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1 **Structure-sensitivity of alumina supported palladium catalysts for N₂O**
2 **decomposition**

3

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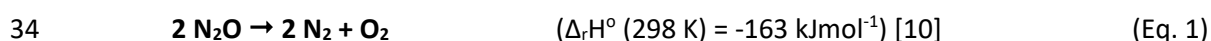
13 **Abstract**

14 The catalytic activity of Pd/ γ -Al₂O₃ for N₂O decomposition was found to be highly dependent on the
15 preparation methodology and the number of reaction cycles. Chloride species on the surface of a 2.6
16 wt. % Pd-Al₂O₃ catalyst prepared by wet impregnation were identified as inhibiting the activity.
17 Multiple reaction cycles were shown to remove these species, and a subsequent increase in activity
18 was observed; 10.3 mol_{N₂O} h⁻¹ kg_{cat}⁻¹ in the first use, increased to 28.7 mol_{N₂O} h⁻¹ kg_{cat}⁻¹ on the fourth
19 use both at 550 °C. Additionally, removal of physisorbed water from the support prior to metal
20 deposition increased the thermal stability of Pd nanoparticles and increased the catalyst activity.
21 Catalysts were subsequently prepared using a deposition technique with an increased concentration
22 of Cl⁻ ions resulted in increased Pd-Cl species in the final catalyst and the catalytic activity was
23 consequently increased due to the improved control of Pd particle size.

24

25 Keywords: Nitrous Oxide Decomposition, Particle Size, CO Chemisorption, HAADF-STEM, Pd-Al₂O₃.

27 Nitrous oxide (N₂O) is a highly potent greenhouse gas, this being evidenced by its global warming
28 potential of *ca.* 300 relative to CO₂ [1–3]. 60 % of the global N₂O emissions are anthropogenic and
29 include industrial chemical processes, sewage treatment, combustion sources (both stationary and
30 mobile) and the agricultural sector [4–7], while adipic acid production accounts for around 80 % of the
31 global industrial emission of N₂O [6,8]. There are also small industrial uses such as hospital and dental
32 surgeries [9]. Consequently, it is of great importance to develop catalysts that can efficiently
33 decompose N₂O (Eq. 1):



35 There are many catalysts that can be used for N₂O decomposition including perovskites [11–15], ceria-
36 based catalysts [16–18], spinels [19–21] and supported metal catalysts [22–26]. This work focuses on
37 palladium/alumina (Pd-Al₂O₃) catalysts as these have not been extensively studied to date [27–31] and
38 similar catalytic systems have been demonstrated to exhibit high activity and stability in similar
39 applications [32–37]. Pekridis *et al.* reported a T₁₀₀ (i.e. the temperature to reach 100 % conversion)
40 of 425 °C using a 2 wt. % Pd-Al₂O₃ catalyst prepared by wet-impregnation. They also showed that the
41 addition of propane to the gas feed lowered the T₁₀₀ to 400 °C [27]. The rate-limiting step in the
42 decomposition of N₂O is typically the recombination of oxygen to form O₂ [38–44] and propane acts
43 as reductant that can facilitate the abstraction of oxygen from the oxidised active site, significantly
44 increasing the observed rate of N₂O decomposition at lower temperatures [27,28]. In addition to
45 propane [45–49] ethane, methane and CO [49–54] have also been used as reductants. Christoforou *et*
46 *al.* reported that 72 % conversion was possible using 2 wt. % Pd-Al₂O₃ at 600 °C, the addition of
47 propane to the feed lowers the temperature required for 100 % conversion by over 200 °C. [28]. Doi
48 *et al.* utilised a higher weight loading of 5 % with only 60 ppm N₂O in the gas stream and showed that
49 it was possible to decompose this low concentration of N₂O at 300 °C; however, air was used as the
50 balance gas of this reaction and in this case that the addition of oxygen to the feed increases the
51 activity [31]. It is important to note that in most cases the addition of oxygen to the gas feed limits the
52 conversion of N₂O, this is because the oxygen present oxidises the active site of the catalysts
53 [22,27,55].

54 A range of Pd concentrations have been shown to be active for the decomposition of N₂O. Tzitzios *et*
55 *al.* prepared a 0.5 wt.% Pd- Al₂O₃ catalyst by wet impregnation using a nitrate precursor that achieved
56 55 % conversion of N₂O at 550 °C. The group showed that the presence of a reductant (CO) to the feed
57 lowers the temperature required for 50 % conversion (T₅₀) from 536 °C to 366 °C, a decrease of 170 °C
58 in the operating temperature.[56] Parres-Esclapez *et al.* also prepared a 0.5 wt.% Pd-Al₂O₃ catalyst by

59 impregnation using a Pd acetate precursor that converted 34 % N₂O present at 600 °C.[22] Staying on
60 the theme of low Pd loadings, Pachatouridou *et al.* prepared a 1 wt.% Pd-Al₂O₃ catalyst by dry
61 impregnation, that reached 78 % conversion at 600 °C, with a T₅₀ of 525 °C.[57] Tateishi *et al.*
62 demonstrated that a higher weight loading was also good for this reaction with a commercial 5 wt.%
63 Pd-Al₂O₃ catalyst achieving 100 % conversion at 320 °C, but the catalyst that the group prepared by
64 wet impregnation required 500 °C to achieve the same conversion in the same conditions (noting O₂
65 present in gas feed) [30].

66 In this work, we investigate the importance of surface species and particle size of Pd-Al₂O₃ catalysts
67 for the decomposition of N₂O in the presence and absence of a reductant, propane. The effect of
68 removing surface species such as water and chloride ions have been investigated by different pre-
69 treatments and support pre-treatments. In addition to comparing how activity changes based on these
70 pre-treatments, we have evaluated how the surface sensitivity of these catalysts can be used to
71 control the particle size and consequently, catalyst activity. Through pre-treatment of the catalyst
72 support prior to the metal deposition, the catalytic activity is significantly increased, resulting in a
73 decrease of the N₂O T₁₀₀ by 150 °C to 400 °C, in the presence of propane.

75 2.1 Catalyst Preparation

76 2.6 wt.% Pd-Al₂O₃ was prepared by wet impregnation as described by Pekridis *et al.* [27], PdCl₂ was
77 dissolved in deionised water to give a solution with a concentration of 6 mg mL⁻¹. γ-Al₂O₃ (0.98 g, Sigma
78 Aldrich, average particle size < 50 nm) was then added to the solution (4.6 mL) and heated slowly to
79 55 °C with stirring to remove the water via evaporation until a slurry was formed. The slurry was then
80 dried in an oven at (120 °C, 2 h) and calcined (600 °C, 4 h, heating rate 10 °C min⁻¹ in flowing air).
81 Where stated further heat treatments were carried out at 600 °C for 1 h at 20 °C min⁻¹ in flowing air.
82 In some cases γ-Al₂O₃ was calcined before catalyst preparation at 600 °C for 4 h at 10 °C min⁻¹ in flowing
83 compressed dry air. The following denominations were assigned to various catalysts: **SC** – Support
84 calcined at 600 °C for 4 h at 10 °C min⁻¹ in flowing compressed dry air before catalyst preparation. **5HT**
85 – catalyst prepared, calcined and subjected to 5 more heat treatments at 600 °C for 1 h at 20 °C min⁻¹
86 in flowing compressed dry air. **4R** – catalyst that has been through four reaction cycles. **5R** – catalyst
87 that has been through five reaction cycles.

88 2.1 wt.% Pd-Al₂O₃ was prepared by a modified impregnation method as described by Morad and co-
89 workers [58]. PdCl₂ was dissolved in water to give a solution with a concentration of 6 mg mL⁻¹, HCl
90 was added to acidify the solution until a concentration of 0.58 M was achieved. De-ionised water was
91 added to the solution (3.49 mL) to a total volume of 16 mL in a 50 mL round bottom flask. The solution
92 was heated to 60 °C in an oil bath. γ-Al₂O₃ (0.98 g, Sigma Aldrich, average particle size < 50 nm) was
93 added to the solution slowly over a period of 10 min. The slurry was left to stir for 15 min and then
94 the temperature was increased to 95 °C and left to dry for 16 h. The resulting solid was calcined at
95 600 °C for 4 h at 10 °C min⁻¹ in flowing compressed dry air. As with the wet impregnation samples, one
96 catalyst was prepared with γ-Al₂O₃ that had been calcined before catalyst preparation at 600 °C for 4
97 h at 10 °C min⁻¹ in flowing compressed dry air and was also denoted support calcined (**MI SC**). The
98 catalyst that was prepared by modified impregnation using untreated Al₂O₃ was denoted **MI**.

