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# Exploring the feasibility of continuous CWAO of bisphenol A at near-ambient temperature and pressure through use of hydrophobic Pt catalysts

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ABSTRACT

Hydrophobic Pt CWAO-catalysts can achieve complete removal of bisphenol A from a flow of contaminated water in a trickle-bed reactor at an operating temperature of 120°C, total air pressure of 8 bar and a liquid-hourly space velocity of 26.6 $h^{-1}$ Although increasing the throughput of contaminated water while lowering the operating temperature results in bisphenol A conversions below 100%, these more demanding conditions allow structurally similar catalyst formulations to be differentiated from one another. At 60°C and 8 bar total pressure of air, 2%Pt supported on a SiC-TiC composite material has the highest initial activity from a group of three hydrophobic catalysts with similar surface areas and Pt particle diameters, but it begins to deactivate progressively after 15 hours on stream. This catalyst contains some localised hydrophilicity arising from the presence of surface $TiO_2$, which forms when the exposed TiC component of the support material oxidises during catalyst preparation. At 80 °C and ambient air pressure, the activity is lower but there are no signs of deactivation during 24 hours on stream. The results are consistent with metallic platinum providing the active sites for CWAO of bisphenol A, with oxygen being directly activated from the gas phase at elevated pressures, but with dissolved oxygen also contributing to the reaction particularly at ambient air pressure. Continuous and irreversible deactivation, which occurs at air pressures ≥4 bar, appears to be associated with high occupancy of the active sites by adsorbed oxygen, resulting in leaching of platinum into the aqueous phase.

## 1. Introduction

BPA (bisphenol A) is described as an *emerging contaminant* [1,2], and yet it is a common pollutant in municipal wastewater [3]. Although its presence in wastewater originates from its widespread use as a monomer in the synthesis of epoxy resin and polycarbonate plastic [4], it usually enters the water stream through the waste produced by its disposable end-products (*e.g.* bottles, packaging, paper, sanitary materials) [5]. As an endocrine disrupting chemical, BPA is associated with mutagenic and carcinogenic effects, and it is also suspected to be an obesogen [6] (a compound that leads to human weight-gain [7]). The safe limit for BPA ingestion set by the European Food Safety Authority (EFSA) is currently 4 μg per kg of human bodyweight per day [8], but that limit is now under review, with EFSA suggesting that a $2 \times 10^4$-fold reduction (to 0.2 ng $kg^{-1}$ $day^{-1}$) may be required [9].

Current biological methods used in the recycling of wastewater are not particularly effective at eliminating BPA [3,5,10]. Therefore, the burden on municipal water treatment plants could be reduced by transferring responsibility for controlling BPA release further upstream, before it enters the wastewater stream. This would require effective *end-of-pipe* decontamination systems to be installed at polluting sites. Ideally, these systems would have low capital and operating costs, require minimal intervention and maintenance, and would be largely passive in terms of their control. Perhaps, by example, their ease of application should be comparable to the exhaust-gas aftertreatment systems fitted inside the tailpipes of road vehicles [11–13]. One

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potential technology is CWAO (catalytic wet air oxidation), in which air is used as the source of $O_2$ for deep oxidation (*i.e.* mineralisation) of aqueous organic compounds to $CO_2$ [14–17]. However, there are high costs associated with installing and operating a multiphase reactor utilising current commercial catalyst technology [18], but these would be reduced by the development of more active catalysts which could be operated at lower temperatures and pressures [19].

In the field of CWAO research, BPA and related chemicals have not received as much attention as other organic pollutants such as phenol, carboxylic acids, nitrogen-containing compounds and short-chain alcohols (*e.g.* see reviews [15,17,20–25]). From the existing body of work in the open literature, the most promising catalysts for CWAO of BPA appear to be supported precious metal nanoparticles (Ru [26–28], Pt [29], Ag[30]), modified ceria [30], dispersed Fe [31,32] and titania-based materials [33–35]. When these catalysts are tested in flow reactors, they typically require a temperature greater than 120 °C and a partial pressure of $O_2$ ($p_{O_2}$) in excess of 1 bar ($10^5$ Pa), *i.e.* where the total air pressure, $p_T$, > 5 bar, in order to achieve high purification rates for a feed of liquid water containing 10–100 mg $dm^{-3}$ of BPA. Recently, however, Hao *et al.* have demonstrated that CWAO of BPA is feasible under ambient conditions [36], using nano-structured materials derived from $MnO_2$, but this study was carried out in a batch reactor. An outstanding challenge, therefore, is to achieve rapid and continuous removal of BPA from a flowing wastewater stream under ambient or near-ambient conditions of temperature and pressure.

In this study, we have used a trickle-bed reactor to evaluate a group of catalysts comprised of platinum nanoparticles dispersed on hydrophobic support materials. Similar catalysts have previously been shown to be highly active for continuous CWAO of phenol [37,38]. Starting from a set of benchmark conditions (T = 120 °C; $p_T$ = 8 bar; [BPA] = 10 mg $dm^{-3}$; liquid hourly space velocity = 26.6 $h^{-1}$), we have examined the effects of changing the operating parameters (space velocity, temperature and pressure) on three performance criteria: BPA conversion, selectivity to $CO_2$ formation, and catalyst durability.

