Platinum-rhodium gauzes are frequently used to catalyse the high temperature ammonia oxidation step for production of synthetic nitrogen-based fertilisers. The gauzes suffer from Pt loss in the form of platinum dioxide (PtO$_2$), due to the highly exothermic nature of the oxidation reaction. Industrially this is mitigated by installing one or more palladium-nickel catchment gauzes directly downstream of the combustion gauzes, to capture the lost Pt. The Pd-Ni catchment gauzes undergo severe structural modification during operation. In this study, we undertake a systematic study in a laboratory-scale furnace system to determine the role of each of the constituent gases O$_2$, H$_2$O and PtO$_2$ on the structural changes of the Pd-Ni gauzes. In addition, some samples are exposed to real industrial conditions in an ammonia combustion pilot plant reactor. Fresh and spent catchment gauzes are analysed by means of scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), thermogravimetric analysis (TGA) and inductively coupled plasma mass spectroscopy/optical emission spectroscopy (ICP-MS/OES). By combining analysis of samples from furnace and pilot scale experiments, the main findings are that Pd-Ni gauzes undergo internal oxidation to nickel(II) oxide (NiO); which in the presence of steam results in Ni depletion and that PtO$_2$ vapour causes severe grain reconstruction. Furthermore, in laboratory-scale experiments no significant Pd loss is observed, which is in contrast to observations from the pilot plant where the samples are exposed to real post-ammonia oxidation conditions. Pd loss is likely attributed to some gas species contained in the real post-ammonia oxidation gas stream.

**Introduction**

Ammonia oxidation is one of the key reaction steps in the production of synthetic nitrogen-based fertilisers. Industrially, the reaction is typically carried out at 900°C and a pressure of 1–13 bar over metallic Pt-Rh catalytic gauzes (1). During operation, the Pt-Rh catalyst undergoes several structural changes, such as grain growth of the wire core, surface formation of so-called cauliflowers and enrichment of Rh on the wire surface, due to a significant loss of Pt (2, 3). The Pt is mainly lost as gaseous PtO$_2$ and it is anticipated to be caused by hot spots on the Pt-Rh gauze due to the extreme
exothermic nature of the oxidation of ammonia to NO (2) (selectivity ~96% (1)), Equation (i) (4):

\[
4\text{NH}_3(g) + 5\text{O}_2(g) \rightarrow 4\text{NO}(g) + 6\text{H}_2\text{O}(g) \\
\Delta H^0_{r,298 K} = -908 \text{ kJ mol}^{-1}
\]  

(i)

Depending on plant conditions, the Pt loss is in the range of 0.05–0.4 g per tonne nitric acid (HNO₃) produced i.e., noble metal loss in a modern plant producing on average 1000 tonnes HNO₃ per day, represents a huge financial cost for the fertiliser industry (1). State of the art technology to reduce this cost proceeds via catchment of the formed PtO₂ vapour by Pd-Ni alloy gauzes, located just downstream of the Pt-Rh ammonia oxidation catalyst. The predecessor of this catchment technology, a palladium-gold (80:20 wt%) alloy gauze, was developed by Degussa in the late 1960s (5). The Pd-Au gauzes quickly outperformed other catchment systems, such as glass wool filters, Raschig rings and marble chips (6). Later, cheaper metals such as Ni and cobalt replaced Au in the Pd-Au alloy, as they gave an enhanced catchment efficiency in addition to lower costs (7). Still, the Pd-Ni catchment unit has several drawbacks. During operation, the Pd-Ni gauze wires reconstruct completely and swell in size. This results in a significant loss of mechanical strength and additionally, it is the dominant cause of a large pressure drop increase over the gauze pack during the campaign, see Figure 1. Furthermore, during operation, the gauze is depleted in Ni and depending on plant conditions, 0.2–0.4 g Pd is lost per gram Pt captured (6).

