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**Research Article** 

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## <sup>1</sup> Elucidating Structure–Property Relationships in the Design of Metal <sup>2</sup> Nanoparticle Catalysts for the Activation of Molecular Oxygen

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12 **S** Supporting Information

ABSTRACT: A novel synthetic strategy for the design of metal 13

nanoparticles by extrusion of anionic chloride precursors from a 14

porous copper chlorophosphate framework has been devised 15

for the sustainable aerobic oxidation of vanillyl alcohol (4-16

hydroxy-3-methoxybenzyl alcohol) to vanillin (4-hydroxy-3-17 methoxybenzaldehyde) using a one-step, base-free method. The

18 precise nature of the Au, Pt, and Pd species has been elucidated

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for the as-synthesized and thermally activated analogues, which 20 exhibit fascinating catalytic properties when subjected to diverse 21

activation environments. By employing a combination of 22

structural and spectroscopic characterization tools, it has been shown that analogous heat treatments have differing effects on

23 extrusion of a particular metal species. The most active catalysts in this series of materials were the extruded Pt nanoparticles that 24

were generated by reduction in H<sub>2</sub>, which exhibit enhanced catalytic behavior, when compared to its Au or Pd counterparts, for 25

- industrially significant, aerobic oxidation reactions. 26
- KEYWORDS: nanoparticle, catalysis, vanillyl alcohol, structure-property correlations, aerobic oxidation, vanillin, EXAFS 27

#### INTRODUCTION 28

29 Design of versatile metal nanoparticle (NP) catalysts has been a 30 progressive area of research within the field of heterogeneous 31 catalysis in recent years, due to their significant potential in a 32 variety of chemical transformations, including industrially 33 desirable selective aerobic oxidations. Monometallic (Au, Pt, 34 Pd) and bimetallic NPs have been successfully employed in the 35 selective oxidation of alcohols,<sup>1</sup> including glycerol,<sup>2</sup> cinnamyl 36 alcohol,<sup>3</sup> crotyl alcohol<sup>4,5</sup> and benzyl alcohol,<sup>6,7</sup> to name but a 37 few. Prodigious design of bimetallic equivalents has recently 38 demonstrated their propensity for C-H activation, particularly 39 in the oxidation of aromatics.<sup>8,9</sup> In addition to bulk chemical 40 applications, heterogenized Pd NPs have also found a niche for 41 cross-coupling reactions, alongside their ubiquitous homoge-42 neous counterparts.<sup>10</sup> The key to engineering catalytically 43 active NPs reproducibly appears to be contingent on the 44 development of robust design strategies that can control the 45 size and shape of the particles at the nanoscale, which still 46 proves to be a challenge.<sup>1</sup>

A variety of preparation methods for generating NPs on solid 47 48 supports have been previously studied with specific focus on

control of the nanoparticle size and shape.<sup>11-14</sup> These include 49 wet impregnation,<sup>15</sup> deposition-precipitation<sup>16</sup> and sol- 50 immobilization techniques,<sup>17,18</sup> with the latter showing a 51 greater propensity for the generation of smaller particle sizes, 52 but often resulting in polymer-capped particulates and hence a 53 reduction in accessible surface area. More importantly, these 54 research efforts have clearly illustrated that changes in size, 55 ranging from average diameters of less than 1 nm up to 10 nm,  $_{56}$  can have a substantial effect on catalytic activity,  $^{11,12,19}$  with  $_{57}$ smaller particle sizes affording superior conversion rates in most 58 cases. In fact, studies involving cluster-based nanoparticle 59 catalysts even highlighted the integral importance of site- 60 isolation as well as particle size in enhancing efficiency of 61 catalytic oxidations and hydrogenations.<sup>20-25</sup> The nature of 62 support materials has ranged from metal oxides<sup>26</sup> and 63 carbonaceous materials,<sup>27</sup> to microporous alternatives such as <sub>64</sub> zeolites<sup>28,29</sup> or metal-organic frameworks (MOFs),<sup>30,31</sup> and 65

