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Catalytic Oxidation of Ethylbenzene to Acetophenone Using Alumina-Supported Dichromate: Process Optimisation and Development of a Continuous Process

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Abstract:

Potassium dichromate supported on neutral alumina is a heterogeneous catalyst for the liquid phase oxidation of hydrocarbons. The material has been used to catalyse the oxidation of ethylbenzene to acetophenone using air as the consumable oxidant with high selectivity and is truly catalytic in the metal, unlike homogeneous Cr(VI) systems. Optimisation of reaction conditions has been achieved in terms of air flow rate, agitator speed, and catalyst quantity. An induction period prior to achievement of maximum catalytic turnover, which is proportional to both temperature and the concentration of catalyst, may be reduced by doping the substrate with 5−15% acetophenone (w/w) and eliminated by doping with 30% (w/w) acetophenone. A rate of conversion of *ca.* 3.8% h^{-1} (0.39 turnover s^{-1}) may be achieved at a reaction temperature of 130 °C for a period of *ca.* 10 h before catalyst deactivation occurs. However, this rate may be maintained for periods in excess of 24 h by continuous addition of substrate to the reaction vessel in order to maintain a constant molar ratio of substrate to product. It may thus be concluded that, at high agitator speeds, the rate-limiting factor is adsorption/desorption at the catalyst surface (and is therefore affected by the overall polarity of the medium) rather than mass transfer between solid−liquid−gas interfaces. The catalyst has been successfully recovered and reused with no induction period, and initial activity is comparable with that for fresh catalyst, although deactivation occurs readily thereafter.

Introduction

The oxidation of organic substrates provides routes to a wide range of important functionalised molecules including alcohols, aldehydes, ketones, epoxides, and carboxylic acids. Traditional methods of oxidation often involve the use of stoichiometric quantities or large excesses of poisonous high oxidation state chromium, manganese, and osmium reagents.[1] Environmental and economic factors make the use of these reagents increasingly unacceptable.[2] Oxidation processes based on lower oxidation state transition metals such as Co(II), Mn(II), and Cu(II) in acetic acid media are also known,[3] and some are catalytic in the metal, using molecular oxygen as the consumable oxidant. However, the conditions are often harsh, the reagent mixture is corrosive (bromide is used as a promoter), and the chemistry is rarely selective. Environmentally acceptable catalytic partial oxidations of inexpensive substrates (including hydrocarbons) that operate under moderate conditions in the liquid phase with a high degree of selectivity are clearly desirable.

Considerable research effort has gone into the design of heterogeneous oxidation catalysts[4−6] leading to a wide variety of interesting materials including metalloporphyrins, zeolites and other molecular sieves, pillared clays and supported reagents, and other amorphous solid catalysts. All of these materials suffer from drawbacks including the need for expensive or hazardous co-oxidants (*e.g.*, organic hydroperoxides) and low activity in liquid phase reactions. Among the most interesting of the newer catalysts are synthetic molecular sieves with transition metals (*e.g.*, Ti, V) incorporated into their structures.[7] Vanadium silicate molecular sieves, for example, have recently been shown to be capable of oxidising 4-chlorotoluene to 4-chlorobenzaldehyde although the reaction uses peroxide as the source of oxygen, involves the use of a polar organic solvent (acetonitrile), and gives a range of products.[8] The microporous nature of such catalysts will preclude the use of large molecules, will limit diffusion rates (and hence reaction rates) in the liquid phase, and is likely to lead to catalyst deactivation through pore blockage.

A large number of supported reagents have been used in the liquid phase oxidation of organic substrates. The low cost of the support (commonly chromatographic materials such as silica gel), the mesoporosity of many of these supports, and the other general advantages of supported reagents (ease of handling, use, and recovery, low toxicity, and the avoidance of solvents) make them very attractive in the context of this area of chemistry. However, in oxidations, supported reagents have generally acted as *stoichiometric* reagents, making their large-scale use difficult and expensive. We have proven the possibility of developing genuinely

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Table 1. **Effect of air flow rate on the oxidation of ethylbenzene with EPAD**

air flow rate (mL min^{-1})	conversn rate in first 10 h[a] % h^{-1}	turnover s^{-1}	final conversn[b] (%)	mass balance (%)[b]
200	3.3	0.34	44.2	87.1
400	3.8	0.39	46.8	84.6
600	3.8	0.39	47.6	83.7