Despite the fact that the aforementioned drawbacks of the Pd-Ni catchment system have been known for several decades, only a handful of studies related to this topic have been published in the last 50 years (5–18). Ning et al. (8) report on the surface reconstruction of the catchment gauze and both Fierro et al. (9) and Ning et al. (10) discuss the catchment mechanisms. Recently, Pura et al. (11) suggested that the alloying element Ni is not participating in the catchment process, but that grain boundary attack may be a mechanism responsible for grain reconstruction. This was further investigated by Pura et al. (18) suggesting that a rapid loss of Ni from grain boundaries causes the initial porosity in the wire. Still, sufficient understanding of the occurring reactions is not achieved and knowledge on how to improve or modify the Pd-Ni based catchment systems is still lacking. The common denominator between all the mentioned investigations is that they are based on gauzes used in industrial operation, where several different parameters such as temperature and gas composition are in play simultaneously. To the best of our knowledge, no or only minor focus has been put on systematic, single-parameter studies to unravel the underlying reasons for the grain reconstruction phenomena.

Here we report the results of systematic studies to understand the role of the individual constituents of the reaction gas mixture (O₂, H₂O and PtO₂ diluted in N₂) in the reconstruction of Pd-Ni gauzes, at conditions relevant for high-temperature ammonia oxidation. By exposing pure Pd and Pd-Ni wires and woven gauzes in a laboratory-scale furnace to the individual gas components in a systematic manner, we investigate which gas species cause reconstruction. We will also discuss the role of Ni with respect to Pt catchment, Ni loss and the existing Ni species during operation (metal, oxide and hydroxide). Finally, we compare the laboratory-scale results with two samples treated in a pilot plant at the Yara Technology Center facility (Herøya, Norway), where the samples experience the real conditions of high temperature ammonia oxidation in terms of gas mixture, linear gas velocity, temperature and pressure.

**Experimental**

Wires and woven gauzes of the industrial alloys Pd-Ni (95:5 wt%) and pure Pd were supplied by K. A. Rasmussen (wire diameters of 76 μm and 120 μm) which were used for the laboratory-scale experiments. In addition, pure Pd catchment gauzes
(76 µm) were used in pilot plant experiments with a pure Pt net and a lanthanum cobaltite (LaCoO₃)-based ammonia oxidation catalyst, the latter in the form of 3 mm cylindrical pellets. For the laboratory-scale furnace experiments, samples were heat treated in a six-zone furnace at 900–1050°C (ambient pressure) in a quartz tube (inner diameter = 6 mm) in various gas atmospheres containing synthetic air (5.0, Praxair, USA), steam and PtO₂ vapour. The composition of the water vapour mixture was 33 vol% H₂O, 14 vol% O₂ and 53 vol% N₂. PtO₂ vapour was generated from a rolled up Pt gauze (~0.4–0.8 g) located upstream of the sample at 1050°C, producing a p(PtO₂) of approximately 1 × 10⁻⁸ bar (2.5 mg Pt loss over 20 days in a flow of 1 l air per min). During heat treatment, samples were positioned perpendicular to the length direction of the quartz tube to enhance gas exposure to the gauze and wire in the gas flow. Samples from the Yara pilot plant were treated at 900°C and 5 bar in a gas mixture containing 10 vol% NH₃ in compressed air, before the ammonia oxidation combustion catalyst. This implies that the gas mixture contained approximately 9 vol% NO, 15 vol% H₂O and 6 vol% O₂, 2000 ppm or 100 ppm N₂O (pure Pt or oxide catalyst) and the rest N₂ when exposed to the catchment alloy. The pilot plant samples were exposed to exactly the same conditions as industrial catchment gauzes and are compared with laboratory-scale samples (as described above) and industrial samples treated at 900°C at 5 bar for 47 days below an industrial Pt-Rh (95:5 wt%) catalyst in the industrial gas mixture (10 vol% NH₃ in compressed air).

Various sample surfaces and cross-sections were examined with a high-resolution Hitachi Regulus 8230 field-emission scanning electron microscope (FE-SEM). Images were obtained by collecting the secondary electrons produced by the electron beam (FE-SEM). Images were obtained by collecting the secondary electrons produced by the electron beam. Qualitative EDX analysis (mapping and point quantification) was performed on selected samples using an acceleration voltage of 1 kV. Qualitative EDX analysis (mapping and point quantification) was performed on selected samples using an acceleration voltage of 1 kV. Samples were mounted with carbon tape on a copper plate or prepared for cross-section imaging by casting the wire in a conducting resin (PolyFast, Struers, UK) before grinding and polishing (1 µm diamond finish). Wet chemical etching of the polished sample was performed in HNO₃ (heat-treated gauze) or aqua regia (unreacted gauze) for 30 seconds at room temperature. Light microscopy was performed with a Zeiss Axio metallurgical microscope. ICP-MS/OES analysis was performed on selected samples by SINTEF Molab AS (Norway). Prior to analysis, samples were fully dissolved in aqua regia. The Pt content was determined by ICP-MS whereas Pd and Ni concentrations were determined by ICP-OES. The standard deviation was in the range of 1–2% of the measured value.