Reduction

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f1

66 mesoporous silica-derived hosts<sup>32</sup> such as MCM-41 or SBA-15. 67 Nanoporous materials have been extensively explored for their 68 intrinsic catalytic properties;<sup>33</sup> however, isolated single-sites in 69 the form of doped frameworks<sup>34–36</sup> or supported nanoparticles 70 have proved to be superior. The latter have afforded a better 71 understanding of the nature of the active site at the molecular 72 level, which has resulted in the development of heterogenized 73 NP catalysts with unprecedented activity.<sup>21–24</sup>

<sup>74</sup> We have recently demonstrated a novel strategy for <sup>75</sup> generating uniform sized, small NPs (ca. 5 nm) by extrusion <sup>76</sup> of MCl<sub>x</sub> precursor complex anions (M = Au, Pt or Pd) from a <sup>77</sup> crystalline microporous copper chlorophosphate framework <sup>78</sup> (Figure 1).<sup>7</sup> The framework is of Cu-2 topology<sup>37</sup> and has



**Figure 1.** Representative crystal structure of the  $[PtCl_4]^{2-}$  supported  $Rb_9Cu_6(P_2O_7)_4Cl_2$  framework (Pt – gray spheres, Cl – green spheres, Rb – pink spheres, Cu – green polyhedra, P – orange polyhedra, oxygen omitted for clarity).

79 flexible anion-exchange properties.<sup>38</sup> In this article, we 80 rationalize and demonstrate the efficacy of our design strategy 81 for the in situ generation of nanoparticles within a microporous 82 host architecture, wherein the porous framework can be 83 employed synergistically as an active species, and not just as 84 a heterogeneous support, thereby affording exciting prospects 85 for bifunctional catalysis. We have meticulously probed the 86 nature of the active site using a combination of X-ray 87 absorption spectroscopy (XAS), X-ray photoelectron spectros-88 copy (XPS), and transmission electron microscopy (TEM), for 89 affording structure-property correlations, which highlight the 90 efficacy of catalyst activation protocols on metal (NP) extrusion 91 and ensuing catalytic activity. These findings further confirmed 92 the structural and compositional integrity of the active sites, 93 that subsequently led to the design and creation of well-defined 94 and isolated heterogeneous NP catalysts for the aerobic 95 oxidation of vanillyl alcohol (Scheme 1), using a one-step, 96 base-free method.

<sup>97</sup> The production of vanillin is significant in the fine chemicals <sup>98</sup> industry, as its primary use in vanilla flavorings and fragrances <sup>99</sup> make it the single-most highly produced additive in this field.<sup>39</sup> <sup>100</sup> Demand for food-grade vanillin has led to a production rate of <sup>101</sup> approximately 12 000 tons per annum, of which natural vanilla <sup>102</sup> extracts contribute only 20 tons.<sup>40</sup> It is also used in other <sup>103</sup> industries, including as an intermediate toward pharmaceuticals <sup>104</sup> such as L-3,4-dihydroxy-phenylalanine (L-DOPA), a key <sup>105</sup> therapeutic agent used to combat Parkinson's disease. Current Scheme 1. Aerobic Oxidation of Vanillyl Alcohol to Vanillin and Vanillic Acid



synthetic methods employ one of three routes: (i) an 106 established method that utilizes the degradation of lignins, 107 which is a solvent intensive process involving multiple 108 extraction and distillation steps;<sup>40</sup> (ii) a cheaper synthetic 109 pathway from guaiacol (Schemes 2 and 3), but which involves 110 s2s3









the use of mineral acids and heavy-metal promoters such as Pb, 111 Bi, and/or Cd;<sup>40,41</sup> or (iii) a biosynthetic pathway, which 112 involves high production costs.<sup>42,43</sup> Schemes 2 and 3 represent 113 the processes mostly employed in industry today, both of which 114 are composed of the same principles: first, a condensation 115 reaction with either glyoxylic acid (Scheme 2) or formaldehyde 116 (Scheme 3), followed by an oxidation step and subsequent 117 decarboxylation. The route via glyoxylic acid requires the 118 decarboxylation step to form the desired product, vanillin. The 119 formaldehyde route, however, produces small quantities of 120 vanillin (16%) after the oxidation step, with the decarboxylation 121 converting some of the overoxidation products back to vanillin, 122 in order to obtain an overall yield of  $61\%^{41}$  (detailed scheme in 123 Figure S1.1). It is to be noted that both methods involve 124 multistep processes to achieve these yields. 125