[a] Number of turnovers per catalytic chromium site per second, based on a chromium loading of 0.075 mmol g^{-1}. [b] Final weight of the contents of the reactor (after 24 h of operation) as a percentage of the initial weight. Mass loss is attributed to loss of the low-boiling water/ethylbenzene azeotrope from the reactor due to the high air flow rate.

catalytic supported reagents,[9] and one of these is the basis of the commercial catalyst "EPAD".[10] Under carefully controlled pH and temperature conditions, it was found that treatment of neutral alumina with potassium dichromate yields a material possessing a high surface area and chemisorbed Cr(VI) species (although the exact nature of the reagent−support interaction is still unknown). Substitution of the support material with basic alumina, for example, reduces catalytic activity, and no other supports have been found to yield genuinely catalytic materials at present. This material has been shown to promote a range of alkyl side chain and CH_2 bridge oxidations.[10] A previous paper[11] demonstrated novel catalytic oxidations of ethylbenzenes to acetophenones using EPAD. Indeed, the catalyst has been used to catalyse a range of other alkyl aromatic oxidations.[9,12] Here, we report on further studies of the ethylbenzene oxidation reaction using this material. These studies have shown the batch process to be hindered by problems of lengthy induction periods and catalyst deactivation, limiting overall reaction rates. We have optimised the reaction conditions by careful control of a range of parameters (*i.e.*, air flow rate, agitator speed, catalyst quantity, and reaction temperature) and improved catalyst performance by surmounting the problems of induction periods and catalyst deactivation, thus demonstrating the feasibility of running this process continuously.

Results and Discussion

Optimisation of Reaction Conditions. *1. Effect of the Air Flow Rate.* The effect of changing the air flow rate is shown in Table 1 and Figure 1. It was found that increasing the air flow rate from 200 to 400 mL min^{-1} increased the conversion rate during the first 10 h of operation but increasing the air flow rate to 600 mL min^{-1} had no further effect on the conversion rate. This suggests that, at air flow rates greater than 400 mL min^{-1}, there was no further improvement in mass transfer. It was also found that the mass balance decreased with increasing air flow rate. This was expected as the loss of ethylbenzene from the reactor increases with increasing air flow rate. A small amount of benzoic acid (*ca.* 3% by GC area) was produced as a by-product after 24 h of operation.

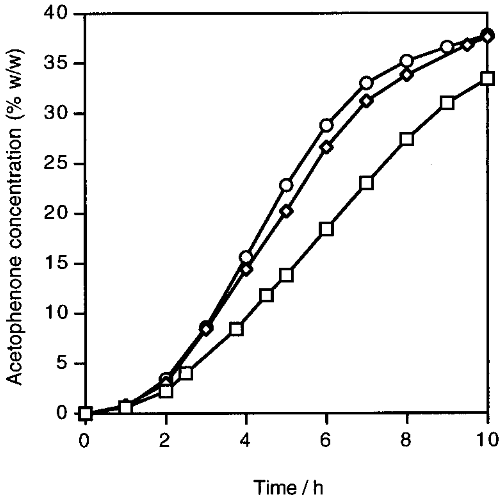

Figure 1. **Effect of air flow rate on the oxidation of ethylbenzene using the catalyst EPAD: (□) 200 mL min^{-1}; (◇) 400 mL min^{-1}; (○) 600 mL min^{-1}.**

Table 2. **Effect of agitator speed on the oxidation of ethylbenzene with EPAD**

agitator speed (rpm)	conversn rate in first 10 h[a] % h^{-1}	turnover s^{-1}	final conversn[b] (%)	mass balance (%)[b]
500	3.0	0.31	43.6	88.1
1000	3.0	0.31	43.7	86.5
1500	3.8	0.39	46.8	84.3
2000	3.6	0.37	45.2	84.6

[a] Number of turnovers per catalytic chromium site per second, based on a chromium loading of 0.075 mmol g^{-1}. [b] Final weight of the contents of the reactor (after 24 h of operation) as a percentage of the initial weight. Mass loss is attributed to loss of the low-boiling water/ethylbenzene azeotrope from the reactor due to the high air flow rate.