99 2.2 N₂O decomposition studies

100 All reactions were performed at atmospheric pressure in a continuous-flow fixed-bed reactor. A
101 reactor tube (4.6 mm internal diameter, stainless steel) was packed with catalyst (0.0625 g) between
102 two layers of quartz wool. Reactions were performed over the temperature range of 200 – 600 °C,
103 with a flow rate of 100 ml/min (GHSV 76690 h⁻¹). The gas feed was composed of 1 % N₂O in He or 1 %
104 N₂O and 1 % C₃H₈ in He. All outgoing gaseous products were analysed online using an Agilent 7890B
105 Gas Chromatograph (GC) (columns: Hayesep Q (80-100 mesh, 1.8 m) MoSieve 5A (80-100 mesh, 2 m)

106 fitted with a thermal conductivity detector. Pre-treatment of the γ -Al₂O₃ in the reactor prior to the
107 addition of the metal was carried out using 13 % O₂ and 87 % N₂ from separate cylinders (BOC grade
108 N4, 99.99 %).

109 2.3 Catalyst Characterisation

110 X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Fisher Scientific K-alpha⁺
111 spectrometer. Samples were analysed using a micro-focused monochromatic Al X-ray source (72 W)
112 over an area of approximately 400 microns. Data was recorded at pass energies of 150 eV for survey
113 scans and 40 eV for high resolution scan with 1 eV and 0.1 eV step sizes respectively. Charge
114 neutralisation of the sample was achieved using a combination of both low energy electrons and argon
115 ions. Data analysis was performed in CasaXPS using a Shirley type background and Scofield cross
116 sections, with an energy dependence of -0.6.

117 Solid-state Magic Angle Spinning Nuclear Magnetic Resonance (MAS-NMR) spectra were obtained at
118 the EPSRC UK National Solid-state NMR Service Durham University. Solid state ¹H Proton spectra were
119 recorded at 399.88 MHz using a Varian VNMRS spectrometer and a 4 mm (rotor o.d.) magic-angle
120 spinning probe. They were obtained using a background suppression pulse sequence, 128 repetitions
121 with a 1 s recycle delay and a spin-rate of approximately 14 kHz. Spectral referencing was to external,
122 neat tetramethylsilane carried out by setting the resonance from adamantane to 1.9 ppm.

123 Powder X-Ray Diffraction (XRD) analysis was performed on a PANalytical X'Pert Pro diffractometer
124 using a Ni-filtered CuK α radiation source operating at 40 KV and 40 mA. Standard analysis was
125 performed using a 40 minute run with a back filled sample holder. Patterns were identified using the
126 International Center for Diffraction Data Powder Diffraction File.

127 *In-situ* XRD was performed using a PANalytical X'Pert Pro diffractometer using a Ni-filtered CuK α
128 radiation source operating at 40 KV and 40 mA, fitted with a cell that allows temperature control and
129 gas flow using Bronkhorst MFC's. 'Data collector' program controls temperature settings, run time and
130 repeats. Patterns were identified using the International Center for Diffraction Data Powder
131 Diffraction File.

132 High-Angle Annular Dark-Field Scanning Transmission Electron Microscopy (HAADF-STEM) was
133 performed using a JEOL ARM 200CF AC-STEM instrument and the samples were prepared using the
134 dry dispersion route: The catalyst powder was ground between two clean glass slides and then dry
135 transferred onto a holey carbon TEM grid.

136 Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) was performed by Exeter
137 Analytical Services using HF digestion to get an accurate Pd loading. The sample was digested by Anton
138 Paar Multiwave 3000 microwave with nitric and HF acids – then the HF was neutralised with the
139 addition of Boric Acid. A reagent blank was carried out. Internal standard was added to the resulting
140 solutions and the blank and sample were run against Fe standards by ICP-OES using Thermo Fisher
141 iCAP Duo 7400.

142 CO Chemisorption was performed using a ChemBET TPR/TPD pulsar with a reduction in 10 % H₂/Ar up
143 to 150 °C before carrying out CO chemisorption at room temperature using 10 % CO/He using an
144 attenuation of 2, TCD sensitivity of 150 and CO flow of 15 mL min⁻¹. An automated pulse program was
145 used with a pulse length of 400 seconds, loop volume 125 μL, 16 pulses and a stable baseline.

147 Pd-Al₂O₃ catalysts have previously been shown to catalyse N₂O decomposition at high reaction
 148 temperatures (>500 °C) [22,27,30,56,57]. Initially, their stability was investigated through the use of
 149 multiple reaction cycles. The catalyst was heated step wise from 200 – 600 °C in 50 °C increments
 150 under a mixture of N₂O (1 %) in helium and the N₂O conversion was recorded every 50 °C. Following
 151 this, the catalyst bed was cooled under flowing helium and the reaction process repeated. In each
 152 cycle, the catalyst was exposed to the same pre-treatment as the initial test, as described in the
 153 experimental section. The catalytic activity could then be compared across the reaction cycles and
 154 differences investigated through material characterisation.

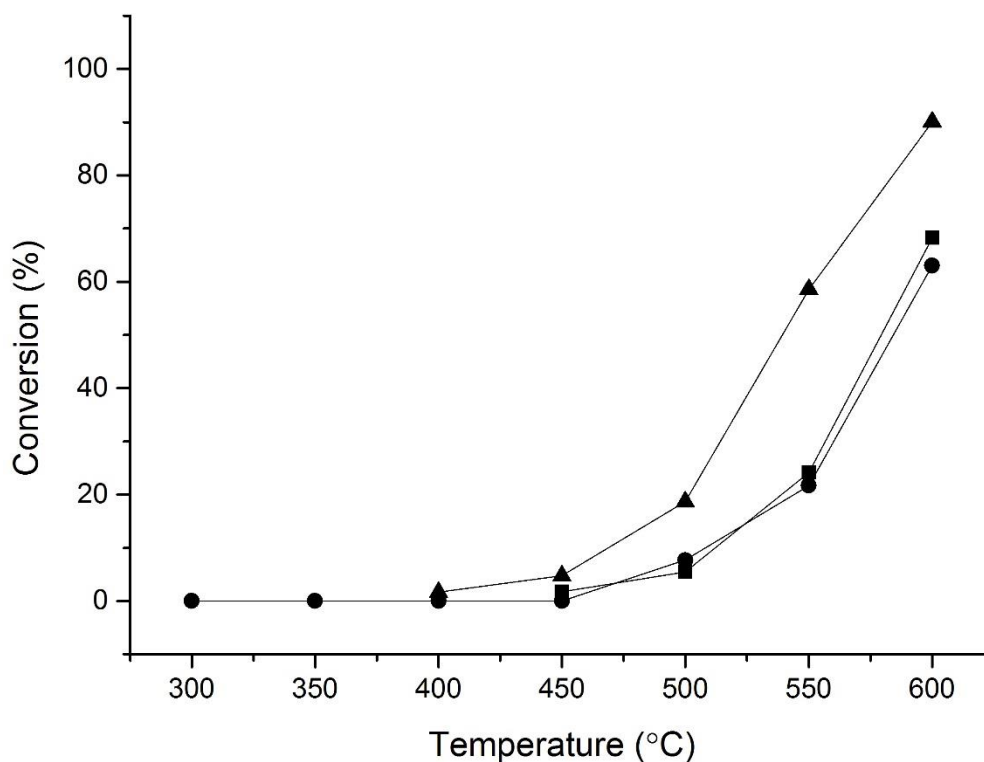
155 Firstly, a blank reaction was performed with only quartz wool and no catalyst. No conversion of N₂O
 156 was measured over the temperature range of 300 – 600 °C, indicating the reactor was not active over
 157 the temperature range of interest (Table 1, entry 1). Decomposition of N₂O was studied using 2.6 wt. %
 158 Pd-Al₂O₃ prepared by wet impregnation, with a pre-treatment (1 h at 600 °C, 13 % O₂, 87 mL min⁻¹)
 159 over the temperature range 300 – 600 °C. The fresh catalyst (Table 1 entry 2) was able to convert 10.3
 160 mol_{N₂O} h⁻¹ kg_{cat}⁻¹ at 550 °C, while the catalyst by Tzitzious *et al.* converted 20.9 mol_{N₂O} h⁻¹ kg_{cat}⁻¹ at the
 161 same temperature.[56]

162 Table 1. The effect of multiple reaction cycles or heat treatments on N₂O conversion over 2.6 wt. %
 163 Pd-Al₂O₃ catalysts.

Entry	Catalyst (2.6 wt. % Pd-Al ₂ O ₃)	T ₅₀ ^a (°C)	Conversion at 550 °C (%)	Decomposition Rate at 550 °C (mol _{N₂O} h ⁻¹ kg _{cat} ⁻¹)
1	Blank	-	0	0
2	Fresh	577	24	10.3
3	2R	565	39	16.7
4	3R	542	56	24.0
5	4R	527	67	28.7
6	5R	540	57	24.4
7	5HT	584	22	9.4

^a temperature required for 50 % N₂O conversion;

164 The catalytic activity was found to increase with each reaction cycle up to the fourth use (Table 1
 165 entries 3-5). After the second reaction cycle the decomposition rate increased from 16.7 to 24.0, this
 166 increased to a maximum at the 4th use (4R) 28.7 mol_{N₂O} h⁻¹ kg_{cat}⁻¹. For the fifth cycle a decrease in the
 167 decomposition rate was observed to 24.4 mol_{N₂O} h⁻¹ kg_{cat}⁻¹. The observed increase in activity after
 168 multiple uses was investigated further by replicating the five heat treatment cycles *ex situ*, i.e. in a
 169 furnace (flowing air at 600 °C for 1 h) to simulate the reaction conditions. The activity of this catalyst
 170 (denoted 5HT) did not compare to that of the multiple use catalyst, but was comparable to the fresh
 171 catalyst (Table 1, entry 7 and Fig. 1). The decomposition rate at 550 °C was 9.4 mol_{N₂O} h⁻¹ kg_{cat}⁻¹.