## 2. Materials and methods

### 2.1. Catalyst preparation

Catalysts with low affinity for $H_2O$ were prepared by dispersing 2% Pt (by mass) on three SICAT™ silicon carbide support materials: (*i*) 1.6 mm trilobe extrudate of β-SiC with a nominal surface area of 25 $m^2$ $g^{-1}$ (for the catalyst referred to as 2%Pt/SiC(A) below); (*ii*) 1.6 mm trilobe extrudate of β-SiC with a nominal surface area of 30 $m^2$ $g^{-1}$ (for 2%Pt/SiC(B) below); (*iii*) 1.6 mm trilobe extrudate, made from a β-SiC and TiC composite, with a nominal surface area of 90 $m^2$ $g^{-1}$ (for 2%Pt/'SiC-TiC' below). The support materials were impregnated to incipient wetness with a solution of platinum acetylacetonate (≥ 96.5% purity based on Pt) dissolved in toluene (≥ 99.8%), before being dried and calcined (see Supporting Information for full method). To allow comparison with a hydrophilic catalyst, 2% Ru (by mass) was dispersed on alumina granules containing 5% ceria (by mass), by impregnating the support with ruthenium acetylacetonate (≥ 97%), to produce the catalyst referred to as 2%Ru/5%$CeO_2$-$Al_2O_3$ (see Supporting Information for full method).

### 2.2. Catalyst characterisation

Pre- and post-reaction characterisation of the catalysts was carried out using powder x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) with energy dispersive x-ray spectroscopy (EDX), temperature programmed reduction (TPR), thermogravimetric analysis, nitrogen physisorption (BET method) and helium pycnometry (pore volume measurement). Equipment details and methodology are provided in Supporting Information.

### 2.3. Catalyst evaluation

Catalyst activity, selectivity and durability were evaluated using a fixed bed, continuous-flow trickle bed reactor (the operating procedure and a schematic diagram of the reactor system are included in Supporting Information, while further details can be found in Žerjav *et al.* [35]). In our initial tests, in which a hydrophobic catalyst achieved 100% conversion, an aqueous BPA solution (10 mg $dm^{-3}$) was fed to the reactor (containing a 2 g charge of catalyst) at a rate of 0.275 $cm^3$ $min^{-1}$; the resultant liquid hourly space velocity (LHSV) was 26.6 $h^{-1}$. Synthetic air (20.8% $O_2$ and 79.2% $N_2$) was added at a rate of 120 $cm^3$ $min^{-1}$ (equivalent to a gas hourly space velocity of 11600 $h^{-1}$) concurrently with the aqueous BPA to the reactor, which was maintained at a total pressure of 8 bar throughout the initial tests. The exit stream from the reactor was periodically sampled, and its BPA content was analysed using HPLC separation followed by UV detection (λ = 210 nm). The extent of BPA mineralisation was determined by measuring the TOC (total organic content) of the exit stream, which also allowed the selectivity of the catalytic reaction to $CO_2$ formation to be monitored. When a blank reactor was tested under the initial conditions, the inlet and outlet concentrations of BPA were the same throughout 24 hours of testing, indicating that there was no conversion of BPA in the absence of a catalyst. After completion of the initial tests, several of the key parameters (LHSV, T, $p_T$) were altered systematically to allow discrimination between different catalyst formulations, and to provide insights into the reaction pathway and the mechanism of deactivation.

Activity profiles of BPA and TOC conversion against time on stream were not based on the average of several data-sets, but were plotted using data from individual performance tests. During some tests, periodic pulsing of the liquid feed gave rise to variability in BPA conversion of ±5% between individual data points, which can be seen in the sawtooth appearance of several of the activity profiles shown below.

## 3. Results and discussion

### 3.1. Effects of operating variables on CWAO activity

Initial testing was carried out on 2%Pt/'SiC-TiC', which had previously been found to be highly active for CWAO of phenol [38]. The XRD pattern (Fig. S1 in Supporting Information) showed that this catalyst contained metallic Pt crystallites, with a mean diameter of 19 nm (calculated using the Scherrer equation). XPS analysis (Fig. S2 in Supporting Information) indicated that the exposed platinum was in the form of $Pt^0$. As $Pt^0$ will activate $O_2$ and is hydrophilic (so is more likely than the hydrophobic support material to provide adsorption sites for the BPA in the aqueous phase), these results are consistent with the active sites in this catalyst being Pt atoms at the surface of the relatively large metallic nanoparticles of platinum.