TGA was conducted with a NETZSCH (Germany) STA 449 F1 Jupiter®, with an alumina TG-pin stage. The experiments were performed by stacking six (6) fresh Pd-Ni (or Pd) gauzes on top of each other and heating to 140°C to remove humidity and other surface species on the sample. Thereafter, the sample was ramped to 900°C (10°C min⁻¹) before a 24 h dwell. After the experiment was completed, the same setup and temperature program was rerun with a fully oxidised sample for the background correction. In all experiments O₂ (5.0) and N₂ (5.0) from Praxair were used and the pO₂ was 0.2 bar over the sample.

**Results and Discussion**

**As-Received Palladium-Nickel and Palladium Catchment Gauzes**

Prior to exposing the as-received Pd-Ni and Pd wires to any gases, SEM and EDX analysis was performed on both wire surfaces and their cross-sections. In Figure 2, representative overview images of the wire surface (Figure 2(a)) and the cross-section (Figure 2(b)) of the 120 µm Pd-Ni alloy are shown. Overall, EDX analysis confirms the cross-sections of the alloys to contain minute quantities of oxygen, with slightly enhanced amounts at the surface, see Table I. In addition, EDX analysis of three randomly selected points on the Pd-Ni cross-section reveal the Ni content to be in the range from 4.4–5.0 wt%, close to the value provided by the supplier. EDX mapping did not reveal any obvious heterogeneities or impurities, neither within the grains nor along the grain boundaries. Based on this we conclude the Pd-Ni alloy to be a homogeneous solid-solution, of ~95:5 wt% Pd-Ni, within the uncertainty of the EDX analysis. Finally, it should be noted that light microscopy of chemically etched cross-sections reveal sharp grain boundaries and a grain size of 5–20 µm for 76 µm wires, of both Pd and the Pd-Ni alloy, see Figure 2(c) for the Pd-Ni alloy.

**Effect of Oxygen**

When the metallic Pd-Ni gauze (wire diameter 76 µm) is exposed to air in the TGA instrument at 900°C for 24 h, a mass gain of 1.47 wt% is...
recorded, see Figure 3(a). The observed mass gain is slightly larger than the theoretical value (1.36 wt%) for complete oxidation of Ni to NiO for a 95:5 wt% Pd-Ni alloy. When exposing the metallic Pd gauze to similar conditions, only a minor mass gain is observed (not shown). With reference to Ning et al. (10) and Gegner et al. (19), we assign the observed mass gain of the Pd gauze to a small oxygen solubility and formation of PdO on the Pd surface. The minor mass gain observed for pure Pd may indeed contribute in the slightly larger observed mass gain relative to theory for the Pd-Ni sample. The internal oxidation of the Pd-Ni alloy is shown visually in Figure 3(b)–(d). Here, cross-sections of the Pd-Ni wire heated for 1 h and 4 h, analysed by SEM and EDX, show small precipitated particles approaching the wire centre with time. By EDX point analysis, the precipitated particles are found to consist of oxygen and nickel in an approximately 1:1 molar ratio, indicating NiO formation (Figure 3(c)).

