ORCA – Online Research @ Cardiff

This is an Open Access document downloaded from ORCA, Cardiff University's institutional repository:https://orca.cardiff.ac.uk/id/eprint/113770/

This is the author's version of a work that was submitted to / accepted for publication.

Citation for final published version:

Saunders, Korrin, Davies, Dafydd, Golunski, Stanislaw , Johnston, Peter and Plucinski, Pawel 2018. Making the most of precious metal nanoparticles in the purification of industrial wastewater by catalytic wet air oxidation. Johnson Matthey Technology Review 62 (4) , pp. 429-437. 10.1595/205651318X15299289846952

Publishers page: http://dx.doi.org/10.1595/205651318X15299289846952

Please note:
Changes made as a result of publishing processes such as copy-editing, formatting and page numbers may not be reflected in this version. For the definitive version of this publication, please refer to the published source. You are advised to consult the publisher's version if you wish to cite this paper.

This version is being made available in accordance with publisher policies. See http://orca.cf.ac.uk/policies.html for usage policies. Copyright and moral rights for publications made available in ORCA are retained by the copyright holders.

https://doi.org/10.1595/205651318X15299289846952 *Johnson Matthey Technol. Rev.*, 2018, **62**, (4), 429–437

JOHNSON MATTHEY
TECHNOLOGY REVIEW

www.technology.matthey.com

Making the Most of Precious Metal Nanoparticles in the Purification of Industrial Wastewater by Catalytic Wet Air Oxidation

Revealing synergy between platinum and catalyst support

Korrin Saunders, Dafydd Davies, Stan Golunski
Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Cardiff CF10 3AT, UK

Peter Johnston
Johnson Matthey Plc, Orchard Road, Royston SG8 5HE, UK

Pawel Plucinski*
Department of Chemical Engineering, University of Bath, Bath BA2 7AY, UK

***Email:** P.Plucinski@bath.ac.uk

The aim of catalytic wet air oxidation is to use air to remove organic contaminants from wastewater through their complete oxidation, without having to vaporise the water. To date, the widespread exploitation of this process has been held back by the low activity of available catalysts, which means that it has to be operated at above-atmospheric pressure in order to keep the water in the liquid phase at the elevated temperatures required to achieve complete oxidation. Here we present an overview of an ongoing study examining the key requirements of both the active phase and the support material in precious metal catalysts for wet air oxidation, using phenol as the model contaminant. The major outcome to date is that the results reveal a synergy between platinum and hydrophobic support materials, which is not apparent when the active phase is ruthenium.

1. Need for Catalytic Wet Air Oxidation

The generation of wastewater from both industrial and domestic processes, can lead to the release of hazardous organic pollutants, which, if left untreated, can cause severe problems for our ecosystems. Therefore, with the ever-growing concern for the environment, and strict national water quality regulations, it is necessary to develop greener and more efficient processes to treat such pollutants. Industrial wastewater streams can contain recalcitrant, non-biodegradable, toxic organic compounds (1), such as phenol and its derivatives. Phenolic compounds are important chemical precursors for many industrial processes, where they are widely used as raw materials for production of petrochemicals, dyes, pesticides, plastics and pharmaceuticals (2). As a result, these compounds are commonly encountered in industrial effluents and surface water. Phenol itself is both toxic and corrosive, and, if allowed to enter water streams, it can cause severe problems for aquatic life (3, 4). Phenol is therefore often used as a model organic pollutant for contaminated wastewater due to its generic properties and prevalence in industrial processes (5).

Efficient and economical technologies for the removal of toxic organic contaminants in wastewater streams are imperative to produce reusable process water and environmentally friendly effluents (6). There are several different methods for the treatment of toxic wastewater, including biological, thermal and advanced oxidation technologies. The choice of an appropriate treatment method often depends on the toxicities and concentrations of the

 © 2018 Johnson Matthey

pollutants in the wastewater. Biological treatment is the most commonly used depolluting method (7) and is widely applied to residual wastewaters. Microorganisms are used to degrade pollutants, however these processes require long residence times and are not suitable for the treatment of toxic contaminants due to biomass poisoning (1). Thermal treatment methods include incineration, which, unlike biological methods, is more suited to wastewater with a high concentration of contaminants. Incineration, however, is extremely energy extensive, requiring high operating temperatures and pressures, thus making it a high cost process. Incineration can also lead to the release of atmospheric pollutants, such as dioxins and furan (8), and so can create new environmental problems rather than presenting an entire solution. Both processes have their advantages, however neither are effective for wastewaters which contain organic pollutants in the range of a few hundred to a few thousand parts per million – these wastes are too dilute to incinerate, yet too toxic to be biologically treated (5).

A more versatile process for toxic wastewater treatment is wet air oxidation (WAO), in which complex organic contaminants are converted into simpler biodegradable molecules or ideally into carbon dioxide and water. WAO can cope with water streams that are too dilute for incineration, but too concentrated for biological treatment, without releasing hazardous emissions such as NOx, SO_2 and HCl (9). Furthermore, the use of air as a clean source of oxidant makes it more environmentally friendly than those technologies that rely on strong oxidising agents. However, the process requires a combination of high temperature (to achieve high rates of reaction) and high pressure (to keep the wastewater in the liquid phase) (10), which can make it highly energy intensive.

