Recovery of Palladium from Spent Activated Carbon-Supported Palladium Catalysts

Precipitation by sodium borohydride allows high grade recovery of palladium

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Activated carbon-supported palladium catalysts are liable to progressive deactivation even in the absence of any gaseous contaminants during the oxidation of hydrogen under ambient conditions. The high value of palladium coupled with environmental considerations means that new, efficient and cost effective methods for the quantitative recovery of palladium from such materials are required. In the present study, a process for extracting precious metals from spent catalyst or inorganic waste was developed. Palladium was extracted from the spent catalyst with an acid solution containing dilute hydrochloric acid and hydrogen peroxide at leaching temperatures of around 90ºC. Palladium in the leached solution was then precipitated by use of sodium borohydride solution. The effectiveness of the method for recovery of precipitated palladium was investigated by ultraviolet-visible (UV-vis) spectrophotometry, X-ray diffraction (XRD) and scanning electron microscopy (SEM). The recovered metallic palladium was of a sufficient grade to manufacture fresh activated carbon-supported palladium catalysts.

1. Introduction

Hydrogen is prone to leakage and can form an explosive atmosphere due to its wide range of flammability limits. Methods of hydrogen elimination before accumulation of a detonable mixture in confined spaces are thus very important. Catalytic combustion of hydrogen is the most common method used in commercial hydrogen detection and elimination systems. Palladium is frequently used as the active component of the catalysts for such systems (1–4). These systems can respond to hydrogen when maintained at temperatures of 80ºC, and in some cases less (5). However, for reasons which remain unclear, the catalyst is liable to progressive deactivation even in the absence of any gaseous contaminants (2).

The high value of palladium makes its recovery economically desirable: for example, in 2011 22% of the palladium market was supplied by recovery from

autocatalysts and jewellery scrap (6). In addition environmental considerations mean that effective recovery of the residual precious metals from spent catalysts is of paramount importance for a process to be environmentally acceptable (7,8).

Spent organic-based catalysts which contain precious metals have traditionally been treated by incineration to recover the precious metal content. However, palladium is recovered in oxide form, which is not ideal for the production of fresh catalyst (9).

Hydrometallurgical techniques are also widely used for the recovery and separation of precious metals from spent catalysts. The processes can be categorised into two types: support dissolution and precious metal dissolution (10). In the first of these, the support is dissolved with a nonoxidising acid or base, after which the precious metals remain as a residue. A major disadvantage is that this process requires large quantities of reagents.

In the second type of process the precious metals are extracted from the support by an acidic oxidant solution, leaving the bulk of the support undissolved. Different leaching mixtures such as sulfuric acid, hydrochloric acid or chloride salts in the presence of oxidising agents such as nitric acid, bromine or chlorine have been used for palladium recovery (11–15). Disadvantages of this technique are the environmental impact of the reagents, the high cost of nitric acid and the potential for evolution of hazardous nitric oxides. In addition, after leaching, nitric acid must be completely removed from the solution, adding to the complexity and cost. Separation of Pd from solution has also been carried out by reduction in phosphoric acid solution by formalin at 150ºC (16); in hydrochloric acid by formic acid (17); by polyoxometallates (18); by bioreduction (19); and by reduction using aluminium powder (20).

Lastly, the development of new innovative and sustainable chemical processes with high energy efficiency and ideally 100% selectivity will require a new generation of catalytic materials with tailored functionality at the surface. Since the material properties change at the nanoscale, nanosized catalytic materials are expected to enable highly complex catalytic processes to be created on the basis of a controlled sequence of surface reactions and active sites. Nanostructured catalysts show great promise in the field of environmentally friendly, flexible and efficient materials processing (21). The kinetics of adsorption/desorption of hydrogen on the catalytic surface is closely related with its diffusion rate, and it is possible to improve these diffusion rates by use of nanoscale catalytic surfaces. The ability to obtain recovered palladium in a form which can be effectively re-used to generate fresh catalysts will be an advantage in this regard.