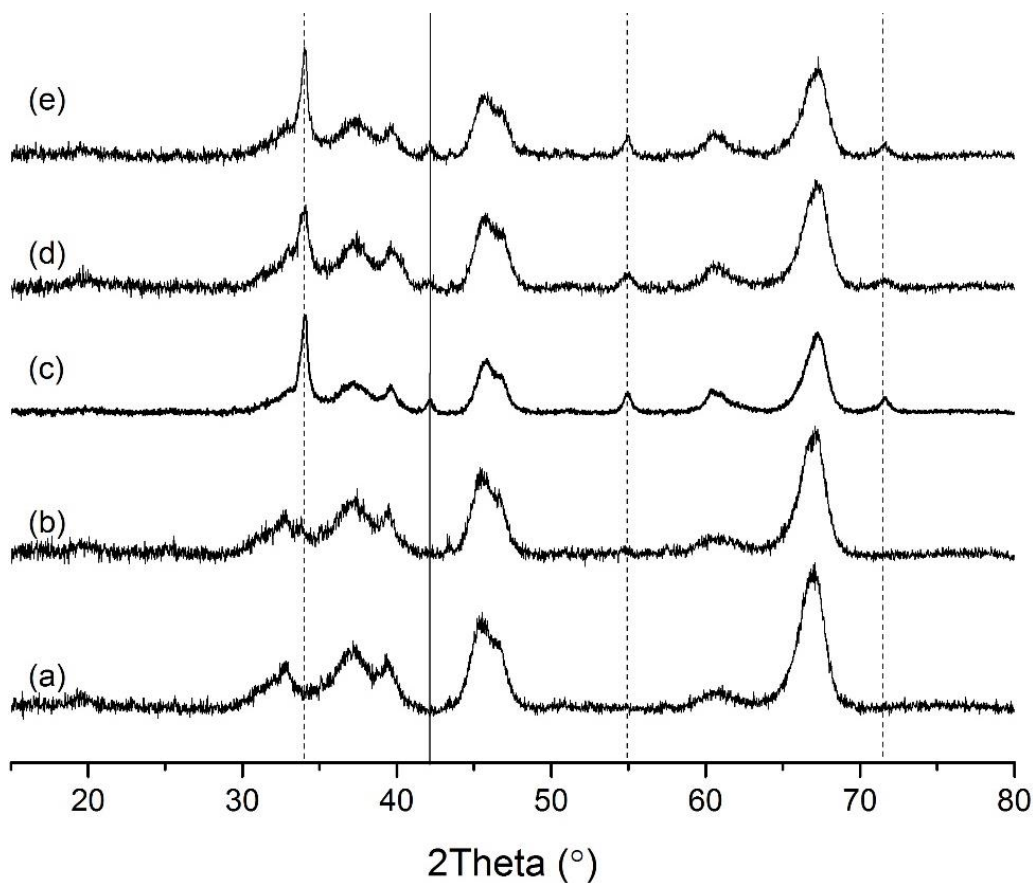


172

173 Fig. 1. The effect of multiple uses or heat treatments on N₂O decomposition using a 2.6 wt. % Pd-Al₂O₃
 174 catalyst. Reaction Conditions: 1 % N₂O/He, total flow 100 mL min⁻¹, GHSV: 76690 h⁻¹ Legend: ■ - 2.6
 175 wt. % Pd-Al₂O₃ Fresh, ● - 2.6 wt. % Pd-Al₂O₃ **5HT**, ▲ - 2.6 wt. % Pd-Al₂O₃ **5R**.

176

177 The Pd-Al₂O₃ catalysts were then characterised in an attempt to understand the origin of the activity
 178 differences observed over multiple reaction cycles and heat-treatments compared to the fresh
 179 sample. The samples of interest were the fresh 2.6 wt. % Pd-Al₂O₃ catalyst, the catalyst after five
 180 reaction cycles (**5R**) and the catalyst after five heat-treatments (**5HT**). Fig. 2 illustrates the X-ray
 181 diffraction patterns; the support exhibits only alumina reflections, as does the fresh 2.6 wt. % Pd-Al₂O₃
 182 catalyst, reflection are assigned to γ-Al₂O₃ (3 1 1) 2θ = 37.1 °, (4 0 0) 2θ = 46.0 ° and (4 4 0) 2θ = 66.6 °
 183 [59]. There is no reflection present for Pd in the fresh catalyst, which indicates that the particle size of
 184 Pd is below the XRD nanoparticle detection limit. In contrast, the **5R** and **5HT** catalysts exhibited
 185 reflections due to Pd as PdO (1 0 1) 2θ = 33.855 °, PdO (3 1 1) 2θ = 54.900 ° and PdO (2 1 1) 2θ = 71.485
 186 ° [60]. A Pd⁰ reflection was observed at Pd (1 1 1) 2θ = 42.034 ° [61]. In the used (**4R** and **5R**) and **5HT**
 187 catalysts there are reflections present due to both PdO and Pd, this presence of reflections suggests
 188 that Pd nanoparticles have sintered as the particles are now observable by XRD.



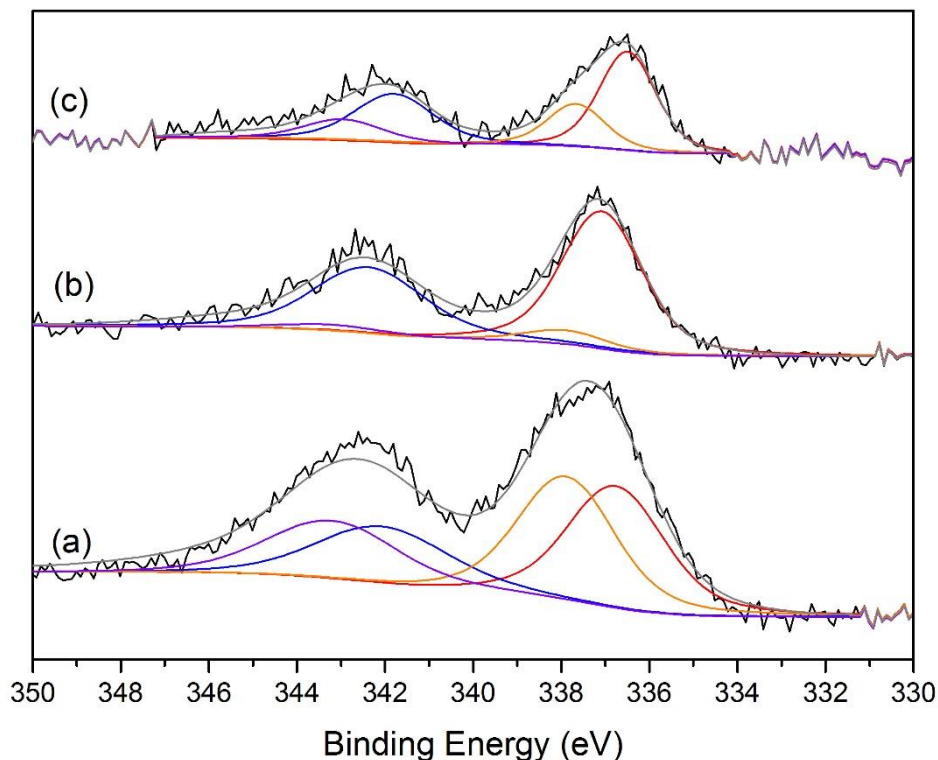
189

190 Fig. 2. XRD patterns for γ -Al₂O₃ and 2.6 wt. % Pd-Al₂O₃ catalysts; (a) Al₂O₃ support, (b) 2.6 wt. % Pd-
 191 Al₂O₃ Fresh, (c) 2.6 wt. % Pd-Al₂O₃ **4R**, (d) 2.6 wt. % Pd-Al₂O₃ **5R**, (e) 2.6 wt. % Pd-Al₂O₃ **5HT**, dashed
 192 line – PdO, solid line – Pd, all unlabelled reflections are due to γ -Al₂O₃.