The process economics and wider environmental impact of WAO can be substantially improved by the addition of a catalyst i.e. by changing the operating mode to catalytic wet air oxidation (CWAO). Not only does this reduce the severity of the reaction conditions, but it can also open up reaction pathways which can lead to the oxidation of even refractory pollutants (1). The operating costs of CWAO can be as low as half that of WAO, due to the milder operating conditions and shorter residence times (11) (typically WAO operates at temperatures of 210–350°C and pressures of 20–200 bar (9, 12)). Significantly, complete oxidation is often achieved with CWAO, ensuring the negligible release of organic compounds.

Since the 1970s, when supported copper oxide was one of the first catalysts reported for CWAO (13), numerous homogeneous and heterogeneous catalyst formulations have been found to be active (14), including graphene oxide (15), N-doped carbon nanotubes (16), highly defective mixed-metal oxides (17) and pillared clays (18), as well as more conventional metal oxides and supported metals (1, 3, 19). Here, we report on an ongoing investigation of supported platinum and ruthenium nanoparticles, which are among the most active and stable CWAO catalysts (11, 20, 21), especially when the support contains ceria (4, 22, 23). The results from a study of compositional variables provide insights into the design of optimised CWAO catalysts, which can allow: (i) lower operating temperatures; (ii) shorter induction times before maximum conversion is achieved for the conversion of organic contaminants to CO_2; (iii) lower loadings of the active-metal content of the catalyst.

2. Method

2.1 Catalyst Preparation and Characterisation

Alumina (γ-Al_2O_3) and silicon carbide (β-SiC) were the most frequently used support materials (provided by Johnson Matthey as 3 mm pellets); the precursor salts were platinum(II) 2,4-pentandionate (Alfa Aesar, UK), ruthenium(III) 2,4-pentandionate (Sigma Aldrich, USA) and cerium(III) nitrate hexahydrate (Sigma Aldrich, USA). The solvents used for preparing the impregnating solutions were HPLC-grade toluene (Sigma Aldrich, USA) and water (Fischer Scientific, USA).

The catalysts were prepared by impregnation to incipient wetness at room temperature. The Pt and Ru precursors were dissolved in small amounts of toluene, whereas water was used as the solvent for the cerium salt. For granular catalysts, the pelleted support materials were first crushed and sieved to achieve a grain size-range of 0.425–0.6 mm. The slurries of support material and impregnating solution were left for 24 h to ensure effective impregnation, after which the solvents were removed by evaporation using a rotary evaporator (200 mbar; water bath temperature: 90°C). The samples were thoroughly dried overnight in an oven at 120°C, before being calcined at 500°C in static air for 2 h, following heating at a ramp rate of 10°C min^{-1}. Bimetallic catalysts were prepared by the same route, except that the two metals were either co-impregnated

 © 2018 Johnson Matthey

onto the support, or a monometallic catalyst was initially prepared and then post-impregnated with the second metal before the drying and calcination steps were repeated. For screening experiments, activated carbon (12–20 mesh size) and ruthenium supported on 3 mm pellets of extruded carbon (2% Ru by mass) were used as supplied (by Johnson Matthey).

Characterisation of the catalysts using Brunauer-Emmett-Teller (BET) measurements, temperature-programmed reduction, X-ray diffraction and cryo-electron tomography provided information on their exposed surface area, reducibility, structure and composition, and wettability (24).

2.2 Catalyst Notation

In the text below, the nominal catalyst compositions are represented as follows:

mass loading of precious metal(s) in catalyst / identity of support material(s)

For example, 2%Pt/5%ceria/alumina signifies a catalyst prepared by: (i) impregnating γ-Al_2O_3 with enough cerium(IV) nitrate solution to produce a support material which when dried and calcined contained 5% CeO_2 by mass; and (ii) impregnating the resultant mixed-oxide support material with platinum precursor solution to produce a catalyst, which after further drying and calcination contained 2% Pt by mass.

2.3 Catalyst Evaluation

Catalyst performance testing was carried out in a three-phase downward flow trickle-bed reactor, of the type described by Enache and co-workers (25), using a co-current testing procedure based on that used by Suárez-Ojeda and co-workers (26). Air was co-fed (at a flow-rate of 144 cm^3 min^{-1}) together with an aqueous solution of phenol (concentration: 1000 mg $litre^{-1}$; feed-rate: 1.1 cm^3 min^{-1}) which trickled under gravity through the catalyst bed (8 g) at a liquid-hourly space velocity of 25–27 h^{-1}. The liquid-phase products and unconverted phenol in the outlet stream were separated by high-performance liquid chromatography (HPLC) before being analysed with an ultraviolet-visible (UV-vis) detector, which had been calibrated using known concentrations of phenol, quinones and organic acids (Sigma Aldrich, USA).

