is also a heterogeneous component to the reaction rate.

Conclusion

In conclusion, we have demonstrated the efficacy of Pd-Fe supported catalysts towards the oxidation of phenol using H₂O₂ generated *in situ* from molecular H₂ and O₂, in a relatively short reaction time, with superior results achieved in comparison to using preformed H₂O₂. We have also identified some of the phenol oxidation intermediates that are responsible for the leaching of active metals from the surface of the catalyst support, namely Fe. We consider that through additional catalyst optimisation and reactor design it may be possible to ensure minimal leaching of metal while maintaining the excellent rates of phenol conversion reported.

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