193

194 The improvement in activity on repeated uses may have been caused by the removal of residual Cl
 195 species that has been reported to poison the catalyst [62]. This would be achieved over the reaction
 196 cycles through a process of converting any remaining Pd-Cl species to PdO. X-Ray photoelectron
 197 spectroscopy (XPS) was used to investigate the surface composition and oxidation state of Pd in more
 198 detail (Fig. 3). In general, two peaks at 336.8 eV and 334.9 eV are observable in the Pd 3d core level
 199 XPS spectra, with the peak at 336.8 eV ascribed to PdO-Al₂O₃ as previously reported by Batista *et al.*
 200 [63] while the peak at 334.9 eV can be attributed to Pd⁰ on Al₂O₃ [64,65]. Depending on catalyst
 201 preparation techniques Pd-Cl species can also be present in the spectra and correspond to the peaks
 202 at 338.2 eV [66]. Each Pd species has two peaks assigned to it due to the spin orbit splitting value of
 203 5.3 eV [67,68]. All catalysts show only PdO and Pd-Cl species and the concentration of these species
 204 was observed to change as the catalyst was subjected to reaction conditions. Specifically, the
 205 proportion of Pd-Cl species decreased while PdO species increased, overall. The **5R** catalyst shows an
 206 increase in PdCl species over the **4R** catalysts. This is not because the catalyst has gained Cl, but
 207 because the % Pd present has decreased meaning more of the surface of the Pd is in the form PdCl as
 208 sintering has taken place. (**Error! Reference source not found.**). When the catalyst was heated in the

209 furnace (**5HT**) almost all the PdCl species were removed (Fig. 3), however, the catalytic activity is not
 210 improved above that of the fresh catalyst. As the number of heat treatments increases the surface
 211 concentration of total atomic Pd % (as given by XPS) decreases (Table 2), this indicates that the % of
 212 Pd at the surface has decreased, which can indicate Pd sintering or agglomeration has taken place.



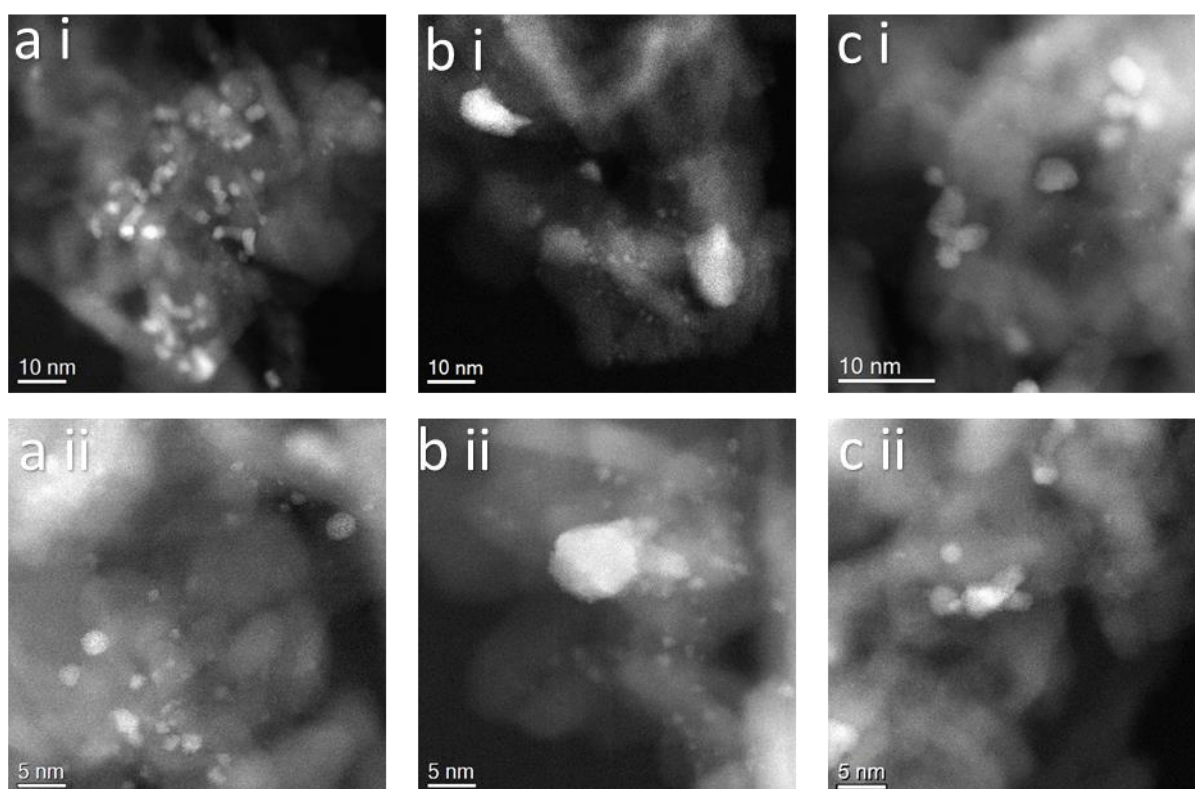
213
 214 Fig. 3. XPS spectra for various 2.6 wt. % Pd-Al₂O₃ catalysts (a) Fresh, (b) **5HT**, (c) **5R**. Each spectra is
 215 fitted with two peaks corresponding to PdO (Red and Blue lines) and Pd-Cl (Orange and Purple
 216 species).

217
 218 Table 2. Surface composition of Pd-Al₂O₃ catalysts as reported by XPS analysis.

Catalyst	Pd 3d (at.%)	% of PdO (337 eV) (%)	% of PdCl (339 eV) (%)
2.6 wt. % Pd- γ -Al ₂ O ₃ Fresh	0.46	50	50
2.6 wt. % Pd- γ -Al ₂ O ₃ 4R	0.40	78	22
2.6 wt. % Pd- γ -Al ₂ O ₃ 5R	0.11	72.7	27.3
2.6 wt. % Pd- γ -Al ₂ O ₃ 5HT	0.25	92	8

219
 220 The XRD patterns indicate that with increased reaction cycles and heat treatments Pd sintering took
 221 place. Furthermore, XPS measurements indicated that in addition to sintering the population of Pd-Cl
 222 species decreased across the samples. However, the N₂O decomposition activity of the **4R** sample
 223 when compared to the **5HT** sample is suggestive of another factor not examinable by XPS or XRD.
 224 Therefore, HAADF-STEM was performed on the samples to provide a greater insight into the particle
 225 size changes suggested by XRD and XPS. Comparison of fresh **5R** and **5HT** 2.6 wt. % Pd-Al₂O₃ samples

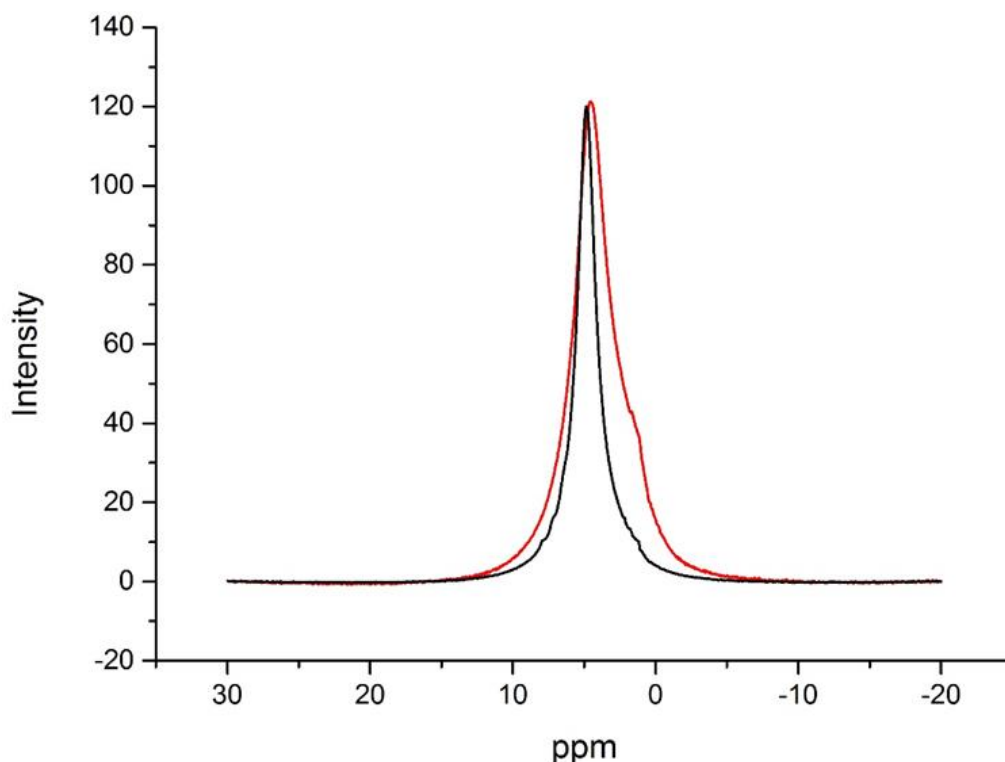
226 by electron microscopy are shown in Fig. 4. The fresh catalyst possesses Pd particles in the range of 1-
227 5 nm (Fig. 4a). Large Pd particles (> 10 nm) of PdO are present after five reaction cycles (Fig. 4b),
228 however, small particles persist. These large particles were not present in the fresh catalyst and are,
229 therefore, consistent with analysis of the XRD and XPS results. That is PdO particles have sintered to
230 form large nano-particles greater than 10 nm. Liu *et al.* showed that sintering is a common mechanism
231 by which metal surface area and dispersion decreases [69,70]. In the 5HT sample, HAADF-STEM shows
232 that there are a range of particle sizes visible with both large particles (> 5 nm) and small (< 2 nm)
233 present. In general, the presence of the large nanoparticles indicates that during the heat treatments
234 sintering occurred and despite the removal of Cl⁻ ions an increase in activity was not realised, due to
235 the concomitant the loss of metal surface area. The increase in activity of the Fresh catalyst with
236 multiple use is due to incremental removal of Cl⁻ ions, with a slight decrease in activity seen after the
237 4th cycle (**4R**) as the effect of the removal of Cl is negated by the formation of larger Pd nano-particles,
238 as seen by HAADF-STEM in the **5R** sample. Representative particle size distributions could not be
239 constructed due the presence of non-spherical agglomerates of nano-particles that would produce a
240 statistically irrelevant distribution.