The maximum operating pressure inside the trickle-bed reactor was 13.1 bar_g, which allowed testing at temperatures up to 190°C (the boiling temperature of water at this pressure). As most of the testing was carried out at lower temperatures, the operating pressure was also lowered, with 7 bar_g becoming the standard testing pressure. For catalyst screening and in studies of induction time, a catalyst bed temperature of 160°C was used, but this was lowered to 140°C (in the study of support and promoter effects) and then to 120°C (in the metal thrifting study) in order to discriminate between highly active materials. Although by changing the catalyst bed temperature, other process variables were affected (such as viscosity of the reaction medium, oxygen solubility in the water and rate of mass transfer), this was taken into account by comparing catalytic activity under self-consistent test conditions in each of the studies.

3. Catalyst Screening

During initial screening of potential catalysts under benchmark test conditions (160°C; 7 bar_g), the parameters deliberately varied were: (i) identity of the precious metal (Pt or Ru) at a fixed loading of 2% (by mass); (ii) composition of the support material (γ-Al_2O_3 or β-SiC); (iii) absence or presence of a promoter (ceria); and (iv) constituent particle size of the catalyst bed (3 mm pellets or sub-mm granules). Clearly, by changing the metal or the support, and by adding a promoter, other characteristics of the catalyst may also change, such as the surface area of the support and the dispersion and oxidation state of the metal – these are discussed later. Included in the screening study were two commercial catalyst samples: activated carbon and 2%Ru/carbon.

As **Figure 1** shows, several key trends and dependencies became apparent during the screening study. One of the most striking trends is the similarity in performance between Ru supported on activated carbon and the bare support material (this pair of performance curves is labelled (a) in **Figure 1**), despite differences in macroscopic particle size. In both cases, the apparent conversion of phenol rose steeply to 100% during the first 2 h of testing, before stabilising. After 7 h of testing, the apparent conversion began to decline steeply, before eventually levelling at 15–20%. We interpret these results as showing that most of the apparent conversion is due to adsorption of phenol on the activated carbon. It is not until the carbon has become saturated with stored phenol, after about 20 h of testing, that the measured conversion (15–20%) reflects the catalytic activity of the carbon materials.

 © 2018 Johnson Matthey

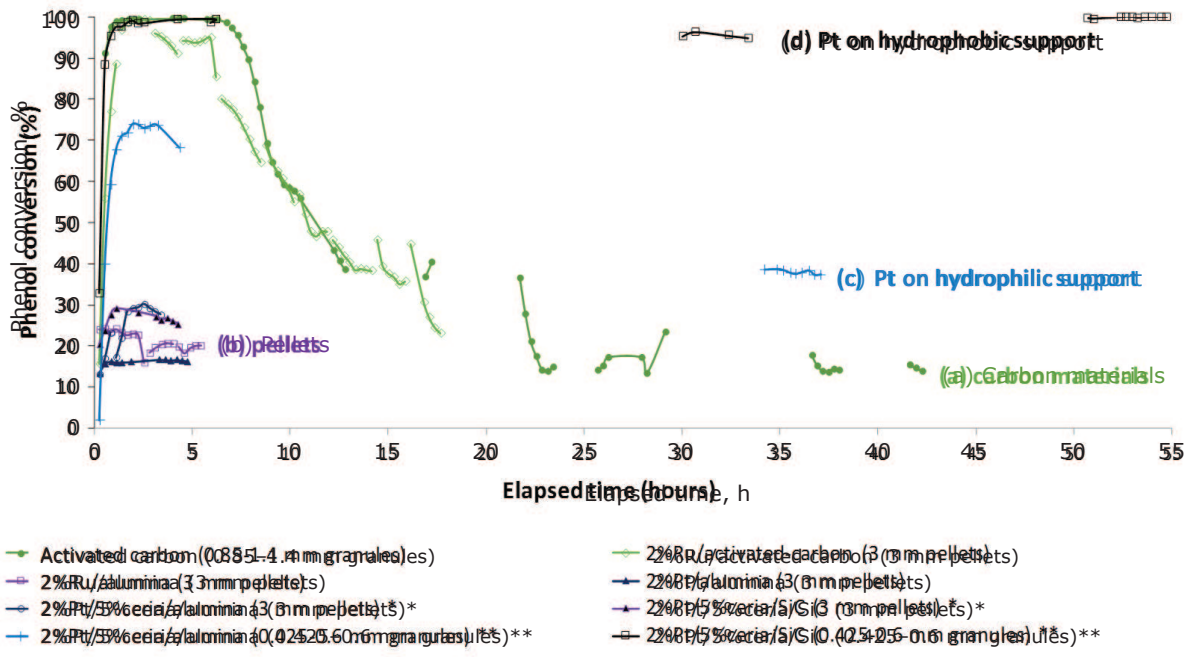

Fig. 1. Phenol conversion measured as a function of time for a range of catalytic materials, at a catalyst bed temperature of 160°C. Breaks in traces show deliberate interruptions in testing. Pairs of catalytic materials with identical compositions are indicated by * and **

As highlighted by the cluster of performance curves showing maximum conversion of 15–30% (labelled (b) in **Figure 1**), it was difficult to discriminate between the effects of the compositional variables when the catalysts were in the form of 3 mm pellets. However, crushing and sieving the pelleted support materials before impregnating with the metal precursor, to produce granular catalysts with particle diameters 0.425–0.60 mm, allowed effective discrimination without compromising the flow characteristics of the catalyst bed. For example, 2%Pt/5%ceria/alumina achieved a maximum conversion of 32% when it was in the pelleted form but, in its granular form, it reached 74% before deactivating to a stable value in excess of 40%.