As shown in Figure 3(e) and Figure 3(f), chemical etching prior to SEM and EDX analysis reveals that the largest NiO precipitates are located at the grain boundaries and that the grain size has increased to 10–30 µm. Additionally, the NiO precipitates are found at equal depth within the grains as in the grain boundaries, indicating that oxygen diffusion is approximately equally fast in grains and grain boundaries (Figure 3(b)–(d)). Notably, at the same time as oxygen diffuses towards the wire centre, EDX mapping show a distinct reduction in Ni concentration in the wire core (Figure 3(b)–(d)). EDX point analysis of the wire core indicate the Ni content to be 4.2 wt% and 2.7 wt% after 1 h and 4 h, respectively. This implies that during the oxidation process the Ni mobility is enhanced, causing a heterogeneous distribution of Ni with more NiO at the outer part of the wire. These observations coincide well with reports by Gegner et al. (19) on internal oxidation of alloys with a non-noble element in a solid solution with a more noble element. Finally, it should be noted that the initial grain growth is seen during the first 24 h, but no significant grain growth is observed after another 20–30 days of heat treatment (see Figure S1 in the Supplementary Information).

### Table I Qualitative EDX Results of Fresh 120 µm Pd and Pd-Ni (95:5 wt%) Alloys

<table>
<thead>
<tr>
<th>Sample</th>
<th>Area</th>
<th>Details</th>
<th>Pd, wt%</th>
<th>Ni, wt%</th>
<th>O, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd-Ni</td>
<td>Surface</td>
<td>Large area</td>
<td>91.3</td>
<td>4.4</td>
<td>4.3</td>
</tr>
<tr>
<td>Pd-Ni</td>
<td>Cross section</td>
<td>Point, centre</td>
<td>95.0</td>
<td>5.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Pd-Ni</td>
<td>Cross section</td>
<td>Point near centre</td>
<td>94.9</td>
<td>5.1</td>
<td>0.0</td>
</tr>
<tr>
<td>Pd-Ni</td>
<td>Cross section</td>
<td>Point off centre</td>
<td>94.5</td>
<td>4.4</td>
<td>1.1</td>
</tr>
<tr>
<td>Pd</td>
<td>Surface</td>
<td>Large area</td>
<td>94.2</td>
<td>0.2&lt;sup&gt;a&lt;/sup&gt;</td>
<td>5.6</td>
</tr>
<tr>
<td>Pd</td>
<td>Cross section</td>
<td>Point, centre</td>
<td>100.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

<sup>a</sup> Possibly overestimated value due to peak overlap between Ni and Cu (sample is mounted on Cu plate). Analysis certificate from K. A. Rasmussen shows a Ni content of <2 ppm in pure Pd wires.

Fig. 2. (a) SEM image of the surface of a fresh 120 µm Pd-Ni wire; (b) SEM image of the cross-section of a fresh 120 µm Pd-Ni wire; (c) light microscope image of a 76 µm Pd-Ni wire after etching in aqua regia for 30 s.
Palladium-Nickel Gauzes Exposed to Wet Air

When water vapour is included in the feed gas (wet air: 33 vol% H₂O, 14 vol% O₂, 53 vol% N₂), the internal oxidation of Ni to NiO occurs in a similar manner as in dry air, see Figure 4(a). However, based on gravimetry, the Pd-Ni gauze has lost 2.4 wt% of its initial mass after heat treatment for two weeks in wet air at 1050°C. ICP-MS analysis of the exposed gauze give a total Ni concentration of only 2.7 wt% relative to Pd, compared to 4.8 wt% on a comparable sample treated in dry air. In addition, SEM analysis reveals that the outer parts of the Pd-Ni wire is depleted in Ni (Figure 4(b)) and that some surface roughness has appeared (Figure 4(c)). The data also shows that only 0.1 wt% Pd is lost during two weeks’ treatment in wet air; far below the industrial Pd loss observed during ammonia oxidation (see below). There is also no observed Pd loss in dry air. This correlates well with the work of Opila (20), which shows no Pd loss in wet or dry oxygen and Ar and other literature on Pd loss in dry air (21). Notably, these findings are in contradiction to the calculations of Factsage (22, 23), which estimate a significant Pd loss as PdOH (22, 23) in wet gas and a smaller loss as PdO₂ and Pd(OH)₂ (22, 23) (see Figure S2 in the Supplementary Information). This leads to the conclusion that the observed mass loss of Pd-Ni in wet air is due to NiO being hydrolysed by the wet air and forming volatile Ni(OH)₂, which in turn causes Ni depletion. This observation is in line with Chen et al. (24).