In the present work, new process conditions have been tested and optimised for the recovery of palladium from spent carbon-supported catalyst. Palladium was extracted from a spent catalyst matrix with a mixture of dilute hydrochloric acid and hydrogen peroxide and then precipitated from the leached solution by sodium borohydride. $NaBH_4$ was selected as a much milder reducing agent which is safer to handle than the conventional alternatives. It has the further advantage that it can be used in aqueous or alcohol solutions. UV-vis spectrophotometry, XRD and SEM were used to monitor the effectiveness of the chosen recovery method and the resultant solid residue was shown to be suitable for manufacturing fresh activated carbon-supported palladium catalysts.

2. Experimental
2.1 Materials
Commercial activated carbon-supported palladium catalysts containing a polytetrafluoroethylene (PTFE) binder in pellets of 100 g were used. The catalyst, sold for hydrogen elimination in confined spaces, was in the shape of rectangle with dimensions of 160 mm × 76 mm. The thickness of the catalyst plate was 1 mm. The palladium loading of the catalyst was determined to be 10% by weight. (Note that due to commercial confidentiality the supplier name and the detailed compositional analysis of the catalyst material have been withheld).

2.2 Chemicals
Hydrochloric acid (37%) and hydrogen peroxide (30%) were used for the preparation of the leaching solution. Sodium borohydride (99%) was used as a reducing agent for palladium. An aqueous solution of 5% sodium hydroxide was used to prevent the self-oxidation of sodium borohydride. All chemicals were of high grade for laboratory usage. Distilled water was used for dilutions.

2.3 Ageing of the Palladium Catalyst
The thermal conductivity of both activated carbon and PTFE is around $0.25\,W\,m^{-1}\,K^{-1}$ (22) while palladium has a thermal conductivity of about $75\,W\,m^{-1}\,K^{-1}$ (23). The thermal conductivity of gases is generally much lower at around $0.02 \pm 0.005\ W\ m^{-1}\ K^{-1}$ (24). The thermal

conductivity of a porous solid such as found in a catalyst support can approach that of gases provided the porosity is high. For this reason, the catalyst body may be classified as a non-thermally conductive material (24, 25). As a result the transport of thermal energy out of a fixed bed catalytic reactor generally proceeds slowly, which can cause an increase in temperature in the catalyst bed at a level approaching the adiabatic temperature rise.

When the surface temperature of the catalyst exceeds 300ºC, the PTFE binder of the catalyst starts to melt, agglomerates the active palladium species and finally leads to the deactivation of the catalyst. For this reason, the normal operating conditions of a hydrogen removal catalyst require a maximum hydrogen concentration in the order of hundreds or thousands of ppmv in air at 25ºC and 1 atm. The maximum allowable effluent gas temperature has been determined to be between 150ºC and 200ºC to maintain the catalyst surface temperature below 300ºC (26). Under normal operating conditions, the lifetime of the catalyst is at least two years. To quickly age the catalyst for the present study, a high fuel content of 3% hydrogen was intentionally chosen. Fresh catalyst was chopped and exposed to 3% hydrogen in air as described previously (26). The completion of ageing was monitored by the loss of catalytic activity with time-on-stream. An effluent gas temperature of ~246ºC was reached indicating that the ageing condition had been met. The deactivated catalyst was subsequently tested for the recovery of palladium.

2.4 Method for the Recovery of Palladium
100 g of the spent catalyst was crushed, ground and sieved below 500 μm. The finely powdered spent catalyst was put into a jacketed 250 ml reactor. The leaching solution of hydrochloric acid and hydrogen peroxide was added slowly to the reactor under magnetic stirring. The reaction was carried out for 180 min at 90ºC. At the end of the leaching process, the mixture was filtered *via* a filtration funnel under vacuum at 90ºC. The Pd concentration of the leached solution was measured using inductively coupled plasma emission spectrometry (ICPES). The leached solution was used as a stock solution for the separation of palladium.

In the separation phase, in order to reduce the leached palladium species to the form of the palladium salt, alkaline sodium borohydride solution was added drop by drop onto 10 g of the stock solution in a 100 ml conical flask. To optimise the precipitation conditions, different concentrations of borohydride solution and different process temperatures were applied. The solution was then filtered off, and the precipitated palladium powder was washed, dried at 105ºC and weighed to calculate the reduction efficiency. **Figure 1** shows the process diagram for the recovery of palladium from the spent Pd/activated carbon (AC) catalyst.