The best performing catalyst identified during the screening study was a formulation containing 2% Pt as the active metal, promoted by 5% ceria and supported on a hydrophobic material (SiC). After the start of the test, there was an induction time of around 1.5 h, when the phenol conversion rose to 100%. During this induction period, two groups of non-selective oxidation products were detected: carboxylic acids (formic, acetic, fumaric, maleic) and aromatic oxygenates (hydroquinone, benzoquinone, catechol, hydroxybenzoic acid). These are consistent with the free-radical reaction pathway proposed by Martín-Hernández *et al*. (21), in which the oxidation of phenol leads initially to the formation of catechol and hydroquinone, which are converted to *ortho*- and *para*-benzoquinone before C–C bond breaking takes place. Once full conversion was reached, the selectivity to CO_2 was >95%. As seen in **Figure 1**, this catalyst retained its high activity during prolonged stop-start testing, and it did not go through an induction period when testing was resumed after being interrupted.

4. Support and Promoter Effects

The underlying causes for the high activity of 2%Pt/5%ceria/SiC were examined by observing the effects of different combinations within the metal-promoter-support system. In order to resolve the differences in activity more readily, the catalyst bed temperature during this phase of testing was lowered from 160°C to 140°C. However, even at the lower temperature, granular materials containing both Pt and SiC achieved a stable phenol-conversion of 98±2% (**Figure 2**), whereas the activity of SiC alone, or SiC with 5% ceria deposited on it, was negligible.

These results are consistent with the interaction between Pt and SiC being critical in determining maximum catalytic activity. The interaction

 © 2018 Johnson Matthey

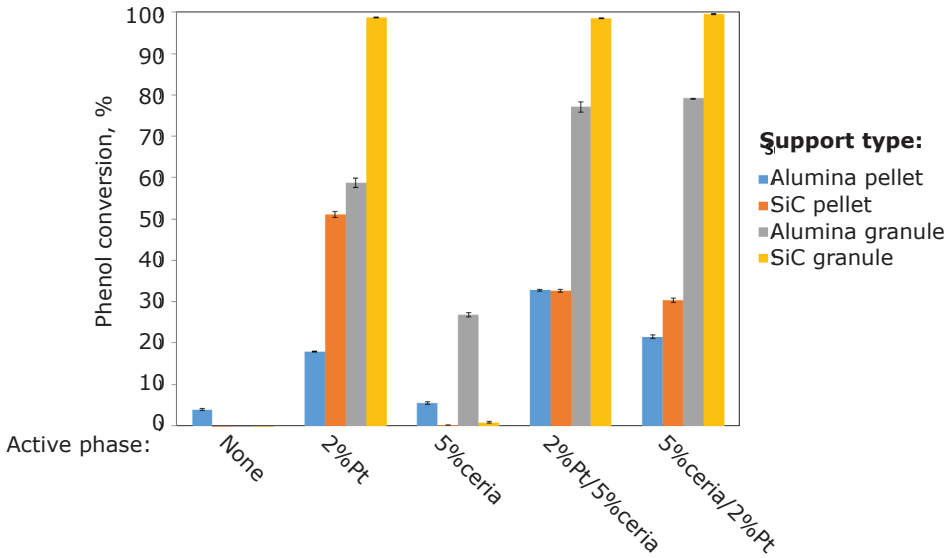

Fig.2. Effect on phenol conversion of changing the combination of active phase and support in the catalytic material. Measurements made at a catalyst bed temperature of 140°C

between Pt and ceria is of secondary importance, but can have a role to play in thrifting the metal loading. As shown in a previous publication (24), the addition of 1–2% ceria to either 1%Pt/SiC or 2%Pt/SiC suppressed activity. However, on adding 5% ceria, both catalysts were promoted, but the effect was much greater for 1%Pt/SiC, resulting in 1%Pt/5%ceria/SiC closely matching the activity of 2%Pt/SiC (**Figure 3**).

When a hydrophilic support (alumina) was substituted for SiC, the maximum stable conversion achieved by granular 2%Pt/alumina was 57%, but this could be increased to 80% by addition of ceria, either by pre-impregnation of the support or by post-impregnation of the Pt/alumina (**Figure 2**). The alumina alone showed some apparent activity (<5% conversion), but only in the pelleted form, suggesting that this was due to phenol storage on the external surfaces of the pellets. Much more substantial activity (>25% conversion) was observed when 5% ceria was deposited on granular alumina, which points to the phenol-conversion over 2%Pt/5%ceria/alumina being essentially the sum of the conversions achieved by 2%Pt/alumina and 5%ceria/alumina.