242 Fig. 4. HAADF-STEM images of 2.6 wt. % Pd-Al₂O₃ Fresh (a), 5R (b), and 5 HT (c).
243

244 These initial results suggest that alongside the presence of Cl^- , the size of the Pd particles strongly
245 contribute to the rate of N_2O decomposition. To try to achieve similar levels of activity as the catalyst
246 which has undergone four reaction cycles a preparatory method to control Pd particle sizes was
247 explored. This would negate the need to carry out multiple catalyst test cycles. As Al_2O_3 is hygroscopic,
248 it was hypothesised that the removal of surface water species and carbonates (the C 1s region of the
249 XPS spectra showed peak at 289.7 eV, that is indicative of O-C=O, carbonate species) could enhance
250 the dispersion of Pd, as these species may block the pore structure of the support [71,72]. Therefore,
251 the alumina support was calcined under flowing air at 600 °C at 10 °C min^{-1} for 4 h before metal
252 deposition (denoted as **SC**) and a 2.6 wt. % Pd- Al_2O_3 catalyst was then prepared by wet impregnation.
253 Analysis of the calcined alumina supported the inference of water removal from the surface through
254 calcination, as illustrated by solid state magic angle spinning (MAS) ^1H NMR (Fig. 5).

255 The properties of the untreated, as-received Al_2O_3 and calcined Al_2O_3 were investigated by NMR (Fig.
256 **5Error! Reference source not found.**). Both spectra contain a single broad peak that is associated to
257 the protons of physisorbed water. The difference in broadness is related to the quantity of water
258 absorbed on the surface of the support. The spectra suggest that there are more physisorbed water
259 molecules present on the untreated sample compared to that of the calcined sample. Both spectra
260 reveal a significant resonance at 4.6 ppm that corresponds to hydrogen bonded water on the Al_2O_3
261 surface. Spectra of the untreated sample has a shoulder present that is not present in the calcined
262 sample, this shoulder at 1.2 ppm is due to the presence of non-hydrogen bonded physisorbed water
263 [73,74]. In this spectra there is also a slight shoulder at 7 ppm; this resonance is due to Brønsted acid
264 sites that are produced when water adsorbs onto a Lewis acidic site [75]. The absence of these two
265 shoulder resonances indicates that water was removed during the calcination treatment.



266

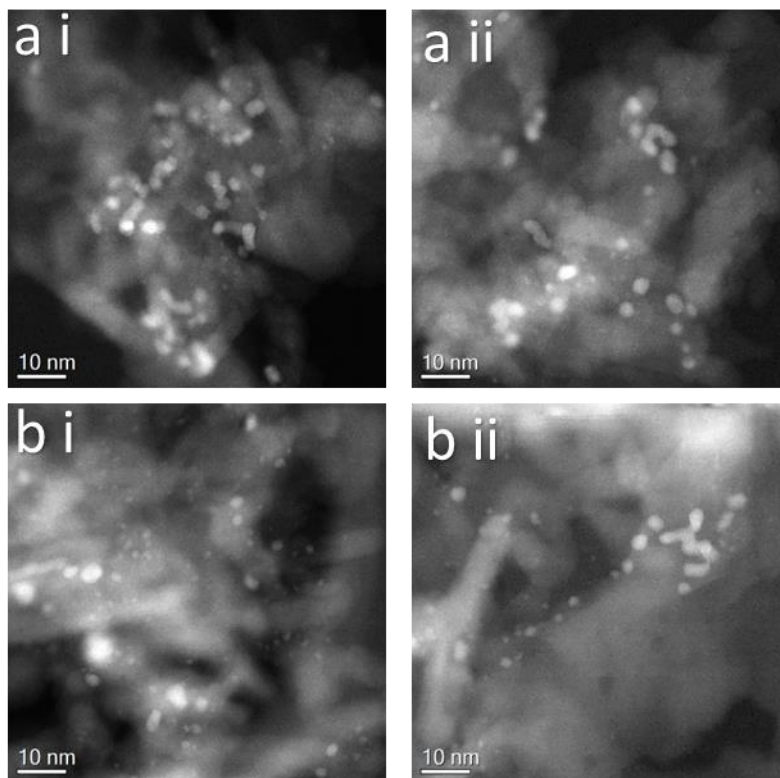
267 Fig. 5. Solid-state ^1H NMR spectrum of Al_2O_3 Fresh (red) and calcined (black)

268

269 Furthermore, calcination of the support led to a change in the point of zero charge (PZC) of the γ -
 270 Al_2O_3 , from PZC = 8.43 for the untreated support, to 8.04 after calcination (see supplementary
 271 information Fig. S1 and Fig. S2). The measured pH of the PdCl_2 solution used to prepare the catalysts
 272 was 1.0, and the Pd solution was confirmed to comprise of $\text{PdCl}_3(\text{H}_2\text{O})^-$ by Raman spectroscopy (see
 273 supplementary information Fig. S3). When the pH of the solution is lower than that of the PZC, the
 274 surface will be protonated and will strongly interact with anions [76,77] therefore the decrease in PZC
 275 of the calcined catalyst will mean the surface is less positively-charged during the catalyst preparation.
 276 This modification in surface charge may be beneficial for the dispersion of the Pd nanoparticles on the
 277 support, as is the case for the preparation of gold catalysts by deposition-precipitation.[78] Therefore
 278 the 2 wt. % Pd- Al_2O_3 **SC** would be expected to have a better dispersion than the palladium supported
 279 on the untreated support. An accurate Pd weight loading on both the fresh and **SC** Pd- Al_2O_3 catalysts
 280 was performed with ICP-OES, both catalysts had a 2.61 wt. % Pd loading.

281 HAADF-STEM shows that similar Pd nanostructures are present in the fresh and **SC** catalysts with
 282 nanoparticles and clusters present in both samples (Fig. 6). However, HAADF-STEM indicates that in
 283 the **SC** catalyst there are an increased quantity of small nanoparticles than in the fresh catalyst (Fig.
 284 6b). The HAADF-STEM of the **SC** catalyst featured many nanoparticles less than 1 nm and some
 285 nanoparticles in the range of 3 – 8 nm. When compared to the **5R** catalyst which has undergone
 286 multiple reaction cycles there are significantly more smaller nanoparticles present in the **SC** catalyst

287 (Fig. 6b). For the **5R** sample (Fig. 4b) there are no nanoparticles that are sub 1 nm, whereas these are
288 easily identifiable in the SC catalyst (Fig. 6b).



289

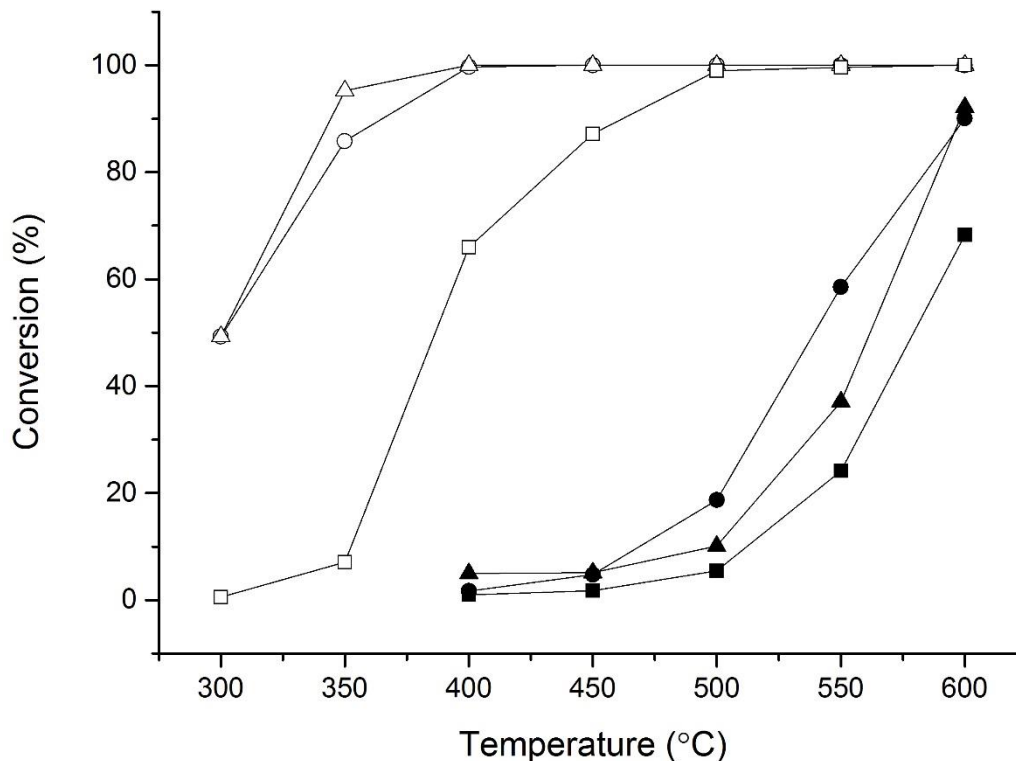
290 Fig. 6. HADDF-STEM images of 2.6 wt. % Pd-Al₂O₃ Fresh (a) and Support calcined (**SC**) (b)