2.5 Characterisation
Elemental analysis of the filtrate solution received after leaching was carried out by ICPES using a Thermo Jarrell Ash Atomscan 25. UV-vis absorption spectra of the samples were taken in the range 200 nm to 400 nm using a Shimadzu UV-1650PC UV-vis spectrophotometer. Wide-angle XRD patterns of the spent catalysts before and after leaching were recorded on a Shimadzu XRD-6000 diffractometer with CuKα radiation (λ of 0.154178 nm at 40 kV
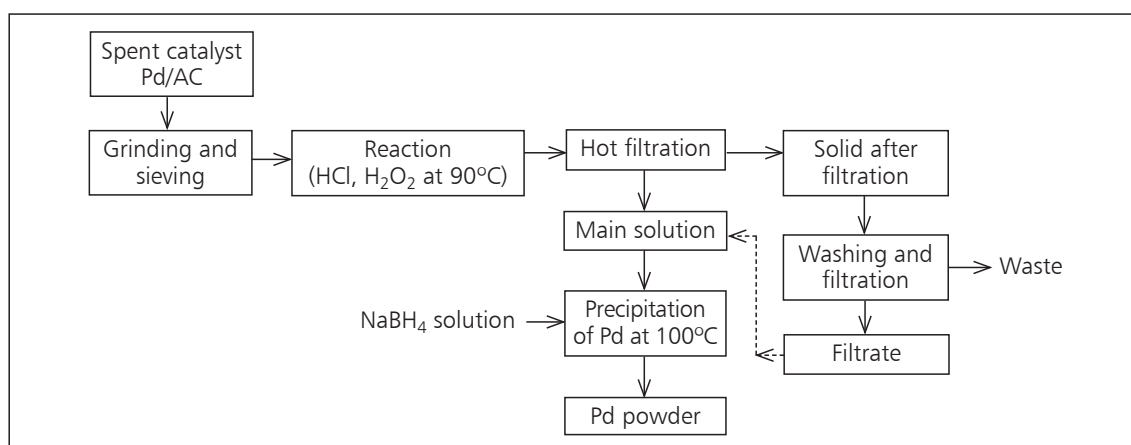

Fig. 1. Diagram showing the recovery of palladium from spent catalyst (AC = activated carbon)

and 30 mA). XRD scans were performed at ambient temperature with a 2θ range between 10º and 60º at a scanning rate of 0.048º min^{-1}. The morphology of the spent catalysts before and after leaching was investigated by SEM using a JEOL 6335F FEG-SEM field emission gun. Additionally, the average particle size of recovered palladium was measured using a Malvern Zetasizer Nano ZSP characterisation system.

3. Results and Discussion
3.1 Effect of HCl and H$_2$O$_2$ Concentrations
Treatment of activated carbon-supported palladium catalysts with a mixture of hydrochloric acid and hydrogen peroxide gives palladium chloride according to the Reaction (i):

$$Pd/AC + 4HCl_{(aq)} + H_2O_{2\,(aq)}$$
$$\rightarrow H_2PdCl_{4\,(aq)} + AC + 2H_2O \quad (i)$$
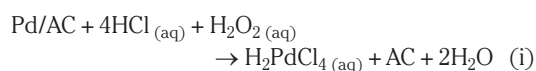
The effects of the hydrogen peroxide and hydrochloric acid concentrations were studied by changing the concentration of hydrogen peroxide while keeping the concentration of hydrochloric acid constant or *vice versa*. In the first case, hydrogen peroxide concentration was increased from 0 to 15% in the presence of 5% hydrochloric acid. The results are plotted in **Figure 2(a)**. It can be seen that the percentage recovery of palladium steadily increased with H$_2$O$_2$ concentration up to 5%, reaching a maximum palladium recovery of ~85%. For H$_2$O$_2$ concentrations above 5%, there was no further increase in palladium recovery. In the second case, HCl concentration was increased from 0 to 20% in the presence of 5% H$_2$O$_2$. The results are shown in **Figure 2(b)**. The percentage

recovery of palladium gradually increased with increasing HCl concentration, reaching a maximum of 99% recovery at 10% HCl. Thus a mixture of 10% HCl and 5% H$_2$O$_2$ was concluded to be effective for extracting palladium from activated carbon-PTFE organic matrix. Similar results have been reported for spent Pd/Al$_2$O$_3$ catalyst by Barakat *et al.* (20).