As already reported (24), the same trends were not repeated when Ru was substituted for Pt. Now, the least active materials were those in which ruthenium was dispersed on SiC granules, resulting in phenol-conversion of only 20% at 140°C,

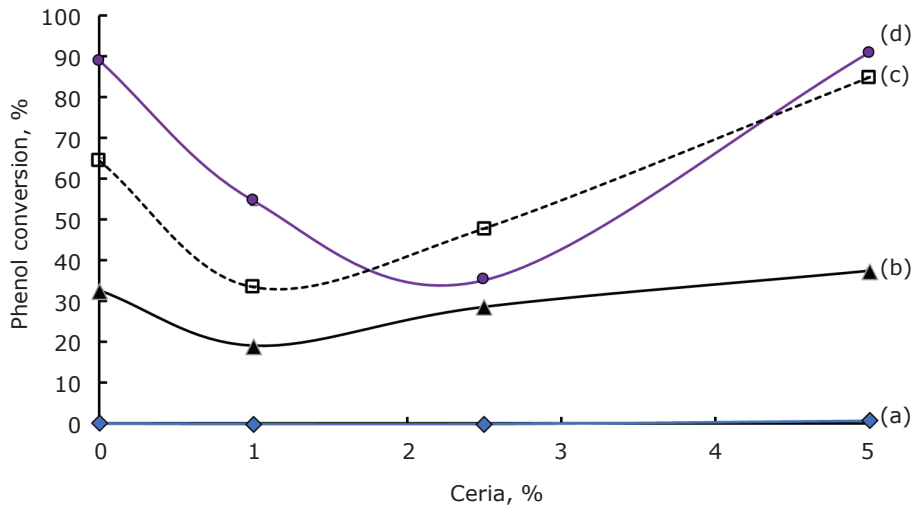

Fig. 3. Effect on phenol conversion of ceria addition to Pt/SiC catalysts with varying Pt loadings, at a catalyst bed temperature of 120°C: (a) ceria/SiC; (b) 0.5%Pt/ceria/SiC; (c) 1%Pt/ceria/SiC; (d) 2%Pt/ceria/SiC. (Reproduced with permission from (24). Copyright 2018 American Chemical Society)

 © 2018 Johnson Matthey

which could not be improved by addition of ceria. However, the activity could be doubled by replacing the SiC with the hydrophilic alumina granules, and then doubled again (to 80% phenol-conversion) by adding 5% ceria.

5. Bimetallic Catalysts

Although a study of the full matrix of compositional variables (including the interactions between Pt and Ru as well as with hydrophobic and hydrophilic supports) has yet to be completed, initial results indicate that there are some specific benefits to be gained by including both Pt and Ru in future catalyst formulations. As observed during the screening phase, it took the most active catalyst (2%Pt/ceria/SiC) around 90 min to reach full phenol-conversion at 160°C. The unpromoted version of this catalyst (2%Pt/SiC) required a longer time (100–120 min) before it stabilised at full conversion (**Figure 4**). It was also during this induction period that the selectivity to CO_2 was below 95%, with measurable (ppm) concentrations of carboxylic acids and aromatic oxygenates being detected in the water exiting the trickle-bed reactor.

When a 1%Pt-1%Ru/SiC catalyst was prepared by post-impregnation of 1%Ru/SiC with Pt, the induction period increased to 170 min (**Figure 4(b)**); changing the sequence of impregnation steps, so that the same catalyst composition was prepared by post-impregnation of 1%Pt/SiC with Ru, led to an induction profile resembling that of 2%Pt/SiC, but the full induction period was 150 min (**Figure 4(c)**). The most notable effect of Ru addition became apparent when 1%Pt and 1%Ru were co-impregnated on SiC. Although the full induction period was again 100–120 min, the phenol-conversion exceeded that achieved by 2%Pt/SiC during most of this time (compare **Figures 4(d)** and **4(e)**), which meant that the exit stream contained a lower concentration of unconverted phenol (and lower concentrations of the non-selective products).

6. Impact of Catalyst Variables on Catalytic Wet Air Oxidation Performance

6.1 Macroscopic Form of the Catalyst

Among the challenges in designing catalysts for continuous CWAO processes is the need to achieve a balance between acceptable back-pressure across the catalyst bed length, and effective mass-transfer of the organic molecules and O_2 between the three phases present within the bed. Starting with relatively large constituent particles (3 mm pellets) in the bed of the trickle-bed reactor used throughout these studies allowed the reactor to operate efficiently in trickle-flow mode. However, probably due to external mass-transfer limitations, differences in catalytic activity (even at low phenol-conversion) could not be resolved when changes were made to the catalyst composition. An important initial outcome, therefore, was that the mass-transfer limitations could be reduced by using granular catalysts with a macroscopic particle size range of 0.425–0.60 mm without compromising the operation of the trickle-bed, which then allowed the effects of the compositional variables to be assessed.