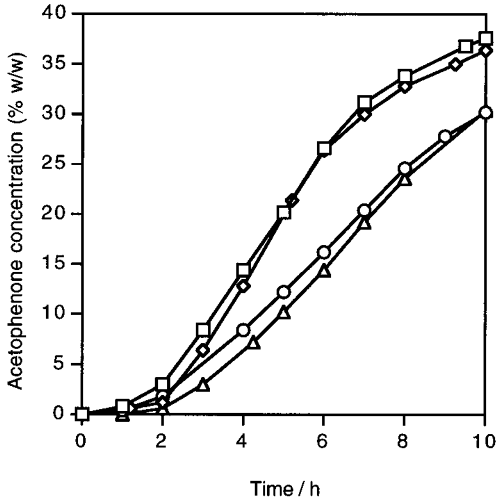

Figure 2. **Effect of agitator speed on the oxidation of ethylbenzene using the catalyst EPAD: (○) 500 rpm; (△) 1000 rpm; (◇) 1500 rpm; (□) 2000 rpm.**

2. Effect of Agitator Speed. Table 2 and Figure 2 show the effects of varying the agitator speed on the performance of the catalyst. There was an increase in both the conversion

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Table 3. **Effect of catalyst quantity in the reactor on the oxidation of ethylbenzene with EPAD**

catalyst quantity (g)	conversn rate in first 10 h[a] % h^{-1}	turnover s^{-1}	final conversn[b] (%)	mass balance (%)[b]
0.00	2.5	0.25	37.1	
0.125	3.5	0.36	47.9	92.7
0.25	3.6	0.37	47.4	91.1
0.50	3.7	0.38	46.5	86.5
1.00	3.8	0.39	46.8	84.6
2.00	3.6	0.37	49.2	82.5
5.00	1.1	0.11	43.9	89.1

[a] Number of turnovers per catalytic chromium site per second, based on a chromium loading of 0.075 mmol g^{-1}. [b] Final weight of the contents of the reactor (after 24 h of operation) as a percentage of the initial weight. Mass loss is attributed to loss of the low-boiling water/ethylbenzene azeotrope from the reactor due to the high air flow rate.

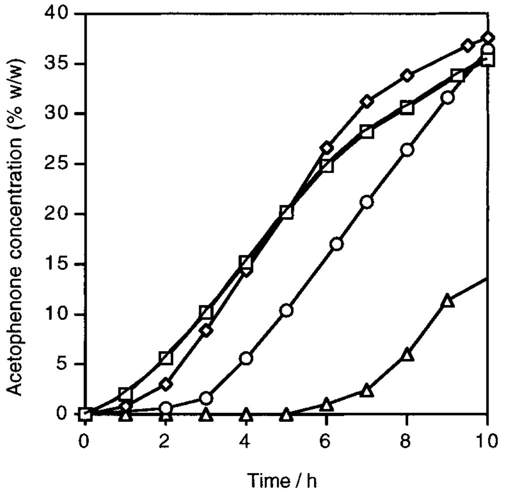

Figure 3. **Effect of catalyst quantity on the oxidation of ethylbenzene using the catalyst EPAD: (□) 0.13 g; (◇) 1.00 g; (○) 2.00 g; (△) 5.00 g.**

rate during the first 10 h of operation and the final conversion as the speed was increased from 500 to 1500 rpm. It was found that, at speeds higher than 1500 rpm, there was no improvement in either the conversion rate or the final conversion after 24 h of operation. This showed that operating at an agitator speed higher than 1500 rpm does not improve the mass transfer and is thus of no benefit. As observed with increasing air flow rate, the mass balance decreased with increasing agitator speed.

3. *Effect of Catalyst Quantity.* The effect of varying the catalyst quantity in the reactor is shown in Table 3 and Figure 3. It was observed that increasing the amount of catalyst in the reactor from 0.13 to 1.00 g did not have any effect on the conversion rate in the first 10 h of operation or on the final conversion. When the amount of catalyst in the reactor was further increased to 2.00 g and subsequently to 5.00 g, an induction period was observed. This induction period was found to increase with catalyst quantity above 2.00 g (Figure 3). This was probably due to poor desorption of the product, acetophenone, until the pores of the catalyst are saturated with the product. The greater the quantity of catalyst used, the greater the extent of product retention in the catalyst, thus resulting in the observed increase in the induction period. Table 3 also shows that the mass balance decreased as the catalyst quantity in the reactor increased.

Table 4. **Effect of operating temperature on the oxidation of ethylbenzene with EPAD**

temp (°C)	conversn rate in first 10 h[a] % h^{-1}	turnover s^{-1}	final conversn[b] (%)	mass balance (%)[b]
115	2.1	0.21	24.7	90.1
130	3.8	0.39	46.8	84.6

[a] Number of turnovers per catalytic chromium site per second, based on a chromium loading of 0.075 mmol g^{-1}. [b] Final weight of the contents of the reactor (after 24 h of operation) as a percentage of the initial weight. Mass loss is attributed to loss of the low-boiling water/ethylbenzene azeotrope from the reactor due to the high air flow rate.