3.2 Effects of Temperature and Time
The effects of leaching time and reaction temperature on palladium recovery were studied over the temperature range 30ºC to 100ºC with leaching times of 1 h, 2 h or 3 h. Spent catalyst was treated with an acid/peroxide mixture having HCl and H$_2$O$_2$ concentrations of 10% and 5%, respectively. As seen in **Figure 3**, the percentage recovery of palladium increased with reaction temperature for each of the treatment time periods. The treatment time was seen to significantly affect the maximum percentage recovery of palladium, and a treatment time of 1 h was not sufficient to extract the highest levels of palladium. The results were closer for the treatment times of 2 h and 3 h. The maximum palladium recovery of >98% was obtained after treatment with an acid/peroxide mixture of 10% of HCl and 5% of H$_2$O$_2$ at 90ºC for 3 h.

3.3 Effect of Reducing Agent
Sodium borohydride was used as the reducing agent to precipitate metallic palladium from the stock solution after filtration. The precipitation of palladium *via* reduction proceeds according to the following reactions:
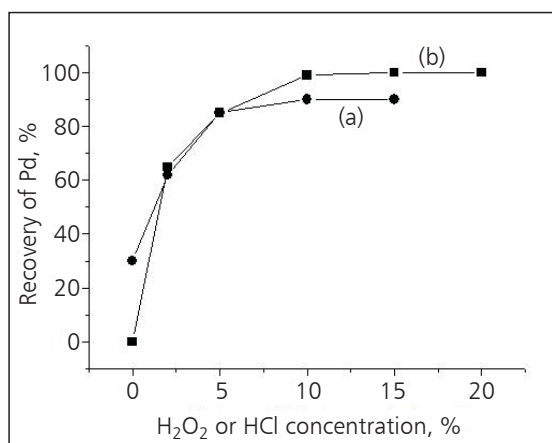

Fig. 2. The effects of: (a) H$_2$O$_2$ concentration (in the presence of 5% HCl); and (b) HCl concentration (in the presence of 5% H$_2$O$_2$) when reacted at 90ºC for 3 h
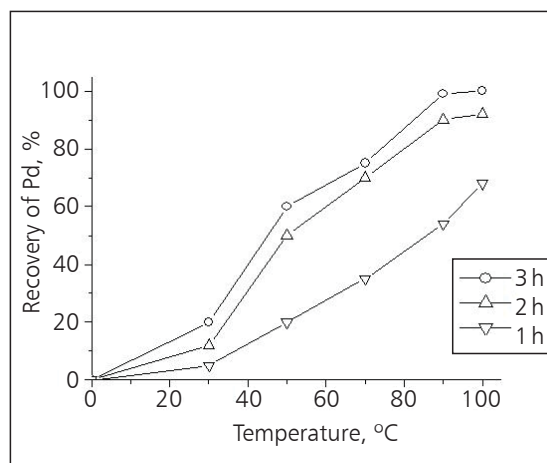

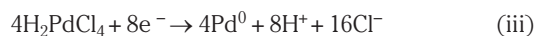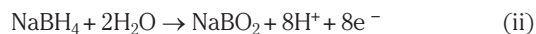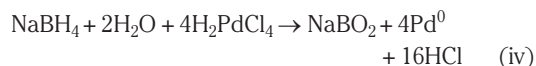Fig. 3. The effects of leaching time and temperature in the presence of 10% HCl and 5% H$_2$O$_2$

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 8H^+ + 8e^- \qquad (ii)$$

$$4H_2PdCl_4 + 8e^- \rightarrow 4Pd^0 + 8H^+ + 16Cl^- \qquad (iii)$$

The overall reaction is:

$$NaBH_4 + 2H_2O + 4H_2PdCl_4 \rightarrow NaBO_2 + 4Pd^0 + 16HCl \qquad (iv)$$

In the absence of any reducible species in the solution, sodium borohydride decomposes into sodium metaborate and hydrogen gas according to Reaction (v):

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2 \qquad (v)$$
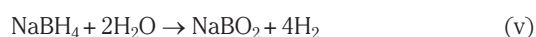
It is apparent from Equations (ii) and (iii) that stoichiometrically four moles of palladium chloride would be reduced to metallic form per one mole of sodium borohydride.