The catalytic activation of molecular oxygen is therefore of 126 significant interest and poses a substantial challenge for the 127 fine-chemicals industry; this is especially true in selective 128 <sup>129</sup> oxidations, with the selective oxidation of vanillyl alcohol to <sup>130</sup> vanillin being a compelling example. Due to the benign nature <sup>131</sup> of molecular oxygen, its utilization as a potential oxidant<sup>44</sup> can <sup>132</sup> help mitigate the use of hazardous reagents, which lead to the <sup>133</sup> generation of greenhouse gases and wasteful byproducts <sup>134</sup> (Schemes 2 and 3).<sup>45</sup> From an academic and industrial <sup>135</sup> standpoint, the concomitant use of a heterogeneous catalyst <sup>136</sup> with molecular oxygen affords many advantages from a socio-<sup>137</sup> economic and environmental perspective, as it offers a viable <sup>138</sup> alternative to homogeneous processes that currently generate <sup>139</sup> stoichiometric quantities of toxic inorganic waste,<sup>46</sup> thereby <sup>140</sup> impeding the atom-efficient synthesis of fine-chemicals and <sup>141</sup> pharmaceuticals.

#### 142 **EXPERIMENTAL SECTION**

143 Chemicals for synthesis and catalytic tests were purchased from 144 Sigma-Aldrich, Fisher Scientific, or Acros Organics and used 145 without further purification.

Material Synthesis. Copper(II) fluoride (0.1168 g, 1.150 mmol), 85 wt % orthophosphoric acid (0.2 mL, 2.922 mmol), 85 wt % RbOH (0.24 mL, 2.037 mmol), RbCl (0.28 g; 2.316 mmol) and a source of MCl<sub>x</sub>; HAuCl<sub>4</sub> (0.0489 g, 0.144 mmol), 50 K<sub>2</sub>PtCl<sub>4</sub> (0.0515 g, 0.124 mmol) or K<sub>2</sub>PdCl<sub>4</sub> (0.0405 g, 0.124 mmol) were mixed in the Teflon liner of a custom-made 23 mL 152 hydrothermal vessel. The vessel was sealed and heated to 448 K 153 for 2 days.

Products formed as brilliant green cuboid crystals for both the Au and Pt material and as light brown crystals for the Pd material. Materials were further activated either by calcination (air, 773 K, 2 h) or reduction (5%  $H_2/N_2$ , 473 K, 2 h) to generate the active nanoparticle catalysts. After calcination, the two and Pd materials appeared unchanged in color, but the Pt catalyst changed to a darker khaki-green. After reduction, the Au material appeared unchanged, the Pt material appeared a more dark green color than the calcined equivalent, and the Pd material appeared black in color.

**X-ray Photoelectron Spectroscopy.** XPS analysis was performed using a Thermo Scientific Theta Probe instrument equipped with monochromated Al K $\alpha$  source in NEXUS, University of Newcastle. A flood gun was used for charge compensation. A pass energy of 200 eV and a step size of 1.0 eV was employed for all survey spectra while a pass energy of two eV and a step size of 0.1 eV was used for high-resolution spectra of the elements of interest. All XPS spectra were calibrated against the carbon and/or oxygen 1s peaks, and highray resolution spectra were fitted with Shirley backgrounds before peak analysis using the CasaXPS software.<sup>47</sup>

X-ray Absorption Spectroscopy. Pd, Pt, and Au XAFS 175 176 studies were carried out on the B18 beamline at the Diamond Light Source, Didcot, U.K. Measurements were performed 177 178 using a quick extended X-ray absorption fine structure (QEXAFS) setup with a fast-scanning Si (111) or Si (311) 179 double crystal monochromator. The normal time resolution of 180 the spectra reported herein was 1 min/spectrum ( $k_{max} = 16$ ); 181 on average, six scans were acquired to improve the signal-to-182 noise level of the data. All samples were diluted with cellulose 183 and pressed into pellets to optimize the effective edge-step of 184 185 the XAFS data and measured in transmission mode using ion 186 chamber detectors. All transmission XAFS spectra were 187 acquired concurrently with the appropriate reference foil placed 188 between  $I_t$  and  $I_{ref}$ . XAS data processing and EXAFS analysis 189 were performed using IFEFFIT<sup>48</sup> with the Horae package<sup>45</sup> 190 (Athena and Artemis). The amplitude reduction factor,  $s_0^2$ , was