Under comparable conditions to those used previously for phenol (T = 120 °C; $p_T$ = 8 bar; LHSV = 26.6 $h^{-1}$) but at a lower concentration of contaminant (10 mg $dm^{-3}$ instead of 1000 mg $dm^{-3}$) because BPA has lower solubility in water, 2%Pt/'SiC-TiC' converted 100% of the BPA throughout 24 h of testing (see Fig. S3 in Supporting Information). However, operating under these conditions of complete conversion with no apparent deactivation did not allow this catalyst to be differentiated from other highly active CWAO catalysts.

Increasing the LHSV from 26.6 to 48.4 and then to 96.8 $h^{-1}$ had no effect on the BPA conversion over 2%Pt/'SiC-TiC', although the TOC conversion decreased from 95% to 70%. It was not until the LHSV was doubled again, from 96.8 to 193.6 $h^{-1}$, that the BPA conversion dropped below 100%, while the TOC conversion decreased to 47% (Fig. 1). The high BPA conversion (100%) at LHSV values of 26.6, 48.4 and 96.8 $h^{-1}$ indicated an excess of active sites under these conditions, so that the surface reaction did not become site-limited until the LHSV was increased to 193.6 $h^{-1}$. The TOC analysis, however, was much more sensitive to the changes in LHSV, indicating that the surface reaction

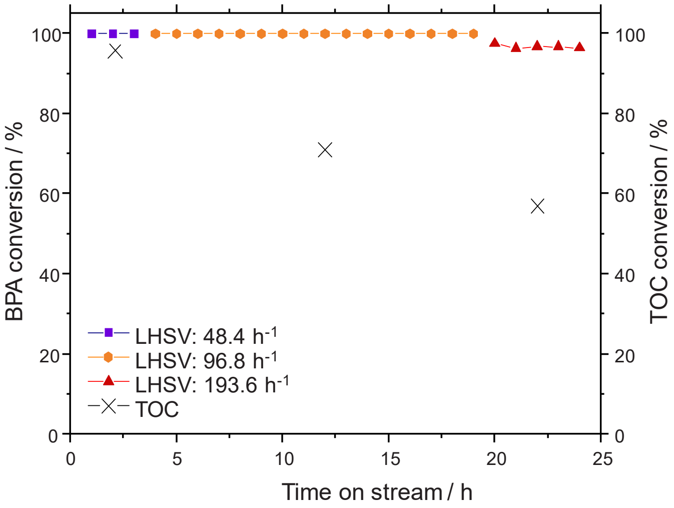

**Fig. 1.** Effect of increasing LHSV on CWAO performance of 2%Pt/'SiC-TiC' at T = 120°C and $p_T$ = 8 bar.

became less selective to $CO_2$ formation and more selective to partial oxidation products when the contact time between the reactants and catalyst was decreased (by increasing the LHSV). These results suggest that mineralisation of the partially oxidised intermediates is a slower process than their formation over this catalyst.

In another approach to lowering the BPA conversion below 100%, we decreased the site-specific rate of reaction by incrementally reducing the temperature of the 2%Pt/'SiC-TiC' catalyst while keeping $p_T$ and LHSV constant at 8 bar and 96.8 $h^{-1}$ respectively (see Fig. S4 in Supporting Information). Starting from 100% at 110 °C, the BPA conversion decreased to 98% when the temperature was lowered to 100 °C, and then to 95% at 80 °C. It was not until the temperature was reduced to 60°C that the initial BPA conversion decreased below 90% (as did the TOC conversion) and the catalyst could now be seen to lose activity over several hours of testing.

### 3.2. *Structure-activity correlations*

Fig. 2 shows the performance of 2%Pt/'SiC-TiC' compared to three other catalysts, when tested under the more demanding conditions identified above (T = 60°C; $p_T$ = 8 bar; LHSV = 96.8 $h^{-1}$). Two of the catalysts were alternative formulations of 2%Pt supported on a hydrophobic support, while the third was 2%Ru/5%$CeO_2$-$Al_2O_3$ (the most active in a series of hydrophilic Ru catalysts identified for CWAO of phenol [37]). The initial activity of each of the Pt catalysts, as indicated by the conversion during the first 1–2 hours of testing, was >5 times that of 2%Ru/5%$CeO_2$-$Al_2O_3$, and this difference in activity was maintained even after the catalysts had undergone on-stream deactivation. Of the three Pt catalysts, 2%Pt/'SiC-TiC' had the highest initial activity as indicated by the initial BPA conversion of 88%, while 2%Pt/SiC(A) had similar activity to 2%Pt/SiC(B), giving rise ~70% initial BPA conversion. 2%Pt/SiC(A) showed the highest rate of deactivation during the first 24 hours of testing before stabilising, whereas 2%Pt/'SiC-TiC' only began to deactivate after about 15 hours, but thereafter its deactivation was continuous. 2%Pt/SiC(B) showed the greatest stability, which resulted in its activity exceeding that of 2%Pt/'SiC-TiC' after 36 hours. At the end of 48 hours of testing, the order of activity was: 2%Pt/SiC(B) > 2%Pt/'SiC-TiC' > 2%Pt/SiC(A).