To optimise the precipitation conditions, different concentrations of alkaline sodium borohydride solution and different process temperatures were applied for a fixed duration of 20 minutes. **Figure 4** shows the change in percentage recovery of palladium *versus* the concentration of $NaBH_4$ at different reduction temperatures. It can be seen that the percentage recovery of palladium increased both with temperature, as also verified by Barakat *et al.* (20), and with sodium borohydride concentration. The percentage recovery increased steadily with temperature, while the effect of $NaBH_4$ concentration disappeared above 7% for the reduction temperature of 90°C. 100% palladium recovery was accomplished
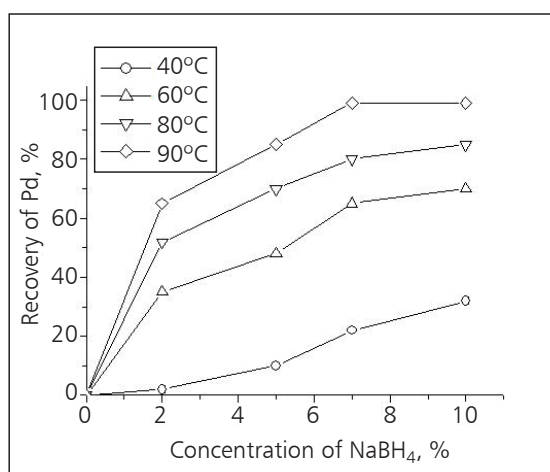
with a $NaBH_4$ concentration and a reduction temperature of 7% and 100ºC, respectively.

3.4 UV Results
Because of ligand-to-metal charge transfer, the transition of $PdCl_4^{2-}$ to H_2PdCl_4 exhibits two absorption bands at 209 nm and 237 nm, as reported by Yang *et al.* (27). These two strong UV absorption bands can be used to measure the reduction of H_2PdCl_4 to metallic palladium. To monitor the reduction upon treatment with different concentrations of $NaBH_4$ at 100ºC, UV-vis spectra of treated solutions were taken. Leached and alkaline sodium borohydride solutions were used in equimolar proportions. **Figure 5** shows the results. It can be seen that the two absorption bands at 209 nm and 237 nm decreased with increasing concentrations of $NaBH_4$. When the concentration of $NaBH_4$ reached 10%, these absorption bands disappeared. This indicates that the H_2PdCl_4 precursor has been completely reduced to metallic palladium.

3.5 XRD and SEM Results
To prove the completeness of palladium recovery from the spent activated carbon-supported palladium catalyst, XRD measurements were taken on the solid residue before and after leaching (**Figures 6(a)**
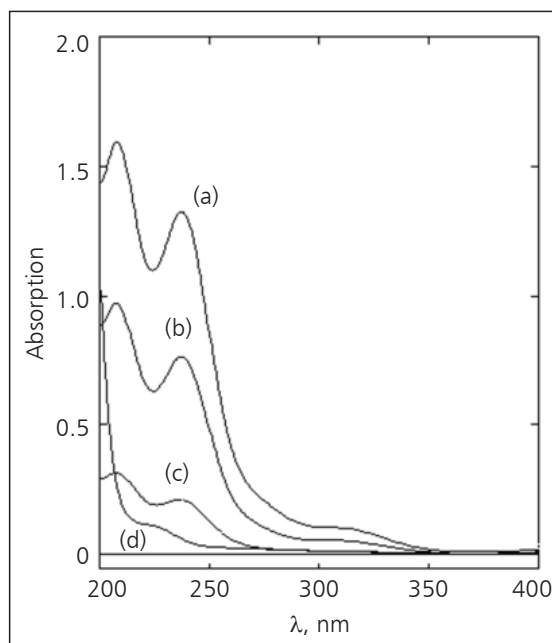
Fig. 5. UV-VIS spectra of the palladium solution after adding the reducing reagent with different percentages of $NaBH_4$ in the first step of chemical reduction: (a) 0%; (b) 2%; (c) 7%; (d) 10%
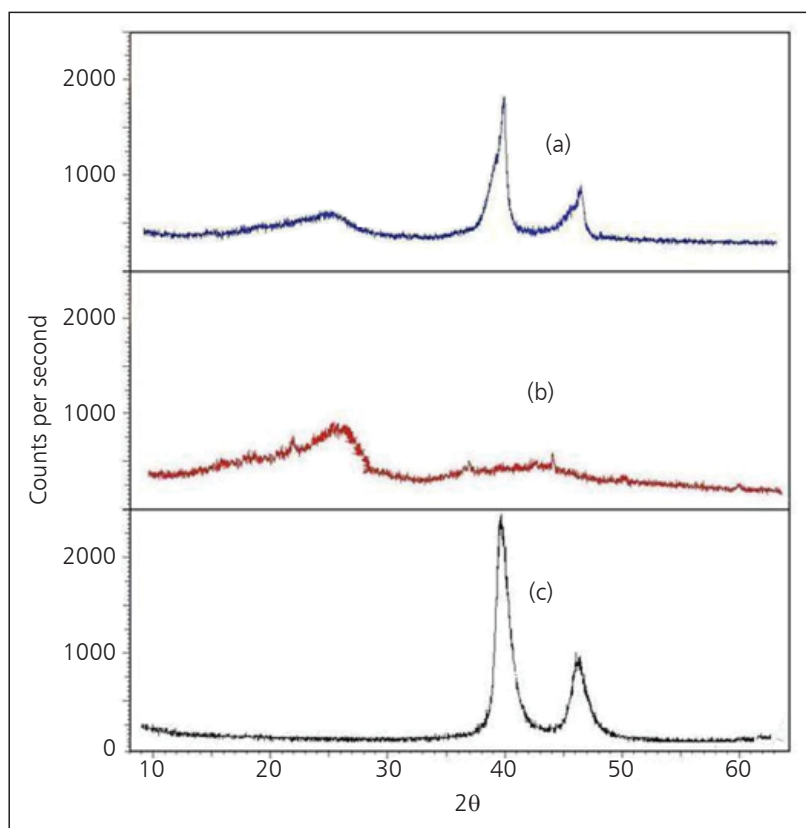
Fig. 4. The effect of addition of sodium borohydride in 5% NaOH to the palladium solution