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derived from EXAFS data analysis of known compounds and 191 used as a fixed input parameter. 192

**Transmission Electron Microscopy.** TEM analysis was 193 performed on a Jeol 2100 Electron Microscope at an operating 194 voltage of 200 kV. The catalyst framework was prone to 195 damage by the electron beam. Therefore, to minimize sample 196 degradation, the TEM images were collected quickly to mitigate 197 the above. 198

**Catalysis.** Catalytic reactions were carried out in a 75 mL 199 PTFE lined, stainless-steel, high-pressure batch reactor. The 200 reactor was charged with vanillyl alcohol (1 g), diethylene 201 glycol dimethyl ether (0.85 g) as an internal standard, *tert-* 202 butanol (30 mL) as a solvent and catalyst (50 mg). The reactor 203 was pressurized with  $\approx$ 20 bar of dry air, stirred, and heated for 204 the required amount of time. Small aliquots of the reaction 205 mixture were taken carefully periodically for GC analysis. 206 Samples were analyzed by GC (PerkinElmer, Clarus 480) using 207 an Elite-5 column equipped with a flame ionization detector 208 (FID). Products were identified against authenticated standards 209 and quantified by calibration to obtain response factors ( $R_{\rm F}$ ) 210 against the known internal standard. 211

#### RESULTS AND DISCUSSION

Figure 2 shows the non-phase-corrected Fourier transform 213 f2 (both magnitude and imaginary component) of the  $k^3$  weighted 214 EXAFS data for the reduced Pd, Pt, and Au catalyst materials, 215 with the fitting parameters generated detailed in Table 1. The 216 t1 EXAFS data of the reduced Pt sample is consistent with that 217 expected for Pt nanoparticles. The long-range structure in the 218



**Figure 2.** Magnitude and imaginary component of the  $k^3$  weighted Fourier transform for the EXAFS data of the reduced Pd (bottom), Pt (middle), and Au (top) samples. Associated scattering paths are included for the imaginary component.

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sample	abs sc	N	R/Å	$2\sigma^2/\text{\AA}^2$	$E_{\rm f}/{ m eV}$	R factor
reduced Au sample	Au-Cl	3.7 (2)	2.29 (1)	0.002 (1)	10 (1)	0.005
reduced Pd sample	Pd-Cl	3.3 (3)	2.35 (1)	0.003 (1)	10 (2)	0.004
	Pd-Pd	1.3 (5)	2.77 (2)	0.004 (2)		
reduced Pt sample	Pt – Pt	8.4 (5)	2.76 (1)	0.005 (1)	7 (2)	0.007
	Pt-Pt	3 (1)	3.91 (2)	0.005 (1)		
	Pt-Pt	10 (3)	4.79 (2)	0.007 (1)		
	Pt-Pt (ms)	13 (3)	5.65 (2)	0.011 (2)		

Table 1. EXAFS	Fitting Parameters f	or the Reduced	Pd, Pt and	l Au Samples"
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<sup>*a*</sup>Fitting parameters: (Au sample)  $S_0^2 = 0.75$  as deduced by KAuCl<sub>4</sub> standard; Fit range 3.5 < k < 12.5, 1.1 < R < 3; no. of independent points = 10; (Pd sample)  $S_0^2 = 0.82$  as deduced by PdCl<sub>2</sub> standard; Fit range 3 < k < 11.5, 1 < R < 3; no. of independent points = 11; (Pt sample)  $S_0^2 = 0.91$  as deduced by Pt foil standard; Fit range 3.5 < k < 14, 1 < R < 6; no. of independent points = 32.