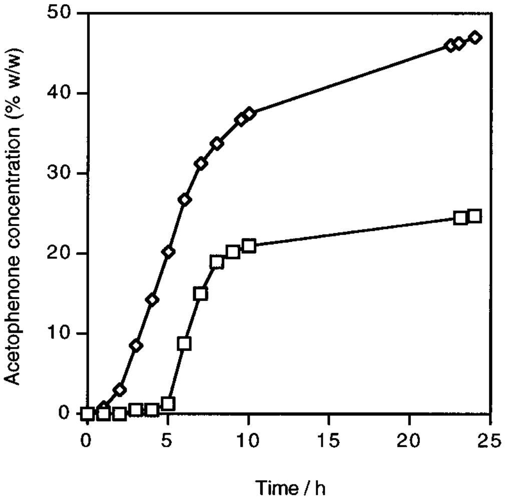

Figure 4. **Effect of temperature on the oxidation of ethylbenzene using the catalyst EPAD: (□) 115 °C; (◇) 130 °C.**

Without catalyst, a conversion of 37.1% was obtained after 24 h of operation (Table 3) and no induction period was observed. This background oxidation is thought to be caused by the presence of small quantities of organic peroxides, present in the ethylbenzene as impurities. The background oxidation was significantly suppressed (<10% after 24 h) by purifying the ethylbenzene with iodide prior to use. Furthermore, as an induction period is observed in the presence of catalyst, it may be concluded that the catalyst itself suppresses the background oxidation.

4. *Effect of Temperature.* Table 4 and Figure 4 illustrate the effect of temperature on catalyst performance. It can be seen that reducing the operating temperature from 130 to 115 °C significantly increased the induction period, although it curiously had little effect on the subsequent catalytic reaction rate. The conversion rate in the first 10 h of operation reduced from 3.8% h^{-1} (0.39 turnover s^{-1}) to 2.1% h^{-1} (0.21 turnover s^{-1}) when the temperature was lowered from 130 to 115 °C, which was largely attributed to an induction period of 5 h in the latter case. At 115 °C, the final conversion after 24 h of operation was approximately half that at 130 °C.

As a result of the above studies, the following experimental conditions were employed for all further work: quantity of catalyst in reactor = 1 g; quantity of ethylbenzene

Table 5. **Effect of recycling catalyst on the oxidation of ethylbenzene with EPAD**

no. of recycles	conversn rate in first 10 h[a]		final conversn (%)	mass balance[b] (%)
	% h^{-1}	turnover s^{-1}		
2.0 g fresh	3.6	0.37	49.2[b]	82.5[c]
first recycle	2.0	0.20	19.8[c]	87.8[d]

[a] Number of turnovers per catalytic chromium site per second, based on a chromium loading of 0.075 mmol g^{-1}. [b] Final weight of the contents of the reactor as a percentage of the initial weight. Mass loss is attributed to loss of the low-boiling water/ethylbenzene azeotrope from the reactor due to the high air flow rate. [c] After 24 h of operation. [d] After 10 h of operation.

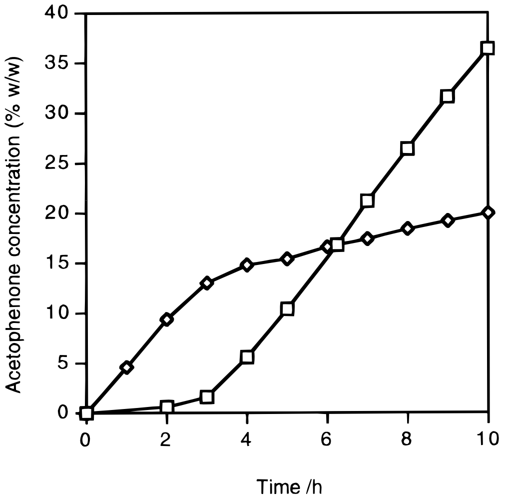

Figure 5. **Effect of recycle of the catalyst EPAD on the oxidation of ethylbenzene: (□) fresh catalyst; (◇) first recycle.**

in reactor = 300 mL (2.82 mol); air flow rate = 400 mL min^{-1}; temperature = 130 °C; agitator speed = 1500 rpm.

Catalyst studies. *1. Leaching.* Samples of the liquid remaining in the reactor following selected experimental runs were analysed by atomic absorption spectrometry in order to determine the dissolved chromium content. There was no evidence to suggest chromium leaching from the catalyst surface. This indicates that the catalysis is truly heterogeneous and that only chemisorbed chromium is present on the catalyst surface.