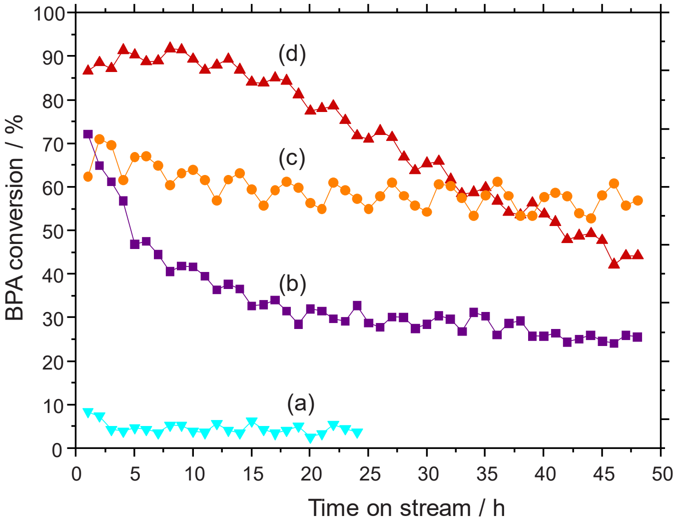

**Fig. 2.** CWAO of BPA at T = 60°C, $p_T$ = 8 bar and LHSV = 96.8 $h^{-1}$ over (a) 2% Ru/5%$CeO_2$-$Al_2O_3$, (b) 2%Pt/SiC(A), (c) 2%Pt/SiC(B), (d) 2%Pt/'SiC-TiC'.

Despite the marked differences in the activity profiles for the three Pt catalysts (Fig. 2), these were not reflected in the characterisation data. In fact, the textural properties of the catalysts (Table 1) were quite similar, even though the Pt was dispersed on three distinct support materials. In each case, the pore volume was 0.3±0.05 $cm^3$ $g^{-1}$, while the BET surface area was 34±5 $m^2$ $g^{-1}$ and the Pt particle size was 16±3 nm. Although characterisation by XRD (see Fig. S1 in Supporting Information) and TPR (Fig. S5 in Supporting Information) indicated that platinum oxide was present in 2%Pt/SiC(A) and 2%Pt/'SiC-TiC', surface analysis by XPS showed that essentially all of the exposed platinum was metallic in the three catalysts (Fig. S2 in Supporting Information).

The most notable difference between the three catalysts was in their surface concentrations of Pt (Table 1). The concentration of Pt at the surface of 2%Pt/'SiC-TiC' was 2.9 mol-%, which was substantially lower than for 2%Pt/SiC(A) (11.1 mol-%) and 2%Pt/SiC(B) (6.8 mol-%). SEM with EDX indicated that the platinum was dispersed more evenly throughout the pelleted support material in 2%Pt/'SiC-TiC' than in the other two catalysts (where no Pt was detected during cross-sectional analysis of the pellet interiors). Another notable feature of the 2%Pt/'SiC-TiC' catalyst was that its BET surface area (34 $m^2$ $g^{-1}$) was much lower than either the nominal or measured surface area of the SiC-TiC support material (90 and 98 $m^2$ $g^{-1}$ respectively).

XPS analysis (Fig. S6 in Supporting Information) indicated that, during preparation of the catalyst, TiC at the surface of the support material had transformed into $TiO_2$, but this was not detected by XRD (Fig. S1 in Supporting Information). Thermogravimetric analysis of the support material heated under air (Fig. S7 in Supporting Information) showed that it underwent a two-step increase in mass of 3.5%, beginning at 300 °C and stabilising just above 500 °C (the calcination temperature used during preparation of the fully formulated catalysts). We conclude, therefore, that TiC at the surface of the SiC-TiC is oxidised during calcination of the catalyst, resulting in the large drop in BET surface area. This conclusion is supported by the results from a set of calcination experiments (Table S1 in Supporting Information), which showed that calcining the SiC-TiC support material in air for 2 hours at just 300 °C resulted in a reduction in surface area from 98 to 32 $m^2$ $g^{-1}$. The fact that the $TiO_2$ on the catalyst surface was XRD-invisible suggests that it forms either as small crystallites which decorate the surface of the Pt nanoparticles, or as an amorphous overlayer which partially obscures the nanoparticles; both surface structures would explain the particularly low surface concentration of Pt detected in 2%Pt/'SiC-TiC'.