219 radial distribution function is indicative of metallic particles, 220 and EXAFS data can be modeled by including the contribution 221 from the nearest three Pt-Pt distances and a multiple scattering Pt-Pt path from the primary Pt coordination shell. 222 The coordination number for the primary Pt coordination shell 223 224 is smaller (8.4) than that expected for a bulk Pt structure (12), indicating the nanoparticulate nature of the Pt sample (Table 225 226 1). In addition, by using an analogous EXAFS analysis, which was previously employed<sup>50</sup> for the calculation of particle sizes 227 from CNs of the first shell of a face-cented cubic (fcc) system, 228 we have estimated that our Pt NPs possess average diameters of 229 230 1.4 nm. The EXAFS data of the reduced Pd sample is similar to the initial Pd precursor used for the preparation of the 231 materials, with the largest contribution in the Fourier transform 232 resulting from the primary Pd-Cl coordination shell. However, 233 the EXAFS data also suggests the presence of Pd nanoparticles 234 as indicated by a second feature in the imaginary part of the 235 Fourier transform, which is consistent with a Pd-Pd scattering 236 distance. The weak Pd-Pd contribution is evidence that only a 237 small fraction of Pd sites are present as metallic species, with 238 the majority of Pd sites consistent with the initial catalyst 239 precursor. The radial distribution plot for the reduced Au 240 sample is dominated by one component, which can be assigned 241 to an Au-Cl scattering path. There is a good degree of 242 correlation between the EXAFS data of the reduced Au sample 243 and the KAuCl4 precursor, indicating that the significant 244 component in this reduced sample is the  $[AuCl_4]^-$  anion. 245 Although there is no observable metallic contribution from the 246 EXAFS data, some NP formation is clearly observed (see XPS 247 and TEM data) and is present at least in a minor fraction. It is 248 also noteworthy that the EXAFS data for the calcined material 249 shows evidence of metallic Au (Figure S2.1); however, the 250 similarity with the Au reference foil indicates mostly larger 251 nanoparticles with more bulk properties. 252

XAS data was also obtained for the calcined Pt and Pd 253 254 materials (Figures S2.2, S2.3); however for the most part, due to XAS being a bulk analysis technique, the data for the Pt and 255 Pd matched quite closely with the standards collected for the 256 respective precursor chloride materials. This highlights the fact 257 that only a small quantity of the chlorometallate anions have 258 been extruded, in comparison with the reduced samples, to 259 form nanoparticles. It is well-known that  $[AuCl_4]^-$  can be 260 reduced thermally in the presence of any gas,<sup>51</sup> which explains 261 262 the presence of metallic species for the calcined Au material. 263 However, the Pt and Pd materials require much more specific 264 reducing conditions, as outlined in the Experimental Section, 265 for the generation of nanoparticles.

<sup>266</sup> High-resolution XPS data were also acquired in order to <sup>267</sup> further probe the nature of the metallic species, and to contrast these findings with the XAS studies. As can be seen in the XPS  $_{268}$  spectra for the Au samples (Figure 3), a signal for Au(0) is  $_{269}$  f3



Figure 3. XPS spectra of metallic Au (blue circles) and KAuCl<sub>4</sub> (purple circles) standards, and as-synthesized (red circles), calcined (green circles) and reduced (orange circles) Au materials. (Black lines indicate background and component peaks.)

present not only in the reduced sample but also in the calcined 270 and as-synthesized materials. It is highly likely that these are 271 generated from small amounts of larger crystalline gold 272 impurities in the synthesis procedure, before the actual 273 formation of the crystalline framework. This is apparent from 274 the observation that the Au(0) 4f<sub>7/2</sub> signal has a binding energy 275 that is typical of bulk gold at 84.1 eV. It was further noted in the 276 calcined sample that the presence of the Au(0) signal increases 277 relative to that of the Au(III) 4f<sub>7/2</sub> signal at 86.8 eV, but a slight 278 shift to lower binding energy for the Au(0)  $4f_{7/2}$  to 83.9 eV was 279 observed. Furthermore, for the reduced sample, almost 280 complete conversion of Au(III) to Au(0) was observed, with 281 a greater shift in the Au(0)  $4f_{7/2}$  peak to a lower binding energy 282 of 83.6 eV. This shift to a lower binding energy for the Au(0) 283 peaks has been observed, as a notable characteristic, for the 284 formation of nanoparticulate gold.<sup>52,53</sup> Miller et al.<sup>52</sup> attribute 285

f4

286 this phenomenon to a change in the local electronic structure 287 close to the Fermi level of the small nanoparticles, in 288 comparison with bulk gold.