2. Recycle of the Catalyst. After 24 h of operation, a sample of the catalyst was separated from the product mixture by filtration and reused without any further processing or regeneration. Table 5 and Figure 5 show that the conversion rate in the first 10 h of operation was 2.0% h^{-1} (0.20 turnover s^{-1}) compared with 3.6 h^{-1} (0.37 turnover s^{-1}) when fresh catalyst was used. This reduction in performance of the catalyst may be due to the presence of deactivating species.

Figure 5 shows that no induction period was observed when the catalyst was recycled. This may be due to saturation of the catalyst pores with product during the first run. When the pores are saturated, all further reaction product is desorbed into the bulk liquid as it is produced.

3. Using Alumina in Place of the Catalyst. An experiment was carried out using the unmodified alumina support in place of the catalyst. A conversion of 13.4% was obtained after 24 h of operation, demonstrating that the support inhibits the inherent background oxidation. This may be explained by the fact that alumina is effective at peroxide removal, as illustrated by its use as a stationary phase in the column chromatography of organic peroxides.[13] Thus, the amount of organic impurities in the substrate was reduced and the level of background oxidation was decreased.

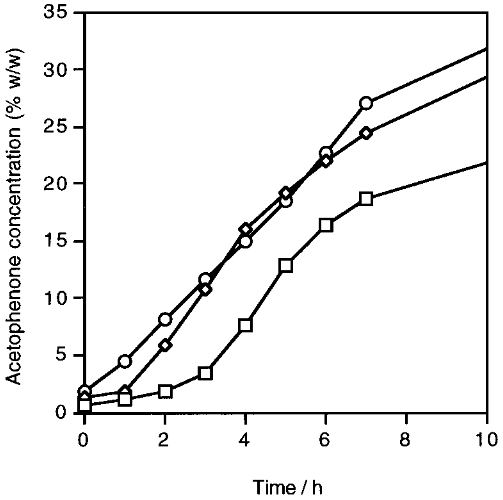

Figure 6. **Effect of doping the initial reaction mixture with acetophenone on the oxidation of ethylbenzene using the catalyst EPAD: (□) no doping; (◇) 10% (w/w) doping; (○) 30% (w/w) doping.**

Development of a Continuous Process. *1. Removal of Induction Period.* In light of the fact that the recycled catalyst shows no induction period, and this appears to be because the reused catalyst is already saturated with product, a number of experiments were performed to investigate the effect of adsorption/desorption of the substrate/product from the catalyst surface. Product desorption is favoured in increasingly polar media, since the acetophenone is notably more polar than ethylbenzene. To this end, the fresh catalyst (5.0 g) was soaked in pure acetophenone for 15 h before use. However, this resulted in total inhibition of the catalyst. Subsequent experiments were carried out in which the initial reaction mixture was doped with increasing quantities of acetophenone: 5, 10, 15, and 30% (w/w). Similar results were obtained with either 5, 10, or 15% doping. The results of the doping are shown in Figure 6. Low levels of doping reduce the induction period from *ca.* 3 to 1 h, and with 30% doping the induction period is eliminated, giving a linear catalytic rate profile during the first 7 h of operation.

2. Investigation of Catalyst Deactivation. The fact that conversion of ethylbenzene to acetophenone was never greater than *ca.* 50% suggests that deactivation of the catalyst was occurring. Since the deactivated catalyst could then be reused, without further processing, giving initial rates of reaction of *ca.* 3.8% h^{-1} (0.39 turnover s^{-1}), it is concluded that deactivation may be attributed to saturation of the catalyst pores with acetophenone. To investigate the nature of the deactivation further, fresh ethylbenzene was pumped into a 2.0 L reaction vessel containing 70% ethylbenzene and 30% acetophenone (w/w) at a rate of 20 g h^{-1} (0.19 mol h^{-1}), and the reaction at reflux was monitored by measurement of water production. Thus a virtually constant molar ratio of substrate to product was achieved. Figure 7