The transformation of TiC to $TiO_2$ at the surface of the support material would be expected to increase the surface hydroxyl functionality, which in turn would increase the affinity of the catalyst for water by allowing dipole interactions with $H_2O$ molecules [39]. Thermogravimetric analysis showed that a negligible amount of water vapour had been adsorbed by 2%Pt/SiC(A) and 2%Pt/SiC(B) following calcination and cooling of the catalysts under ambient air, whereas a small but measurable amount (0.06% of the original mass of catalyst sample) had

**Table 1**
Characterisation of catalysts.

| Catalyst | BET surface area ($m^2$ $g^{-1}$) | Nominal surface area of support material[a]($m^2$ $g^{-1}$) | Surface concentration of active metal[b](mol-%) | Particle size of active metal[c](nm) | Pore volume ($cm^3$ $g^{-1}$) | Support pore volume($cm^3$ $g^{-1}$) |
|---|---|---|---|---|---|---|
| 2%Pt/SiC(A) | 29 | 25 | 11.1% Pt | 13.5 | 0.3 | 0.3 |
| 2%Pt/SiC(B) | 35 | 30 | 6.8% Pt | 18.7 | 0.3 | 0.3 |
| 2%Pt/'SiC-TiC' | 34 | 90 | 2.9% Pt | 18.6 | 0.3 | 0.3 |
| 2%Ru/5% $CeO_2$-$Al_2O_3$ | 110 | - | 2.1% Ru | 25.6 | 0.5 | 0.5 |

[a] value quoted by supplier;
[b] measured by XPS;
[c] from XRD

been adsorbed by 2%Pt/'SiC-TiC' (Fig. S8 in Supporting Information). However, when the water affinity of 2%Pt/'SiC-TiC' was compared to that of the hydrophilic 2%Ru/5%$CeO_2$-$Al_2O_3$ catalyst, by immersing each catalyst in liquid water for 24 hours before drying and then carrying out thermogravimetric analysis (Figs. S9 and S10 in Supporting Information), the surface specific desorption of water for 2%Pt/'SiC-TiC' was only 18% of that released by the Ru catalyst. These results indicate that the macroscopic water affinity was not substantially changed by the surface transformation of TiC to $TiO_2$, suggesting that any increase in hydrophilicity was highly localised, which in turn is consistent with a model in which the surface of the Pt nanoparticles in 2%Pt/'SiC-TiC' is partially covered by either small crystallites or an amorphous layer of hydrophilic $TiO_2$.

### 3.3. *Catalyst deactivation*

Based on the 48-hour activity profile for 2%Pt/'SiC-TiC' (in Fig. 2) we expected this catalyst to deactivate completely over a period of 80–100 hours on stream. In practice, however, we found that the activity took 172 hours to drop to zero (Fig. S11 in Supporting Information). During deactivation, the pH of the aqueous phase decreased (Table S2 in Supporting Information), indicating the formation of acidic by-products from the incomplete oxidation of BPA. Subsequent thermogravimetric analysis of the deactivated catalyst showed that it had retained a substantial amount of adsorbed or un-desorbed species, resulting in a 9.5% loss in mass which occurred in several consecutive steps (Fig. S12 in Supporting Information). We tentatively ascribe the individual steps to desorption of $H_2O$ (75–250 °C), followed by decomposition of surface species such as carboxylates (250–320 °C and 320–450 °C) and carbon-rich phenolic derivatives (450–580 °C), which are known to be formed during CWAO of phenol but are also likely to be intermediates and by-products on the pathway to the mineralisation of BPA [40–42].

The Pt loading, measured by EDX spectroscopy of ground samples, decreased from 1.74% in the fresh catalyst to 1.43% in the deactivated catalyst, which is consistent with leaching of platinum [21] by the organic species in the aqueous phase [22,43]. Characterisation by XRD showed a significant reduction in the intensity of the peaks associated with metallic platinum (at $2\theta = 40°$, 46° and 67.5°) following deactivation of the catalyst (Fig. 3). As 82% of the original platinum content was still present, and there was no indication that the residual platinum was now in an oxidised form (*i.e.* the definitive peak at $2\theta = 54.5°$ corresponding to $PtO_2$ was absent), the attenuation of the $Pt^0$ peaks signifies a change in the size or morphology of the platinum particles, presumably as a consequence of Pt dissolution in the aqueous phase, followed perhaps by some re-deposition of the metal (as reported for Pt/C catalysts during the selective oxidation of glucoside in water [43]). Collectively, our results from post-reaction characterisation indicate that deactivation was associated both with the presence of strongly bound surface species and with significant changes in the platinum component of the catalyst.

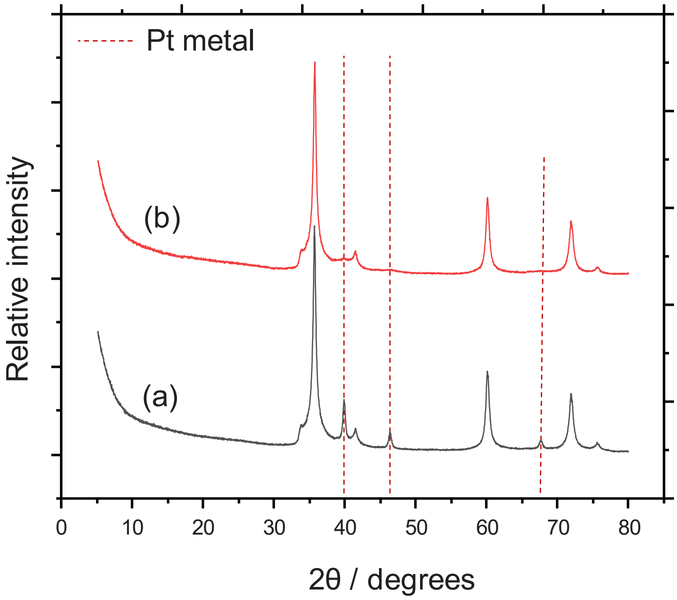

**Fig. 3.** XRD patterns for 2%Pt/'SiC-TiC': (a) as-prepared catalyst; (b) deactivated catalyst (after 172 hours testing at T = 60°C. $p_T = 8$ bar and LHSV = 96.8 $h^{-1}$). Dotted lines indicate the peaks associated with metallic platinum.