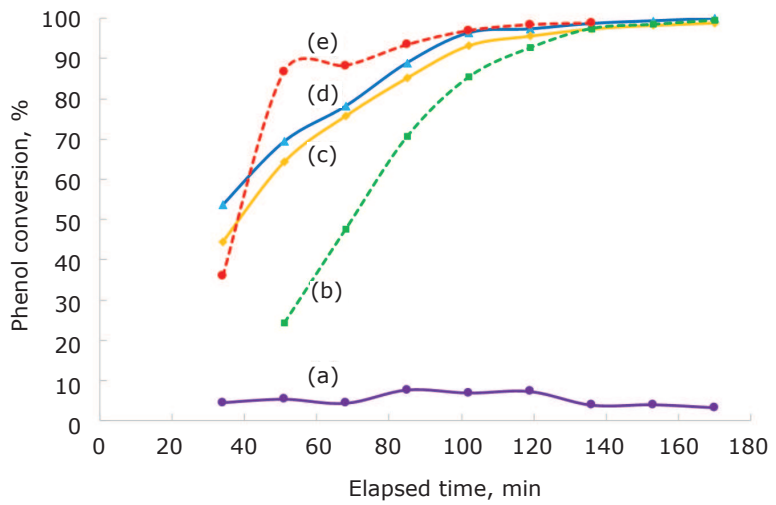

Fig. 4. Phenol conversion measured as function of time for bimetallic catalysts, at a catalyst bed temperature of 160°C: (a) 2%Ru/SiC; (b) 1% Pt post-impregnated on 1%Ru/SiC; (c) 1% Ru post-impregnated on 1%Pt/SiC; (d) 2%Pt/SiC; (e) 1%Pt and 1% Ru co-impregnated on SiC

 © 2018 Johnson Matthey

6.2 Activated Carbon as Catalyst or Support

Extended testing both of activated carbon and of Ru supported on carbon in a continuous reactor has shown that it can be difficult to distinguish between catalytic activity and contaminant-storage in these materials. As yet, it is not certain whether this is a generic property of all carbon-containing catalysts, or if it is specific to the activated carbon used in this work.

6.3 Metal-Support and Metal-Promoter Interactions

The most significant correlation observed between catalyst composition and CWAO activity relates to the wettability of the support material. In particular, there is a definite synergy between Pt and hydrophobic supports, such as SiC. This synergy cannot be explained by textural changes in the catalyst. In fact, the surface area of 2%Pt/SiC (23±2 $m^2 g^{-1}$) was substantially lower than when the same loading of Pt was supported on hydrophilic alumina (99±4 $m^2 g^{-1}$), and yet the mean diameter of the Pt nanoparticles was 7.9±0.2 nm in both catalysts (24).

Although the inclusion of SiC in CWAO catalysts has been reported in the past (27), it has been used specifically to improve durability and not to confer hydrophobicity. In our working hypothesis (see **Figure 5(a)**), we envisage that the presence of a hydrophobic support leads to the adsorption of O_2 directly from the gas phase onto Pt active sites, which are also capable of adsorbing phenol from the aqueous phase. A similar mechanism has been proposed by Lavelle and McMonagle (28) for CWAO of formic acid at near-ambient temperature in a spinning-basket reactor, when using platinum supported on a highly hydrophobic polydivinylbenzene support. Their rationale was that the presence of the hydrophobic support led to a gas envelope forming around the active sites as the reactor rotated, eliminating the rate-limiting requirement for O_2 transport through the aqueous phase. In our catalysts operating in a trickle-bed reactor, the 'gas envelope' is more likely to be in the form of air bubbles within the pores, in which the Pt nanoparticles are located. Of course, some degree of local hydrophilicity is also required in order to allow the aqueous phase (containing the dissolved phenol) to come into contact with the active sites. This is provided by the Pt nanoparticles themselves, but may also be provided by the addition of low loadings of ceria. Otherwise, the promoting effect of ceria is difficult to explain, because its high oxygen storage capacity is unlikely to play a part at the low temperatures used in our studies. The enhanced activity is also unlikely to be due to a strong electronic metal-support interaction, as this requires strongly reducing conditions during either preparation or use of the catalyst (29).

Our results show that the metal-support synergy in 2%Pt/SiC no longer exists when Pt is substituted by Ru. The optimum support is now extensively hydrophilic, leading us to conclude that there are two different pathways for the transport of O_2 from the air-feed to the active sites during CWAO. Characterisation of both groups of catalysts has revealed that a major difference between them is that Pt is present mainly in its metallic form,