In stark contrast to XAS, XPS is a surface sensitive technique, 290 and thus, it is interesting to note the presence of metallic Au 291 NPs in the XPS, even though a larger proportion of the Au 292 present was shown to manifest as  $[AuCl_4]^-$  from the EXAFS 293 measurements (Figure 2). Given that the sampling volume of 294 XPS analysis has a depth less than 10 nm and that the crystallite 295 sizes are approximately 20  $\mu$ m,<sup>7</sup> these results indicate that our 296 materials are composed of isolated fractions of surface NPs and 297 hence represent distinct, discrete regions of Au species.

The large peak adjacent to the Au 4f peaks at lower binding energy (76-78 eV) in the XPS spectra (Figure 3) is associated with a Cu 3p signal originating from the framework. Although this is clearly resolved from the Au peaks in Figure 3, there is soz some overlap with the Pt 4f peaks, as can be seen in Figure 4.



Figure 4. XPS spectra of metallic Pt standard (blue circles) and  $K_2PtCl_4$  standard (purple circles), and as-synthesized (red circles), calcined (green circles), and reduced (orange circles) Pt materials. (Black lines indicate background and component peaks.)

303 For the sake of clarity, only peaks from the Pt have been 304 displayed in Figure 4 (see Figure S3.1 for an exemplar fitting 305 with Cu 3p assignments). From the Pt XPS data, we can observe a similar trend to the Au materials; namely, calcination 306 of the as-synthesized Pt sample results in the generation of a 307 small quantities of Pt(0) that is apparent at 71.2 eV (compared 308 with Pt(II) at 72.4 eV). However, the most striking observation 309 was noted for the reduced sample (Figure 4), where the almost 310 311 complete reduction of the Pt(II) is apparent, with only peaks  $_{312}$  associated with the metallic Pt(0) dominating the spectra. 313 These results, juxtaposed with observations from the EXAFS 314 data (Figure 2 and Table 1), further corroborate our findings 315 relating to the complete reduction of the  $[PtCl_4]^{2-}$  species to 316 metallic NPs.

XPS data from the Pd 3d region of the spectra (Figure 5)  $_{317}$  fs clearly show a transition from a mixture of Pd(IV) and Pd(II)  $_{318}$ 



Figure 5. XPS spectra of  $K_2PdCl_4$  standard (blue circles) and assynthesized (red circles), calcined (green circles), and reduced (orange circles) Pd materials. (Black lines indicate background and component peaks.)

species in the as-synthesized material (binding energies of 338.9 319 and 337.6 eV respectively), to predominantly Pd(II) in the 320 calcined analogues, with some indications for the presence of 321 Pd(0) (335.0 eV), in the reduced samples. A clear contribution 322 of Pd(IV) was noted in some of our samples. A related study<sup>54</sup>  $_{323}$ dealing with the location of supported Pt(II) species noted that, 324 in close proximity, a mixed valence Pt(II)-Pt(IV) bonded 325 dimer was formed, the presence of which was further 326 substantiated by DFT calculations. It is highly plausible that a 327 similar mechanism is operating in our systems, where mixed- 328 valence dimers are formed as precursors to cluster formation, 329 prior to nucleation and eventual nanoparticle growth. This, in 330 conjunction with the EXAFS data, clearly shows that, although 331 the reduction process seems to be much better for extruding 332 nanoparticles than calcination, the presence of metallic Pd(0) is 333 still minor, in comparison with Pd(II) species. We can also 334 conclude that the EXAFS data provide no evidence of any 335 significant  $PdO_x$  phase, with the major contribution in the 336 Fourier transform associated with the characteristic scattering 337 of Pd-Cl (Figure 2). EXAFS data was also acquired for a PdO 338 standard (Figure S2.4), which illustrates two distinct shells 339 (Pd–O and Pd–Pd scattering paths) in the Fourier transform, 340 that are not present in the data obtained for our Pd materials. 341 This supports our assertion that Pd oxide particles are not 342 produced during the synthesis procedure and that the Pd(II) 343 species are predominantly associated with the abundant 344 chlorometallate precursor anions, as in the as-synthesized 345 materials. 346