Raising the testing temperature from 60 °C to 80 °C (while maintaining $p_T$ at 8 bar and LHSV at 96.8 $h^{-1}$) provided insights into the predominant cause of catalyst deactivation. Using a fresh sample of 2% Pt/'SiC-TiC', the conversion at 80°C was initially 95%, but it declined to 65% over 24 hours of testing (Fig. 4), which represented a higher rate of deactivation than at 60°C. This suggests that deactivation is primarily caused by leaching and restructuring of the Pt (which become more rapid at higher temperatures) and not by the blocking of active sites by adsorbed surface species (which would be expected to become more mobile and reactive at higher temperatures).

### 3.4. *Roles of dissolved and gas-phase oxygen*

By varying the total pressure of the air feed through fresh charges of catalyst (at 80 °C), we were able to observe the effects of oxygen availability in the aqueous and gaseous reactant phases on the performance of 2%Pt/'SiC-TiC'. Increasing $p_T$ from 8 bar to 10 bar, or lowering it to 6 bar, had very little effect on the initial conversion of BPA (93±2%), whereas it decreased to 82% at 4 bar and to 30% at 1 bar (Fig. 4). TOC conversion values (measured after 20 hours on stream) were within the range 40–50% at the four above-atmospheric pressures ($p_T$ = 4, 6, 8 and 10 bar), corresponding to $CO_2$ selectivities between 80% and 95%. By contrast, at atmospheric pressure ($p_T = 1$ bar) the TOC conversion (16%) and $CO_2$ selectivity (57%) were much lower,

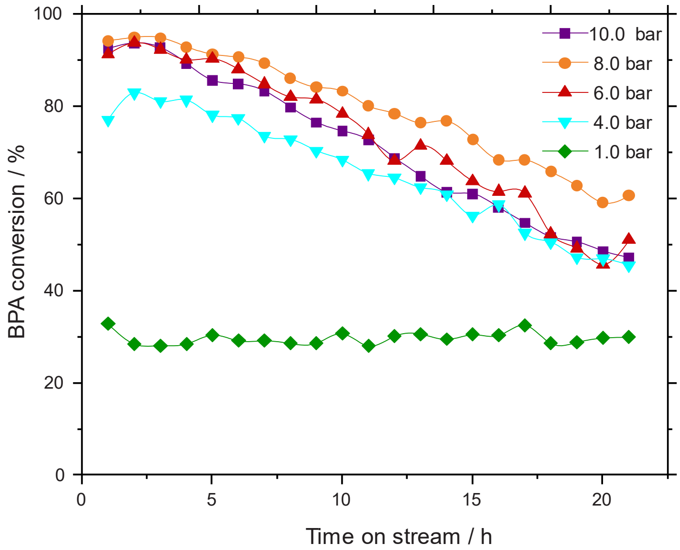

**Fig. 4.** Effect of changing the air pressure on the CWAO performance of 2%Pt/'SiC-TiC' at T = 80 °C and LHSV = 96.8 $h^{-1}$.

indicating that the complete oxidation of BPA was limited by oxygen availability at the catalyst surface. However, the most striking observation was that, whereas the rate of deactivation was similar at 4, 6, 8 and 10 bar (with BPA conversion decreasing by 40±5% over 24 hours), it was negligible at 1 bar, with the BPA conversion remaining stable at 30±2%.Fig. 5 shows the initial BPA conversion values for 2%Pt/'SiC-TiC' at 80°C (from Fig. 4) re-plotted as a function of molar oxygen concentration in the aqueous phase. The oxygen concentration has been calculated using the Tromans equation [44] (Equation 1), which relates oxygen solubility to the partial pressure of $O_2$ and the temperature of water.

$$C_{aq} = p_{O_2} \exp\left( \frac{0.046T^2 + 203.35T\ln\left(\frac{T}{298}\right) - (299.378 + 0.092T)(T - 298) - 20.591x10^3}{(8.3144)T} \right)$$

**Equation 1.** Tromans equation used to calculate concentration of aqueous oxygen at a specific temperature and air pressure, where $C_{aq}$ is molal concentration of dissolved $O_2$ (mol $kg^{-1}$), $pO_2$ is partial pressure of $O_2$ (atm), T is temperature (K).