291

292 The SC catalyst was evaluated for N₂O decomposition and compared to the fresh and **5R** catalysts (Fig.
293 7). The T₅₀ obtained over the **SC** catalyst was found to be 561 °C and compared to the values of 577
294 and 540 °C over the fresh and **5R** catalysts. Therefore, the support pre-treatment step has increased
295 the N₂O decomposition rate to 15.9 mol_{N₂O} h⁻¹ kg_{cat}⁻¹ at 550 °C and is indicative of the formation of a
296 higher density of active Pd nano-particles. Performing, a comparable reaction cycle with the **SC**
297 catalyst resulted in a modest increase of the decomposition rate to 18.8 mol_{N₂O} h⁻¹ kg_{cat}⁻¹ at 550 °C and
298 a decrease of the T₅₀ to 556 °C over the fifth use catalyst (**SC 5R**). We consider the modest
299 improvement in the decomposition rate suggests that the PdCl population has decreased as with the
300 **5R** sample.

301 It has been shown previously that adding a reductant (such as propane [45–49]) to the gas feed lowers
302 the temperature required for 100 % conversion. This is due to the rate limiting step of N₂O
303 decomposition being the desorption and recombination of oxygen to form O₂ [38–44]. Propane acts
304 as reductant that can facilitate the abstraction of oxygen from the oxidised active site, significantly
305 increasing the observed rate of N₂O decomposition at lower temperatures [27,28]. In this case the

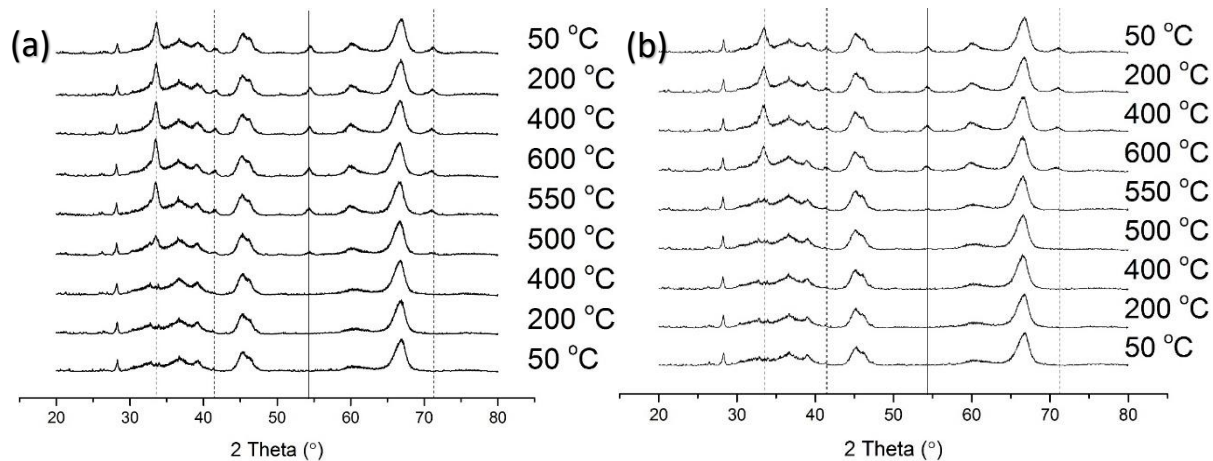
306 presence of propane lowers the temperature required by almost 200 °C. Reactions were carried out
 307 with the addition of propane in the gas feed (1 %). The dramatic increase in decomposition activity is
 308 observed with all catalysts but is most noticeable with the **SC** catalyst, as with N₂O only, 95 %
 309 conversion is achieved at 600 °C, in the presence of propane 95 % conversion is achieved at 350 °C.



310
 311 Fig. 7. The effect on N₂O conversion of heat treatments on 2.6 wt. % Pd-Al₂O₃. Reaction Conditions:
 312 total flow 100 mL min⁻¹, GHSV: 76690 h⁻¹, 300 - 600 °C, Closed symbols: 1 % N₂O/He, Open symbols:
 313 1 % N₂O/1 % C₃H₈/He. Legend: ■ - 2.6 wt. % Pd-Al₂O₃ Fresh, ● - 2.6 wt. % Pd-Al₂O₃ 5R, ▲ - 2.6 wt. %
 314 Pd-Al₂O₃ SC.

315
 316 The superior dispersion Pd on the **SC** catalyst, as evidenced by HAADF-STEM implies that the anchoring
 317 of Pd is stronger on the calcined support. To examine directly the stability of the Pd species on the
 318 surface of the Al₂O₃, *in situ* XRD was performed. The *in situ* XRD profiles of 2.6 wt. % Pd-Al₂O₃ and **SC**
 319 catalysts are illustrated in Fig. 8a and b, respectively. The samples were heated in 1 % N₂O/N₂ and
 320 cooled in N₂ at 50 °C intervals. The *in situ* XRD patterns of 2.6 wt. % Pd-Al₂O₃ shows that small PdO
 321 reflections were present at 500 °C, with the intensity of the PdO reflections not increasing past 550
 322 °C, with Pd⁰ reflections forming at the same temperatures. In the **SC** catalyst PdO and Pd reflections
 323 were not visible until at least 600 °C. The difference in temperature required to observe reflections
 324 corresponding to nanoparticles of PdO and Pd indicates that the Pd nanoparticles are more strongly
 325 anchored to the calcined Al₂O₃ than the untreated support. The effect of the reaction time-on-line was
 326 investigated, (Fig. S4), and the fresh catalyst sharply loses activity over the first 3 h, before following

327 a downward trend over the next 15 h. This catalyst is not stable during long term reactions. However,
 328 the **SC** catalyst shows promise, initially there is a decrease in activity in the first hour but the activity
 329 then improves, and the catalyst is stable over an 18 h period with the conversion of N₂O remaining
 330 constant. These observation are in agreement with the *in situ* XRD data.



331
 332 Fig. 8. *In situ* XRD patterns taken at regular temperature intervals for (a) 2.6 wt. % Pd-Al₂O₃ Fresh and
 333 (b) 2.6 wt. % Pd-Al₂O₃ **SC** heated in 1 % N₂O/N₂ and then cooled in N₂. Solid Line; Pd, Dashed line; PdO.
 334

335 The average particle size of the Pd present on the surface was further investigated with CO
 336 chemisorption of the fresh and **SC** catalysts. It is assumed that all Pd particles are hemispherical and
 337 that one CO molecule will bind to one Pd atom, STEM has shown this is not the case but this will give
 338 an average particle size and metal surface area. Metal nanoparticle dispersion increased modestly
 339 from 24.7 % to 27.5 % with the fresh to the **SC** catalyst (Table 3). The average particle size of Pd
 340 particles in the **SC** catalyst decreased when compared to the fresh catalyst. This decrease in average
 341 particle size indicated that the nanoparticles found on the **SC** catalyst are smaller and further support
 342 the inference that smaller particles are more active than larger particles for N₂O decomposition. This
 343 is due to the smaller particles having a larger surface area per gram of metal and this small change in
 344 particle size facilitates an increased decomposition reaction rate through the increased surface area
 345 available.

346 Table 3. Dispersion and metal surface area as calculated by CO Chemisorption on 2.6 wt. % Pd-Al₂O₃
 347 fresh and SC.