Finally, after the two weeks’ treatment in wet air the NiO precipitates are no longer seen at the grain boundaries. Unfortunately, chemical etching prior to SEM analysis has not revealed the exact position of the grain boundaries and thus the occurrence of grain growth is uncertain. In many ways the situation is similar to the grain growth observed during the initial oxidation process of Ni to NiO. During the initial oxidation, inwards/outwards diffusion of O-Ni increased the mobility of O-Ni, just as treatment in wet air may have increased Ni mobility by Ni diffusion towards the surface. The increased mobility may again contribute to grain growth. However, we are currently not in position to elaborate in detail on how grain growth is interwoven and connected to diffusion and the
oxidation process. We suggest this as a topic for future investigations.

**Effect of Platinum Dioxide Vapour in Dry and Wet Air**

The effect of exposing Pd and Pd-Ni wires to PtO₂ vapour in both dry and wet air is evaluated. First, we investigated if the presence of Ni in the catchment alloy would influence reactivity of PtO₂ toward Pd. Based on this, both materials were heat treated in dry air at 1050°C with Pt gauges installed upstream. The results of exposing the two catchment materials to PtO₂ in dry air at 1 h, 4 h and 10 h are presented in **Figure 5**. Both materials undergo an immediate surface reaction and small Pd-Pt particles or crystals (size ~2–3 µm) are already formed on the wire surfaces after 1 h exposure, as shown in **Figure 5(a) and Figure 5(d)**. The crystals show roughness and have several small ladders on their sides, which increase in size from 4 h to 10 h (**Figure 5(b)–(c) and Figure 5(e)–(f)**). Notably, for Pd-Ni (**Figure 5(a)–(c)**), some smaller (1–2 µm) and more faceted crystals appear with a darker contrast in the SEM images. EDX mapping and point analysis of these crystals indicate NiO formation, in line with previous observations of Ni-oxidation in air. From the SEM images reported in **Figure 5**, it appears as if Pd-Pt based crystals develop at a similar rate in both Pd-Ni and Pd (**Figure 5**). We
therefore conclude that the NiO particles are not participating in the reconstruction and growth process of the Pd-Pt crystals.

With further heat treatment (≥1 day), the interior of the Pd and Pd-Ni wires become subject to the earliest stage of grain reconstruction and ladder-like growth, as if PtO$_2$ is penetrating sub surface from the formed Pt-Pd crystal layer reacting with more fresh metal on the wire, see Figure 6(a) and Figure 6(b). At longer exposure time (≥3 days), the surface crystals show beautiful single crystal shapes. The ladders causing further crystal growth (from ~10–30 µm) are large, slowly growing over a face of an already existing crystal (Figure 6(c)). Prolonged exposure times (20 days) result in complete grain reconstruction to large surface crystals (~20–30 µm) (Figure 6(d)–(f)). The grain reconstruction and crystal formation also causes significant wire swelling; the wire diameter increases by up to 60% after 20 days, see Figure 6(e) and Figure 6(f) and Table II. Additionally, the grain reconstruction of the wire or gauze causes a significant reduction of mechanical strength.

Selected crystals on both the Pd-Ni and the Pd wires are analysed with respect to Pt content by means of EDX analysis and the results are summarised in Table II. Pt concentration in the average top-layered crystals increases rapidly the first day (~10–12 at%), followed by a slower accumulation. This observation goes hand in hand with the fact that the reconstruction starts to occur below the top layer of crystals, after one day on stream (Figure 6(a) and Figure 6(b)), indicating that Pt catchment is preferred on the Pd rich areas below the outermost Pd-Pt crystals. After 20 days on stream (Figure 6(a) and Figure 6(b)), indicating that Pt catchment is preferred on the Pd rich areas below the outermost Pd-Pt crystals. After 20 days on stream, the average surface crystals reach a Pt content of ~22 at% Pt, while the outermost exposed crystals reach a Pt content up to ~40 at% (65 wt%). This is similar to an industrial sample treated for 47 days, where the average Pd-Pt crystal on the wire surface has a Pt concentration of ~30 at%.