At low pressures of air ($p_T < 5$ bar) and therefore low partial pressures of $O_2$ ($p_{O_2} < 1$ bar), BPA conversion showed an almost linear increase as a function of the oxygen concentration in the aqueous phase, before beginning to level at concentrations above 0.7 mmol $dm^{-3}$ (when $p_T > 5$ bar). The near-linear region below 0.7 mmol $dm^{-3}$ agrees well with the partial positive-order dependence on oxygen solubility that has been reported for CWAO of phenol over several types of catalyst (Pt [18], CuO [45], CuO-NiO [46]).

Comparing TOC conversion for the different air pressures (Fig. 6), the trend indicates that, above a threshold that lies between 1 and 4 bar, the mineralisation of BPA over 2%Pt/'SiC-TiC' at 80°C has a near-zero order dependence on the partial pressure of oxygen. We note that near-zero order dependence with respect to $O_2$ has been reported for the gas-phase deep oxidation of volatile organic compounds over supported platinum [47]. We propose, therefore, that there are three pressure-dependent surface reaction regimes during CWAO over hydrophobic Pt catalysts at constant temperature and LHSV. At air pressures between 1 and 4 bar (where $p_{O_2} < 1$ bar), the catalytic activity relies primarily (but not exclusively) on dissolved oxygen (as suggested by the near-linear portion below 0.7 mmol $dm^{-3}$ in Fig. 5); at air pressures between 4 and 10 bar (where the rate of both BPA and TOC conversion is approximately zero order with respect to oxygen partial pressure), gas-phase $O_2$ is the predominant source of reactive oxygen species; this is also the case at air pressures above 8 bar, but now the presence of stable oxygen species on the Pt surface also has an inhibiting effect on the catalytic reaction (as suggested from the inflexions in both Figs. 5 and 6).

The threshold in air pressure that lies between 1 and 4 bar also represents a boundary between negligible and continuous deactivation of 2%Pt/'SiC-TiC' at 80°C, as can be seen from Fig. 4. Based on the

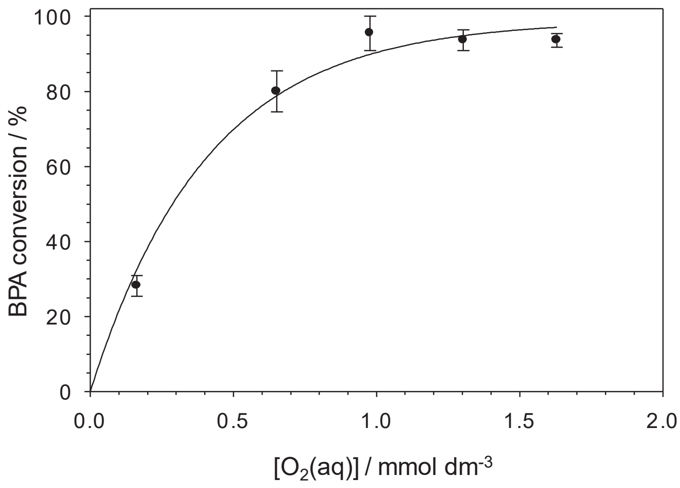

**Fig. 5.** Initial BPA conversion during CWAO over 2%Pt/'SiC-TiC' at T = 80 °C and LHSV = 96.8 $h^{-1}$ plotted as a function of concentration of aqueous oxygen.

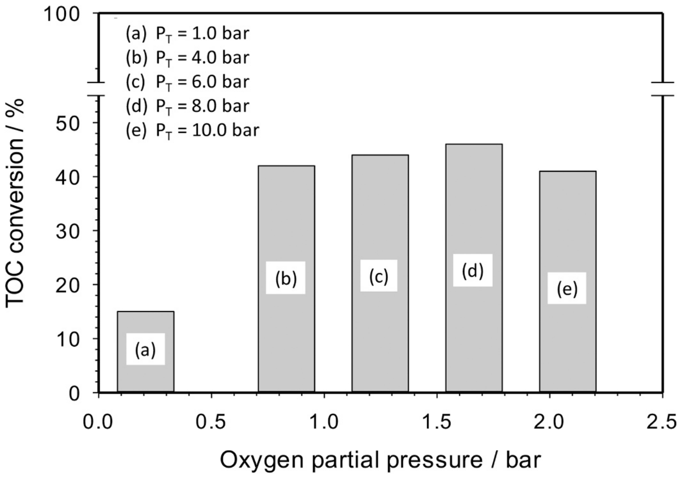

**Fig. 6.** Effect of oxygen partial pressure on TOC conversion after 20 hours of testing, during CWAO of BPA over 2%Pt/'SiC-TiC' at T = 80°C and LHSV = 96.8 $h^{-1}$.

comparison of characterisation data (in Section 3.2) for the fresh catalyst and after its complete deactivation (following the test shown in Fig. S11 in Supporting Information), we envisage that the platinum morphology does not undergo any significant changes under reaction conditions at atmospheric pressure. This would mean that essentially all the active sites, which were on the surface of the relatively large metallic nanoparticles, were retained and remained active during 24 hours of testing (Fig. 4). By contrast, above the pressure threshold (*i.e.* at $p_T = 4$, 6, 8 and 10 bar), we expect that surface oxidation leads to progressive dissolution and re-structuring of the Pt, resulting in irreversible deactivation. As yet, it is not clear whether over-oxidation at the higher pressures induces the formation of ionic platinum, which is more soluble than $Pt^0$ in the aqueous phase, or if increasing chemisorption of $O_2$ favours the formation of acidic intermediates, which promote leaching of metallic platinum through the formation of soluble $Pt^0$ complexes.