Fig. 6. XRD pattern of Pd/AC spent catalyst: (a) before leaching; (b) after leaching; and (c) the recovered palladium powder

and **6(b)**). The XRD pattern of the final reduced palladium sample is also shown (**Figure 6(c)**). In the spectra of the spent catalyst before leaching, the sharp and narrow peaks at $2\theta = 40.1°$ and $46.6°$ were attributed to the presence of crystalline palladium in the form of large crystals, in line with findings reported by A. Drelinkiewicz *et al.* (28) and J. Y. Ying *et al.* (29). These crystalline palladium peaks were clearly separated from the relatively broad 'halo' centred shoulder of activated carbon at around $2\theta = 26°$ (**Figure 6(a)**). After the leaching process, the characterisation peaks of Pd at $2\theta = 40.1°$ and $46.6°$ were not detected indicating the completeness of the leaching process (**Figure 6(b)**). Upon reduction of the H_2PdCl_4 precursor to metallic Pd by $NaBH_4$, the solid reside exhibited only the peaks at $40°$ and $47°$ (**Figure 6(c)**) indicating complete reduction. The unstrained Pd phases should exhibit an XRD pattern according to the powder diffraction files (PDF) database as follows: Pd(1 1 1) ($39.8°$), Pd(2 0 0) ($46.3°$) and Pd(3 1 1) ($81.6°$) (30). This confirms the crystal structure of bulk palladium. The peak at $81.6°$ is not

shown as the XRD scans were performed at ambient temperature with a 2θ range between $10°$ and $60°$.

Scanning electron micrographs for the samples before and after leaching are shown in **Figures 7(a)** and **7(b)**, respectively. The morphology of the spent catalyst samples before and after leaching was compared, confirming the presence of small discrete particulates before the leaching, as seen in **Figure 7(a)**. These micrometre scale zero-valent Pd metal particles disappeared after the leaching process as shown in **Figure 7(b)**. Along with the results obtained by XRD, this confirms that 100% recovery of palladium from the spent Pd/AC catalyst was successfully achieved.