Catalyst	Metal Surface Area (m ² g ⁻¹)	Avg. particle size (nm)	Dispersion (%)
2.6 wt. % Pd-Al ₂ O ₃ Fresh	2.9	1.51	24.7
2.6 wt. % Pd-Al ₂ O ₃ SC	3.2	1.36	27.5

349 The catalytic activity for N₂O decomposition when propane is present with the fresh and **SC** catalysts
 350 is markedly different (Fig. 7). To investigate the effect of particle size, the catalysts were re-prepared
 351 using a modified impregnation (**MI**) technique which has been shown previously to produce catalysts
 352 with a very narrow particle size distribution [58]. Palladium was deposited with the MI technique on
 353 a calcined alumina and an as-received alumina and examined by XPS, XRD, CO chemisorption and
 354 HAADF-STEM. The Pd loading of the MI prepared catalysts was analysed by ICP-OES and was found to
 355 be lower (2.1 wt.%) than the traditionally prepared impregnation catalysts (2.6 wt. %). The materials
 356 were examined by CO chemisorption (Table 4) and this revealed that the average Pd particle size, 1.25
 357 and 1.28 nm was smaller than the analogue impregnation catalysts displayed in Table 3. However, the
 358 metal surface area was found to be lower and can be assigned to the lower Pd loading of the **MI**
 359 catalysts. When comparing the XRD patterns of 2.1 wt. % Pd-Al₂O₃ **MI** catalysts, it is clear that there
 360 are no Pd or PdO reflections (see supplementary information Fig. S5). This indicates that the Pd species
 361 are smaller than the detection limit of XRD, which is consistent with the CO chemisorption data.

362 Table 4. Dispersion and metal surface area as calculated by CO Chemisorption on 2.1 wt. % Pd-Al₂O₃
 363 fresh and **SC** prepared by modified impregnation.

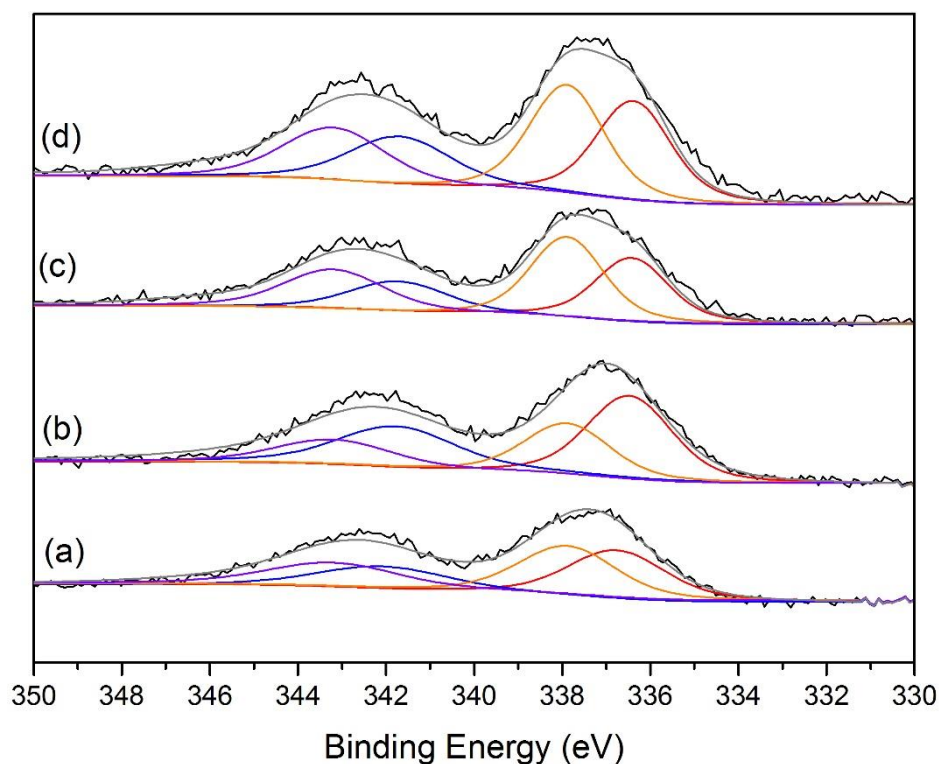
Catalyst	Metal Surface Area (m ² g ⁻¹)	Avg. particle size (nm)	Dispersion (%)
2.1 wt.% Pd-Al ₂ O ₃ Fresh MI	2.8	1.25	29.8
2.1 wt.% Pd-Al ₂ O ₃ SC MI	2.7	1.28	29.3

364

365 The modified impregnation technique requires an excess of HCl to be added during the preparation.
 366 This facilitates the deposition of Pd and the subsequently observed metal particle control, through
 367 altering the support PZC and inducing an increased interaction between the Pd precursor and the
 368 support. Characterisation by XPS shows a high ratio of PdO to PdCl in the modified impregnation
 369 catalysts. For both the un-calcined supported catalyst (2.1 wt. % Pd-Al₂O₃ Fresh **MI**) and the calcined
 370 supported catalyst (2.1 wt. % Pd-Al₂O₃ **SC MI**), there is an elevated population of Pd-Cl species
 371 compared to PdO species, despite undergoing calcination (Fig. 9 **Error! Reference source not found.**)

372 and Table 5). In contrast, when comparing the ratio of PdO to PdCl species for the 2.6 wt. % Pd-Al₂O₃
 373 **SC** catalyst was found to have more PdO present than PdCl.

374



375

376 Fig. 9. XPS spectra for fresh or SC Pd-Al₂O₃ catalysts prepared by impregnation (2.6 wt. % Pd) or
 377 Modified Impregnation (2.1 wt. % Pd). Legend: (a) Fresh, (b) **SC**, (c) **MI**, (d) **MI SC**. Each spectra is fitted
 378 with two peaks corresponding to PdO and PdCl species. Legend: Red and Blue – PdO, Orange and
 379 Purple – PdCl.

380

381

382 Table 5. Surface composition of Pd- Al₂O₃ catalysts as reported by XPS analysis

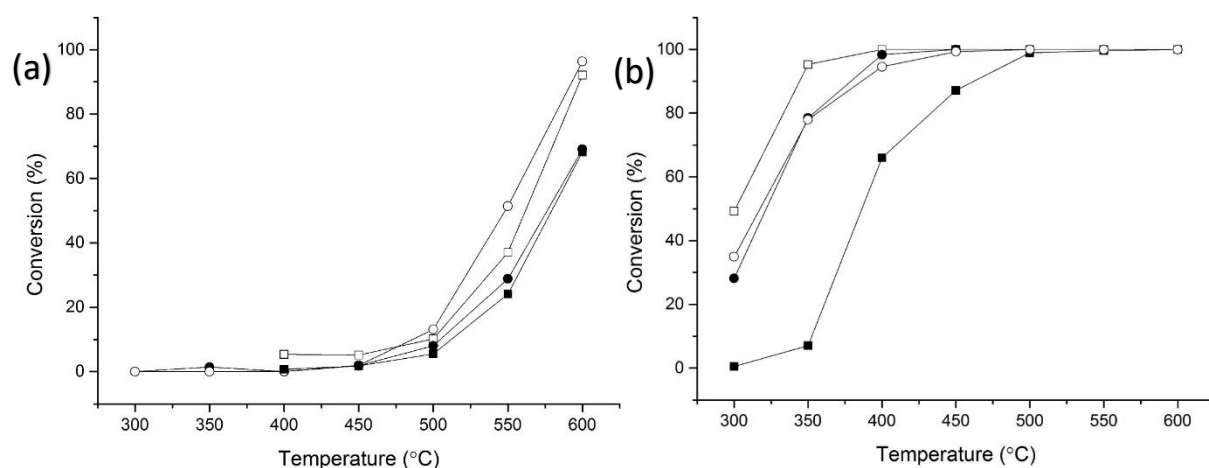
Catalyst	Pd 3d (at.%)	% of PdO (337 eV) (%)	% of PdCl (339 eV) (%)
2.6 wt. % Pd-Al ₂ O ₃ SC	0.48	62.3	37.7
2.1 wt. % Pd-Al ₂ O ₃ Fresh MI	0.39	43.5	56.5
2.1 wt. % Pd-Al ₂ O ₃ SC MI	0.42	47.6	52.3

383

384 The 2.1 wt.% Pd/Al₂O₃ **MI** and 2.1 wt.% Pd/Al₂O₃ **SC MI** catalysts were tested for N₂O decomposition
 385 with and without propane present and compared to the equivalent impregnation catalysts (Fig. 10.a
 386 and b). When only N₂O is present in the gas feed there is still minor difference in activity, with the **SC**
 387 **MI** catalyst modestly outperforming, that of the fresh **MI** catalyst (Fig. 10.a). The **MI** catalysts
 388 outperform the corresponding impregnation catalysts, and further support the supposition that the
 389 N₂O decomposition reaction is sensitive to the active surface composition and structure. This reactivity
 390 can be attributed to the increased dispersion of smaller and more active metal particles available for

391 N₂O decomposition to occur, based on the results from CO Chemisorption (Table 4). However, the
 392 increased Cl⁻ on the surface of the **MI** catalysts restricts the activity to only the minor improvement
 393 observed. The T₅₀ obtained over the **MI** catalyst was found to be 576 °C and compared to the values
 394 of 547 °C over the **MI SC** catalyst. Therefore, the support pre-treatment step has increased the N₂O
 395 decomposition rate from 16.3 mol_{N₂O} h⁻¹ kg_{cat}⁻¹ to 21.9 mol_{N₂O} h⁻¹ kg_{cat}⁻¹ at 550 °C.