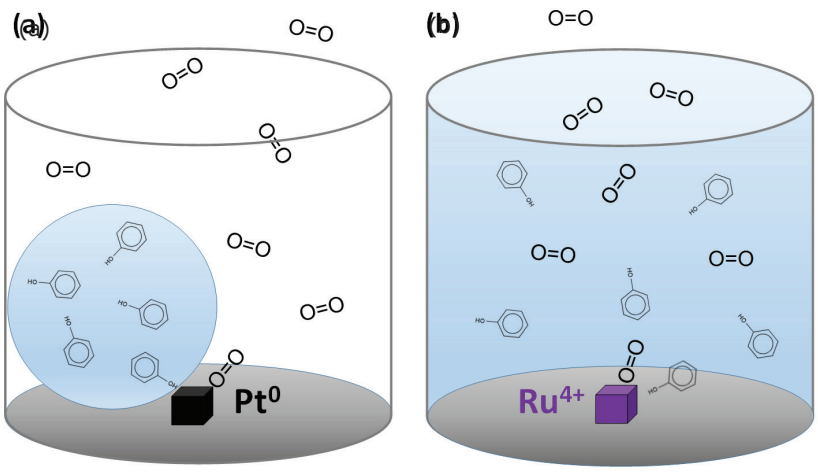

Fig. 5. Two proposed pathways for the activation of phenol and O_2 on the active sites located inside the catalyst pore structures: (a) when Pt is dispersed on a hydrophobic support, gas-phase O_2 is directly adsorbed on the Pt^0 surface, while phenol is adsorbed from the aqueous phase; (b) when Ru is dispersed on a hydrophilic support, dissolved O_2 is activated on RuO_2 immersed in the aqueous phase, from which phenol adsorption also takes place

 © 2018 Johnson Matthey

while Ru is present in its oxidised form (RuO_2) (24). We therefore propose that, during CWAO, RuO_2 adsorbs both phenol and O_2 from the aqueous phase (**Figure 5(b)**). This means that, for maximum rate of reaction through a bed of Ru catalyst, all the active sites should be immersed in the contaminated aqueous phase, which is the favoured state when Ru is dispersed throughout the pore structure of a hydrophilic support material.

Although our studies indicate that the intrinsic activity of Pt supported on a hydrophobic support is greater than that of Ru supported on a hydrophilic support, there may be some benefits to be gained from combining both metals on a hydrophobic support. For example, though the addition of 1%Ru to 1%Pt/SiC does not reduce the total loading of precious metal, it increases the rate at which the catalyst approaches maximum conversion during the first-half of the induction period. This is likely to have a beneficial impact during start-up of a CWAO reactor, by reducing the duration over which the exit stream has to be fed back into the reactor before the purified wastewater can be discharged.

7. Status

Our studies to date have provided insights into the steps that can be taken to optimise Pt and Ru catalysts for CWAO, with the ultimate aim of formulating a catalyst which will operate at temperatures <100°C, so that elevated pressure is not required to maintain the contaminated water in the liquid phase during treatment. The current US Environmental Protection Agency safe limit for phenol discharged in wastewater is 6.2 ppm by mass (30), which is typical of most other national targets. Currently, our best catalyst (2%Pt/5%ceria/SiC) is capable of achieving this target under realistic space velocities at a temperature of 140°C, which requires a minimum pressure of 2.6 bar_g for water to remain as a liquid.

Acknowledgements

This work was started as part of the Johnson Matthey 'Bauhaus' programme and continued as a project within the EPSRC Centre for Doctoral Training in Catalysis (EP/L016443/1). The authors gratefully acknowledge Johnson Matthey and Cardiff University for financial support of the Bauhaus programme, and EPSRC together with Cardiff University and the Universities of Bath and Bristol for financial support of the EPSRC Centre for Doctoral Training in Catalysis.

References

1. K.-H. Kim and S.-K. Ihm, *J. Hazard. Mater.*, 2011, **186**, (1), 16
2. M. Weber and M. Weber, 'Phenols', in "Phenolic Resins: A Century of Progress", ed. L. Pilato, Springer-Verlag, Berlin, Germany, 2010, pp. 9–23
3. 3. G. Busca, S. Berardinelli, C. Resini and L. Arrighi, *J. Hazard. Mater.*, 2008, **160**, (2–3), 265
4. M. A. Lunagómez Rocha, G. Del Ángel, G. Torres-Torres, A. Cervantes, A. Vázquez, A. Arrieta and J. N. Beltramini, *Catal. Today*, 2015, **250**, 145
5. J. Guo and M. Al-Dahhan, *Ind. Eng. Chem. Res.*, 2003, **42**, (12), 2450
6. F. Stüber, J. Font, A. Fortuny, C. Bengoa, A. Eftaxias and A. Fabregat, *Top. Catal.*, 2005, **33**, (1–4), 3
7. D. Janecki, A. Szczotka, A. Burghardt and G. Bartelmus, *J. Chem. Technol. Biotechnol.*, 2016, **91**, (3), 596
8. H. Debellefontaine, M. Chakchouk, J. N. Foussard, D. Tissot and P. Striolo, *Environ. Pollut.*, 1996, **92**, (2), 155
9. F. Luck, *Catal. Today*, 1999, **53**, (1), 81
10. S. T. Kolaczkowski, P. Plucinski, F. J. Beltran, F. J. Rivas and D. B. McLurgh, *Chem. Eng. J.*, 1999, **73**, (2), 143
11. A. Cybulski and J. Trawczyński, *Appl. Catal. B: Environ.*, 2004, **47**, (1), 1
12. J. Levec and A. Pintar, *Catal. Today*, 2007, **124**, (3–4), 172
13. A. Sadana and J. R. Katzer, *Ind. Eng. Chem. Fundamen.*, 1974, **13**, (2), 127
14. L. Zhou, H. Cao, C. Descorme and Y. Xie, *Front. Env. Sci. Eng.*, 2018, **12**, (1), 1
15. S. Yang, Y. Cui, Y. Sun and H. Yang, *J. Hazard. Mater.*, 2014, **280**, 55
16. R. P. Rocha, O. S. G. P. Soares, A. G. Gonçalves, J. J. M. Órfão, M. F. R. Pereira and J. L. Figueiredo, *Appl. Catal. A: Gen.*, 2017, **548**, 62
17. C. Ma, Y. Wen, Q. Yue, A. Li, J. Fu, N. Zhang, H. Gai, J. Zheng and B. H. Chen, *RSC Adv.*, 2017, **7**, (43), 27079
18. H. Sassi, G. Lafaye, H. B. Amor, A. Gannouni, M. R. Jeday and J. Barbier Jr., *Front. Environ. Sci. Eng.*, 2018, **12**, (1), 2
19. F. Arena, R. Di Chio, B. Gumina, L. Spadaro and G. Trunfio, *Inorg. Chim. Acta*, 2015, **431**, 101
20. L. Oliviero, J. Barbier Jr., D. Duprez, H. Wahyu, J. W. Ponton, I. S. Metcalfe and D. Mantzavinos, *Appl. Catal. B: Environ.*, 2001, **35**, (1), 1
21. M. Martín-Hernández, J. Carrera, M. E. Suárez-Ojeda, M. Besson and C. Descorme, *Appl. Catal. B: Environ.*, 2012, **123–124**, 141