### 3.5. Summary of temperature and pressure effects

Based on our earlier CWAO studies, in which we used a phenolic solution as the aqueous phase [37,38], we concluded that hydrophobic Pt catalysts can function by activating oxygen directly from the gas-phase while activating organic molecules from the aqueous phase. We now propose that a similar mechanism can also apply when hydrophobic catalysts are used to treat BPA-contaminated water, but it tends to predominate at the higher pressures normally used for CWAO. At ambient or near-ambient pressure, $O_2$ molecules dissolved in the aqueous phase play a more significant role in generating reactive oxygen species on the catalyst surface. This type of condition-dependent change in the predominant mode of oxygen mass transfer was first proposed by Lavelle and McMonagle [48] for CWAO of formic acid over highly hydrophobic Pt catalysts (albeit in a spinning basket reactor, where the switchover from aqueous to gas-phase $O_2$ occurred as the speed of rotation was increased).

The activation of aqueous $O_2$ can be promoted by increasing the affinity of the catalyst for water, but this needs to occur specifically in the vicinity of the active sites on the surface of the hydrophilic $Pt^0$ nanoparticles. This would explain why 2%Pt/'SiC-TiC' shows much higher initial activity during CWAO of BPA than other catalyst formulations with similar composition and textural characteristics. During thermal pre-treatment of 2%Pt/'SiC-TiC', the surface of the TiC component of the support material oxidises to $TiO_2$ in an XRD-invisible form, which partially covers the $Pt^0$ nanoparticles. We expect that the $TiO_2$ increases the local hydrophilicity around the active sites, without substantially altering the overall hydrophobicity of the catalyst.

Both the activity and the rate of deactivation of hydrophobic Pt catalysts are sensitive to the air pressure (and therefore the partial pressure of $O_2$) inside the reactor. When operating at ambient pressure and near-ambient temperature, the oxidation of BPA is limited by $O_2$ availability, suggesting that there is low occupancy of the Pt surface by oxygen species, due to a low rate of mass transfer of $O_2$. Under these conditions, the catalytic activity is, nevertheless, highly stable. By contrast, at elevated pressures, persistent and irreversible deactivation can take place, resulting in complete loss of activity after 2–3 days of continuous operation. The deactivation is associated with leaching of some platinum from the catalyst surface, and with the restructuring of the remaining platinum. In view of the correlation between elevated air pressure and rate of deactivation, we conclude that high occupancy of the sites on the Pt nanoparticles by oxygen species promotes the dissolution of exposed platinum in the aqueous phase. The dissolution and any subsequent re-deposition of the platinum leads to re-structuring of the Pt nanoparticles into a less active surface morphology.

## 4. Conclusions

In order to overcome the existing barrier of low catalytic activity, current CWAO flow-reactors invariably need to be operated at temperatures above 100 °C, which in turn means that elevated pressures are also required in order to maintain the water in the liquid phase and to ensure high solubility of $O_2$. Our results show that, by using a hydrophobic Pt catalyst with localised hydrophilicity, water contaminated with bisphenol A can be treated at 80 °C and atmospheric pressure. Although the catalyst design and reactor engineering have yet to be optimised for high conversion in a single pass under these mild conditions, there are no signs of the current most active catalyst losing any of its ability to oxidise bisphenol A to $CO_2$ during 24 hours of laboratory testing. The activity and durability of this catalyst suggest that it may yet be possible to develop a passive end-of-pipe CWAO process for the treatment of industrial wastewater, which will operate under normal pressure of air and utilise low-grade waste heat to maintain the catalytic reactor at its optimum temperature.

## CRediT authorship contribution statement

**Korrin Saunders:** Writing – original draft, Visualization, Investigation, Formal analysis. **Stanislaw Golunski:** Writing – original draft, Supervision, Funding acquisition, Conceptualization. **Stuart H. Taylor:** Writing – review & editing, Supervision. **Pawel Plucinski:** Writing – review & editing, Visualization, Supervision, Funding acquisition, Conceptualization. **Albin Pintar:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization. **Gregor Žerjav:** Supervision, Funding acquisition, Conceptualization.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data Availability

Data will be made available on request.

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## Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.apcata.2024.119637.

Information on the data underpinning the results in this article, including how to access them, can be found in the Cardiff University data catalogue at doi:10.17035/d.2024.0310020078.

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