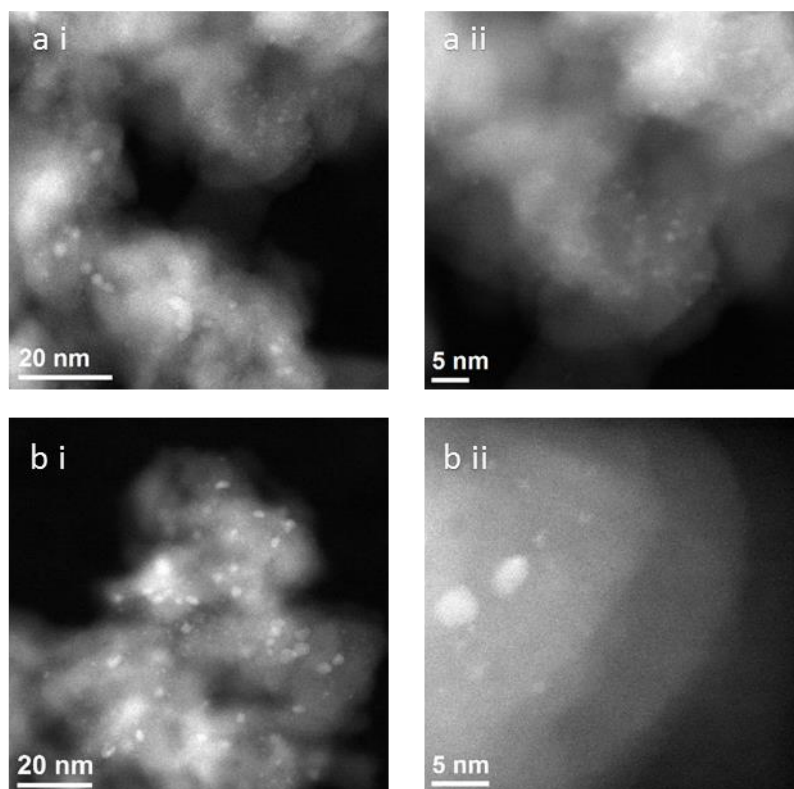
396 When propane was added to the reaction mixture the effect of calcining the support prior to Pd
 397 deposition was negated (Fig. 10b). The activity of the **MI** catalysts was lower, at ca. 78 % N₂O
 398 conversion compared to that of the **SC** catalyst, but higher than that of the fresh supported Al₂O₃
 399 catalyst at 350 °C, compared to 96 % for **SC** and 7 % for the fresh catalyst (Fig. 10a). As the activity of
 400 both **MI** catalysts was comparable the decomposition rate was ca. 30 mol_{N₂O} h⁻¹ kg_{cat}⁻¹ at 350 °C with
 401 propane present. It is possible that residual chlorine species may inhibit the reaction as observed with
 402 the catalysts that underwent increasing reaction cycles. However, it is clear that the influence of
 403 calcining the support prior to metal impregnation is negated with the **MI** catalysts for this reaction
 404 with propane.



405
 406 Fig. 10. The effect on N₂O conversion of catalyst preparation over Pd-Al₂O₃ Fresh (filled symbols) and
 407 **SC** catalysts (open symbols): ■ - 2.6 wt.% Pd Fresh, □ - 2.6 wt.% Pd SC, ● - 2.1 wt.% Pd **MI**, ○ - 2.1
 408 wt.% Pd **SC MI**. Reaction conditions; (a), 1 % N₂O/He, total flow 100 ml min⁻¹, GHSV: 75900 h⁻¹, (b), 1 %
 409 N₂O/1 % C₃H₈/He, total flow 100 ml min⁻¹, GHSV: 75900 h⁻¹.

410
 411 HAADF-STEM images of the fresh **MI** catalyst (Fig. 11a) and the post-reaction **MI** catalyst (Fig. 11b)
 412 show small, uniform particles that sinter after multiple uses. The particles that are present on the
 413 fresh **MI** catalyst are sub 2 nm, with only a few particles larger than 2 nm. After one reaction cycle,
 414 some of the particles present were measured to be ca. 5 nm, indicating that Pd sintering has taken
 415 place. We consider that although the modified impregnation technique does provide increased
 416 control over the metal nano-particle size it does not control the metal-support interaction. In theory,

417 the modified impregnation solution is more acidic due to the presence of HCl so the surface of the
 418 support is more positively charged. The consequence of this should be a stronger interaction between
 419 the precursor and the support, resulting in an increased metal dispersion compared to a conventional
 420 impregnation technique. However, as the support is not calcined it can be hypothesised that the
 421 interaction between the smaller particles produced by MI and the support may not be sufficiently
 422 strong due to the presence of water and can diminish the strength at which the Pd can anchor to the
 423 support and consequently lead to sintering.



424
 425 Fig. 11. HAADF-STEM images of 2.1 wt. % Pd-Al₂O₃ MI (a) MI fresh, (b) catalyst following one reaction
 426 cycle (MI 1R).

427 Table 6. Comparison of the key catalysts in this manuscript with literature examples.

Catalyst	T ₅₀ ^a (°C)	Conversion at 550 °C (%)	Decomposition Rate at 550 °C (mol _{N₂O} h ⁻¹ kg _{cat} ⁻¹)	T ₁₀₀ ^b in the presence of propane (°C)	Ref
Blank	-	0	0	-	This work
2.6 wt. % Pd- Al ₂ O ₃ Fresh	577	24	10.3	550	This work
2.6 wt. % Pd- Al ₂ O ₃ 4R	527	67	28.7	-	This work
2.6 wt. % Pd- Al ₂ O ₃ 5R	540	57	24.4	400	This work

2.6 wt. % Pd- Al ₂ O ₃ 5HT	584	22	9.4	450	This work
2.6 wt. % Pd- Al ₂ O ₃ SC	562	37	15.9	400	This work
2.1 wt. % Pd- Al ₂ O ₃ MI	576	29	12.42	450	This work
2.1 wt. % Pd- Al ₂ O ₃ MI SC	548	52	22.3	450	This work
2 wt. % Pd- Al ₂ O ₃	350	100	2.6	400	Pekridis [27]
0.5 wt. % Pd- Al ₂ O ₃	536	52	20.9	-	Tzitzios [56]
1 wt. % Pd- Al ₂ O ₃	525	59	23.7	-	Pachatouridou [57]

^a the temperature at 50 % N₂O conversion; ^b the temperature at 100 % N₂O conversion in the presence of propane.

428

429 The reactivity data (Table 6) highlights the structural sensitivity of the active site and how important
430 the relationship between Pd dispersion and presence of PdCl is. The increase in Pd dispersion resulted
431 in an increase in activity as seen when the support is calcined before catalyst preparation. However,
432 removal of Cl⁻ from the catalyst surface as with the catalysts that have undergone four or five reaction
433 cycles can lead to an improvement in activity despite the onset of Pd sintering and reduced Pd
434 dispersion. Further activity gains can be observed through careful control of the Pd dispersion, through
435 the MI technique despite a high density of PdCl. Therefore, the balance between a high Pd dispersion
436 and the presence of PdCl appears to favour the former. For comparison the previous literature data
437 are included in Table 6, and these demonstrate that the catalyst preparation conditions are key to
438 designing an active catalyst.

439

440 4 Conclusions

441 The effect of heat treatment conditions on a 2.6 wt. % Pd-Al₂O₃ catalysts have been investigated for
442 the catalytic decomposition of N₂O into N₂ and O₂ in the absence and presence of a reducing agent
443 (C₃H₈). It was found that the use of several reaction cycles increases the conversion of N₂O from 24 %
444 to 57 % at 600 °C. These multiple use catalysts also show improved stability on-stream. It has also
445 been demonstrated that by calcining the support before catalyst preparation, similar conversions as
446 the multiple use catalyst can be achieved in the first cycle of the **SC** catalyst. This procedure enables
447 the high activity to be achieved on the initial use rather than on the 5th cycle (**5R**). We consider that
448 this is due to the removal of water species lowering the PZC of the support, which suggests a reduced
449 interaction between the Pd ion and the support surface, leading to the formation of smaller
450 nanoparticles. When a reductant is present the temperature at which *ca.* 100 % conversion is observed
451 is decrease from 550 °C to 350 °C. The presence of the reductant enhances the decomposition of N₂O
452 to N₂, however a limited amount of O₂ is measured, suggesting that the reductant was acting as a
453 scavenger of oxygen to form cracked, oxidation products and water. When the support was calcined
454 before catalyst preparation, the resultant catalyst was formed of small Pd nanoparticles. Reaction data
455 indicate that small nanoparticles are the more active species, as when the particle size is controlled
456 by using a modified impregnation preparation method the activity of both catalysts is the same,
457 therefore further supporting the hypothesis that the particle size and subsequently the metal
458 dispersion control the activity of a Pd-Al₂O₃ catalysts for N₂O decomposition.

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