 © 2018 Johnson Matthey

22. J. Barbier Jr., L. Oliviero, B. Renard and D. Duprez, *Top. Catal.*, 2005, **33**, (1–4), 77
23. A. Espinosa de los Monteros, G. Lafaye, A. Cervantes, G. Del Angel, J. Barbier, Jr. and G. Torres, *Catal. Today*, 2015, **258**, (2), 564
24. D. Davies, S. Golunski, P. Johnston, G. Lalev and S. H. Taylor, *ACS Catal.*, 2018, **8**, (4), 2730
25. D. I. Enache, P. Landon, C. M. Lok, S. D. Pollington and E. H. Stitt, *Ind. Eng. Chem. Res.*, 2005, **44**, (25), 9431
26. M. E. Suarez-Ojeda, F. Stüber, A. Fortuny, A. Fabregat, J. Carrera and J. Font, *Appl. Catal. B: Environ.*, 2005, **58**, (1–2), 105
27. J. R. Akse and J. E. Atwater, *Top. Catal.*, 2005, **33**, (1–4), 51
28. K. Lavelle and J. B. McMonagle, *Chem. Eng. Sci.*, 2001, **56**, (17), 5091
29. N. Acerbi, S. Golunski, S. C. Tsang, H. Daly, C. Hardacre, R. Smith and P. Collier, *J. Phys. Chem. C*, 2012, **116**, (25), 13569
30. 'Hazardous Waste Management System: Identification and Listing of Hazardous Waste Solvents: Final Decision', SWH-FRL-6185-3, Federal Register, Environmental Protection Agency, Washington, USA, 19th November, 1998, Vol. 63, Issue 223, pp. 64372–64402

The Authors

Korrin Saunders graduated in Chemistry from Cardiff University, UK, in 2014. She is now a member of the Engineering and Physical Sciences Research Council (EPSRC) Centre for Doctoral Training in Catalysis (run jointly by Cardiff, Bath and Bristol Universities), where she is currently in the final year of her PhD project on catalytic wet air oxidation.

After graduating in Chemistry from Cardiff University in 2012, Dafydd Davies was the first PhD student to study catalytic wet air oxidation at the Cardiff Catalysis Institute. After completing his PhD in 2015, he joined Arcadis as a process engineer working on several wastewater treatment projects within the Welsh Water Capital Delivery Alliance.

Stan Golunski began his research career in industry, before becoming Professor of Catalysis and later Co-Director of the Cardiff Catalysis Institute at Cardiff University until July 2018. His research interests lie in the fundamentals and applications of supported nanoparticle catalysts, mainly in the context of water and air purification for environmental protection.

Peter Johnston obtained his PhD from the University of the Witwatersrand, Johannesburg, South Africa. After academic posts at the Universities of Liverpool and Hull in the UK, he joined Johnson Matthey in 1996. Currently he is a Scientific Consultant at Johnson Matthey, Billingham, UK. His interests and activities are in the discovery, development, scale-up and commercialisation of supported platinum group metal and base metal heterogeneous catalysts.

Pawel Plucinski graduated in Chemical Engineering from Wrocław University of Technology, Poland, where he also completed his PhD studies. In 1986, he joined the Technical University of Munich, Germany, (where he was awarded his habilitation in 1993), before moving to the University of Bath, UK, in 1998. His main area of research is in reaction kinetics in heterogeneous systems, including catalytic and interfacial reactions.

 © 2018 Johnson Matthey