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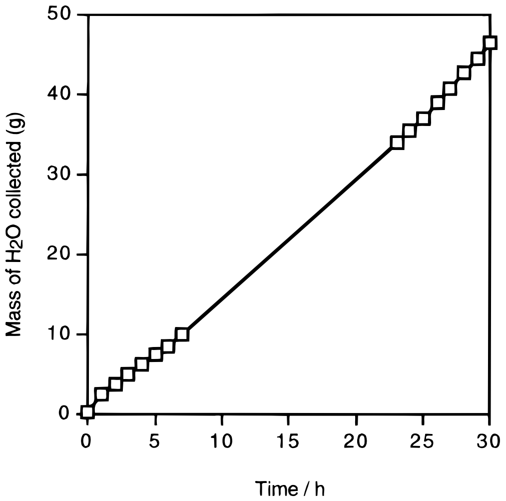

Figure 7. **Doping the reaction mixture with 30% acetophenone (w/w) and adding ethylbenzene to the reactor continuously at a rate such that a constant molar ratio of ethylbenzene to acetophenone results in a linear catalytic rate profile.**

shows that a linear rate profile was achieved throughout the duration of the experiment (31 h), with no induction period or catalyst deactivation. This, in principle, demonstrates the viability of running this process continuously rather than as a batch process.

Conclusions

EPAD is an active, selective catalyst for the liquid phase oxidation of ethylbenzene to acetophenone using air as the oxidant. The catalytically active chromium species is stable towards leaching under oxidation conditions. We conclude from our studies that, at high mixing rates, the rate-limiting factor in the catalytic process is adsorption/desorption at the catalyst surface (and is therefore affected by the overall polarity of the medium) rather than mass transfer between solid−liquid−gas interfaces. The induction period may be removed by doping with 30% acetophenone, and loss of catalyst activity can be eliminated (and hence a continuous conversion rate of *ca.* 3.8% h^{-1} (0.39 turnover s^{-1}) sustained) by maintaining a constant substrate:product molar ratio. This suggests that possibilities exist for running the oxidation of ethylbenzene using EPAD as a continuous process.

Experimental Section

Catalyst Preparation. $K_2Cr_2O_7$ (3 g; 1.02×10^{-2} mol) was dissolved in 100 mL (5.56 mol) of H_2O with warming. Support (Alcan alumina AA101) (50 g; 0.49 mol) was added and the pH adjusted to 4.0 with 36% HCl. The resulting suspension was stirred overnight, filtered, washed with an excess of water, and dried overnight at 65 °C.

The catalyst obtained had a dichromate loading of *ca.* 0.075 mmol g^{-1}, a particle size of 2−30 μm, and a wide pore size distribution with an average of 20 Å. The catalyst had a surface area of 86.9 $m^2\ g^{-1}$, measured by N_2 adsorption. The alumina support itself had a surface area of 102.3 $m^2\ g^{-1}$.

Catalyst Testing. The oxidation of ethylbenzene was carried out using an oxidation reactor consisting of a 500 mL vessel with baffles and overhead stirring. Air was used as the oxidant, supplied *via* a cylinder and air rotameter. The agitator speed was measured using a stroboscope. A thermocouple in the reactor vessel was linked to a temperature-controlled heating mantle to maintain a constant reactor temperature. A chiller unit was used to supply coolant to the condenser at a temperature of *ca.* 1.5 °C, to minimise substrate loss from the reactor. A Dean−Stark trap was fitted to remove water produced during the oxidation. The samples collected during catalytic reaction studies were analysed by gas chromatography using a Hewlett-Packard HP 6890 GC system. Combined gas chromatography/mass spectrometry (Finnigan MAT Magnum GC−MS) was used to identify unknowns. Atomic absorption spectrophotometry (Philips PU 9200 atomic absorption spectrophotometer) was used to measure the concentration of dissolved chromium ions in solution.

The oxidation of ethylbenzene using EPAD was carried out under the following experimental conditions: quantity of catalyst in reactor = 1 g; quantity of ethylbenzene in reactor = 300 mL (2.82 mol); air flow rate = 400 mL min^{-1}; temperature = 130 °C; agitator speed = 1500 rpm. Where indicated in the text, these experimental conditions were systematically varied in order to determine the effect of each parameter on the performance of the catalyst.

Purification of Ethylbenzene. An experiment was performed to remove dissolved peroxides from the substrate prior to use by reaction with aqueous iodide. The procedure used was as follows. NaI (12.0 g; 8.0×10^{-2} mol) was added to 200 mL (11.1 mol) of water and the mixture vigorously shaken with a 300 mL (2.82 mol) batch of ethylbenzene, giving a bright pink organic layer and yellow aqueous layer. The aqueous layer was tapped off, and the process was repeated. A small quantity of thiosulphate solution was added to the organic, giving clear organic and aqueous layers. The aqueous layer was removed, leaving peroxide-free ethylbenzene.

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