At this point it is worth commenting that the Pd-Pt crystal growth rate depends on how a specific part of the gauze or wire is directed toward the high velocity gas stream. The PtO$_2$ molecules have better access to such areas, which is reflected in a

**Table II Relative Increase in Wire Diameter and Qualitative EDX Results of Pt Concentrations in Pd-Pt Surface Crystals on Pd-Ni (120 µm) and Pure Pd (76 µm) Wires, After Heat Treatments at the Indicated Conditions**

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Time</th>
<th>Gas conditions</th>
<th>Wire swelling, %</th>
<th>Pt content, at %</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1050</td>
<td>1 h</td>
<td>Dry air</td>
<td>–</td>
<td>–</td>
<td>1</td>
</tr>
<tr>
<td>1050</td>
<td>4 h</td>
<td>Dry air</td>
<td>5</td>
<td>~0</td>
<td>6</td>
</tr>
<tr>
<td>1050</td>
<td>4 h</td>
<td>Dry air</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>1050</td>
<td>10 h</td>
<td>Dry air</td>
<td>5</td>
<td>~0</td>
<td>3</td>
</tr>
<tr>
<td>1050</td>
<td>10 h</td>
<td>Dry air</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>1050</td>
<td>16 h</td>
<td>Dry air</td>
<td>7</td>
<td>~0</td>
<td>12</td>
</tr>
<tr>
<td>1050</td>
<td>1 d</td>
<td>Dry air</td>
<td>12</td>
<td>5</td>
<td>11</td>
</tr>
<tr>
<td>1050</td>
<td>3 d</td>
<td>Dry air</td>
<td>25</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>1050</td>
<td>5 d</td>
<td>Dry air</td>
<td>37</td>
<td>25</td>
<td>14</td>
</tr>
<tr>
<td>1050</td>
<td>10 d</td>
<td>Dry air</td>
<td>35–45</td>
<td>35</td>
<td>14</td>
</tr>
<tr>
<td>1050</td>
<td>10 d</td>
<td>Dry air</td>
<td>–</td>
<td>–</td>
<td>28</td>
</tr>
<tr>
<td>1050</td>
<td>20 d</td>
<td>Dry air</td>
<td>45</td>
<td>45–60</td>
<td>16</td>
</tr>
<tr>
<td>1050</td>
<td>30 d</td>
<td>Wet air</td>
<td>60–75</td>
<td>–</td>
<td>28</td>
</tr>
<tr>
<td>900</td>
<td>19 d</td>
<td>Pilot plant, Pt catalyst</td>
<td>–</td>
<td>45–55</td>
<td>–</td>
</tr>
<tr>
<td>900</td>
<td>19 d</td>
<td>Pilot plant, oxidation catalyst</td>
<td>–</td>
<td>45–60</td>
<td>–</td>
</tr>
<tr>
<td>900</td>
<td>47 d</td>
<td>Industrial plant</td>
<td>–</td>
<td>45–50</td>
<td>30</td>
</tr>
</tbody>
</table>

$^a$All EDX measurements have an estimated uncertainty of ~10% of the measured value, while the values of swelling have an uncertainty of ~20% of the indicated value due to local variations in sample diameter

$^b$Crystal located on wire edge, making it subject to a large gas flow and PtO$_2$-concentration during laboratory scale experiments
higher Pt content; more reconstruction and larger crystal facets (Table II). This is more prominent in laboratory-scale experiments, where the gas is not passing equally uniformly through the gauze as in the industrial or pilot plant. Correspondingly, on laboratory-scale samples, reconstruction is slower and Pt catchment lesser at the wire crossings and at the side(s) of the wire not directly exposed to the gas stream. These observations are applicable to both the Pd-Ni and the Pd catchment gauzes.

We can now combine the two previous experiments and perform a heat treatment with both wet air and PtO$_2$. If a Pd-Ni gauze is heated for two weeks at 1050°C in wet air with PtO$_2$, a mass increase of 6.5 wt% is observed. From ICP-MS/OES, the resulting Pd-Ni wire contains only 2.8 wt% Ni relative to Pd, at the same time as the gauze has reached a Pt content of 9.3 wt%. This indicates simultaneous Ni loss and Pt catchment. Furthermore, if the Pd-Ni gauze is heated for 30 days in total, the exterior of the wire becomes completely reconstructed, at the same time as the wire is almost fully depleted of Ni, see Figure 7(a) and Figure 7(b). Only the wire core shows the presence of NiO particles. We therefore state that Ni-loss and grain reconstruction are individual effects, caused by the presence of water vapour and PtO$_2$, respectively.