Figure 7(c) shows the SEM image of metallic palladium after recovery. The morphology of the submicron crystallites can be clearly seen. The presence of very tiny particles in the range 250 nm to 550 nm was also verified by Zetasizer measurements. The recovered palladium is therefore demonstrated to be suitable for preparing fresh nanostructured activated carbon-supported catalyst.
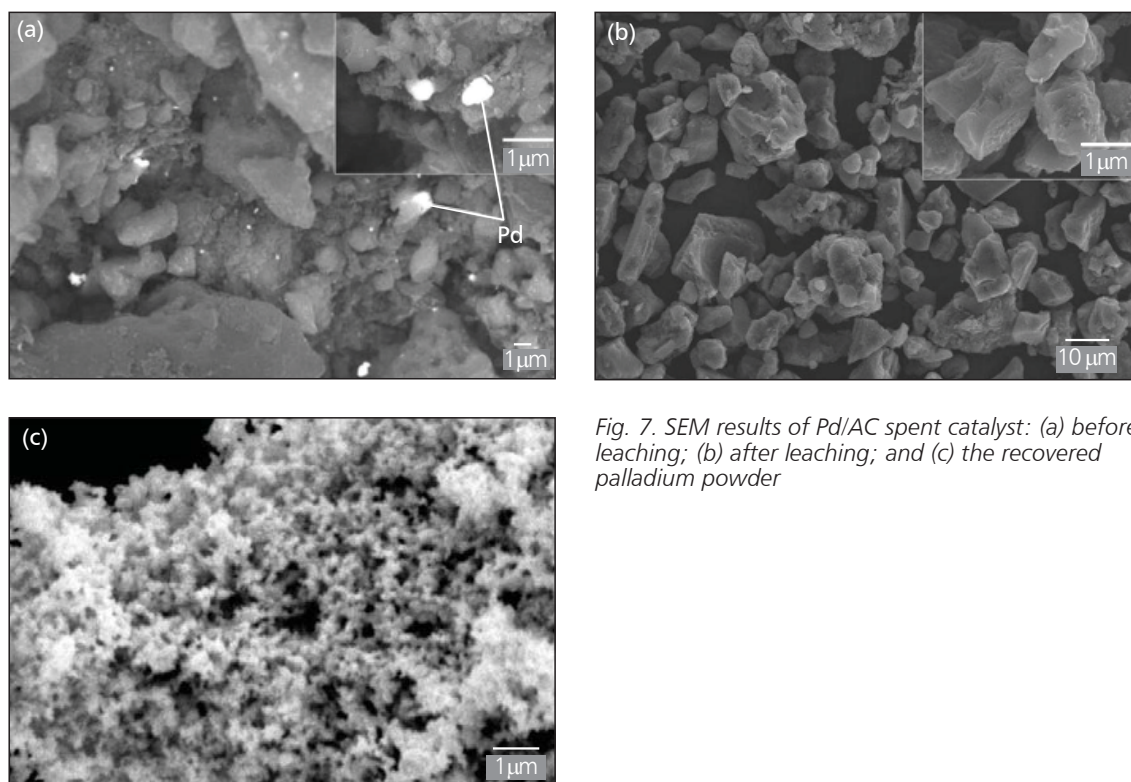
Fig. 7. SEM results of Pd/AC spent catalyst: (a) before leaching; (b) after leaching; and (c) the recovered palladium powder

4. Conclusions

A process for the recovery of palladium from spent activated carbon-supported palladium catalysts was described. Palladium was extracted from the matrix of the spent catalyst with an acid mixture of dilute hydrochloric acid and hydrogen peroxide. Palladium was precipitated from the leached solution by $NaBH_4$. For leaching, a mixture of 10% HCl and 5% H_2O_2 was seen to be sufficiently effective to extract all palladium from the activated carbon-PTFE organic matrix. The maximum palladium recovery was obtained after treatment at 90ºC for 3 h. Complete precipitation of palladium was accomplished using a $NaBH_4$ concentration of 7% and a reduction temperature of 100ºC.

Characterisation by UV-vis, XRD and SEM was used to prove the effectiveness of the developed process. It was shown by these studies that all palladium was recovered from the spent catalyst. The XRD study verified the metallic form of recovered palladium. The reduction of H_2PdCl_4 to metallic palladium was monitored by UV-vis, showing that the optimum concentration of $NaBH_4$ in alkaline solution was 10% to completely reduce the H_2PdCl_4 precursor. The production of metallic nanoparticles by treatment with sodium borohydride was verified by SEM imaging and Zetasizer measurements. The metallic palladium recovered using the method described here is believed to have the required specification to manufacture fresh activated carbon-supported palladium catalysts.

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