Comparing with investigations by Pura et al. (18), we have also observed diffusion and segregation of NiO in the grain boundaries. However, this seems not to cause grain reconstruction or porosity in dry or wet air. Our findings coincide well with the statement by Pura et al. (11), i.e. grain reconstruction is not caused by the presence of Ni or loss of Ni from the Pd-Ni alloy, but rather by catchment of Pt.

**Pilot Scale Experiments – Testing at Industrial Conditions**

Finally, two samples have been exposed in the ammonia oxidation pilot plant at the Yara Technology Center industrial facility. Here, NH$_3$ is included in the gas stream (10 vol% in air) and combusted over an ammonia oxidation catalyst just upstream of the catchment unit. Two scenarios were explored: (i) six pure Pt ammonia combustion gauzes and (ii) a bed of LaCoO$_3$-based ammonia oxidation catalyst pellets, positioned just upstream of a 76 µm pure Pd catchment gauze. As Ni does not significantly affect Pt catchment it was chosen to use pure Pd and not Pd-Ni gauzes in the pilot plant. The experiments were run for nineteen days at 900°C at total pressure of 5 bar, during which each combustion catalyst produced ca. 28 tonnes of nitric acid.

In the first case, when the ammonia oxidation catalyst was a pure Pt gauze, similar features occurred compared to samples heat-treated in the laboratory scale furnace in wet air with Pt upstream. This includes Pt catchment, grain

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Fig. 6. SEM images of Pd (76 µm) and Pd-Ni (120 µm) gauzes heat treated at 1050°C with Pt upstream for 1–20 days: (a) Pd-Ni 1 day; (b) Pd 1 day; (c) Pd-Ni 3 days; (d) Pd-Ni 5 days; (e) Pd-Ni 20 days; (f) Pd 20 days
reconstruction and swelling, see Figure 7(c) and Figure 7(d). The Pd-Pt crystals on the wire surface are in the range of 10–30 µm in size, with an average Pt concentration of ~30 at% (44 wt%), while the gauze in total had a Pt concentration of ~14 at% (23 wt%). The Pt concentration of the surface crystals obtained by EDX is similar to those found in samples treated in the laboratory scale furnace, confirming the validity of the laboratory scale experiments on Pt catchment. In contrast to our laboratory scale experiments, we now observe a significant Pd loss (0.036 g tonne^{-1} HNO_3 produced), very similar to the loss observed with a Pt combustion catalyst (see above). Since the Pd loss in the pilot plant occurs both with a Pt and LaCoO_3 combustion catalyst, it is unlikely to be connected to the Pt catchment or grain reconstruction caused by PtO_2. In addition, there is no known thermal loss mechanism for Pd in wet or dry air that can explain such a large thermal Pd loss in the process gas (20). This leads to the conclusion that Pd loss is most probably caused by interaction with the demanding gas stream conditions of ammonia oxidation and thus by the gas constituents that were not present in the laboratory-scale experiments. Identifying the species or combination of species, present in the combusted process gas that lead to Pd loss is a very relevant topic for future investigations.

**Conclusion**

In this work we have observed that the Pd-Ni catchment system in a dry oxygen containing atmosphere is subject to internal oxidation of Ni to NiO. Further, in a wet oxygen enriched environment, Ni is also oxidised to NiO, but subsequently lost, most probably as Ni(OH)_2. Furthermore, the presence of
PtO$_2$ vapour in wet or dry air causes severe grain reconstruction of both Pd and Pd-Ni wires, which in turn causes wire swelling and pore formation similar to industrial Pd-based catchment systems used during ammonia oxidation. In laboratory furnace experiments, no distinct Pd loss accompanies the Pt catchment. However, pilot-scale testing in an ammonia oxidation atmosphere show significant Pd loss, both with a Pt and LaCoO$_3$-based (non-Pt containing) combustion catalyst. In addition, a second type of pore formation is observed when using the LaCoO$_3$ catalyst in the pilot plant. Therefore, we suspect the Pd loss and the second type of pore formation to be related to gas species present only in the industrial gas mixture, not in our laboratory scale gas mixtures. We suggest this as a topic for further investigation.

Acknowledgements

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