347 It is interesting to note that, although identical conditions 348 were used for thermally activating the analogous metalchloride 349 supported frameworks, the Pt material appears much more 350 readily amenable and susceptible to nanoparticle formation by 351 extrusion, than the Au or Pd. This could be attributed to the 352 differing strength of interactions between the discrete 353 chlorometallate anions within the framework channels and 354 the framework matrix. Further work is currently in progress to 355 study the calcination and reduction protocols in greater detail 356 using in situ X-ray absorption spectroscopy coupled with high-357 resolution electron microscopy (using high-angle annular darkfield imaging and tomography). 358 TEM analysis of the reduced catalysts are shown in Figure 6,



Figure 6. TEM images of reduced (a) Au, (b) Pt and (c)-(d) Pd catalysts, with magnified images of individual Au (e), Pt (f), and Pd (g) nanoparticles (scale bars in (e)-(g) are 2 nm).

361 composed of coexisting crystalline and amorphous phases. The 362 presence of crystalline embedded nanoparticles, with typical 363 diameters of 2–6 nm, can be seen in Figure 6b. High-resolution TEM analysis, shown in Figure 6e,f, display particles with 364 measured fringe spacings of 0.2 and 0.23 nm, which can be 365 attributed to Au(200) and Pt(111), respectively.<sup>55</sup> The mean 366 diameter of the Pt NPs estimated from TEM is 2.6 nm (std dev 367 = 0.7) (Figure S4.1), which is slightly higher than that 368 369 estimated by analysis of the EXAFS data, but certainly in 370 agreement with overall particle sizes, which are less than 3 nm 371 across the bulk of the material. The sizes are smaller than that 372 previously reported for NPs extruded by calcination in air at  $_{373}$  500 °C<sup>7</sup>, with both the lower temperature and reducing 374 conditions favoring smaller NP formation. It should be noted, 375 however, that a thorough high-resolution TEM study was

hindered by the beam sensitivity of the catalysts. The 376 morphology of the reduced Pd catalysts shows some differences 377 compared to the Au and Pt catalysts, with the presence of larger 378 particles (20-50 nm) embedded in an amorphous matrix, as 379 shown in Figure 6c. Due to sensitivity (dynamic changes in 380 crystal orientation) of the sample under the electron beam,<sup>56</sup> 381 the atomic resolution crystallinity of these particles could not 382 be probed in greater detail. However, there is evidence of some 383 Pd nanoparticle formation, as seen in Figure 6g, displaying 384 lattice fringes of 0.22 nm, characteristic of Pd(111).55 The Pd 385 nanoparticles are innately located at the edges of the composite 386 material

All three catalysts (calcined and reduced under identical 388 conditions, as outlined in the Experimental Section) were 389 probed for their catalytic potential, with a view to establishing 390 some initial trends that could be rationalized not only on the 391 basis of the shape and size of the nanoparticles but also, more 392 importantly, on their propensity to readily extrude from their 393 crystalline microporous framework. The aerobic oxidation of 394 vanillyl alcohol to vanillin, an intermediate step in the industrial 395 process to form vanillin from guaiacol (Schemes 2 and 3), was 396 used as a model probe reaction, given its importance from a 397 technological perspective. Interestingly, as reported in Figure 398 f7 7a, all three reduced catalysts displayed high activities for this 399 f7 aerobic oxidation, with the reduced Pt analogue affording close 400 to 100% conversion and selectivities for vanillin in excess of 401 80%, for this one-step process that we have devised (in contrast 402 with the multistep processes that are currently employed). 403 Given the challenging aspects of this aerobic oxidation, 404 turnover numbers (TONs) obtained with the Au and Pd 405 catalysts were modest. However, the performance of the 406 corresponding Pt analogue far exceeded that of its Au and Pd 407 counterparts, with the reduced Pt catalyst, to the best of our 408 knowledge, yielding unprecedented turnover values for this 409 aerobic oxidation at moderate reaction conditions (Figure 8). 410 f8 This clearly highlights the superior role of the Pt NP catalyst, in 411 this series of materials, for aerobic oxidation reactions. From 412 the XPS and EXAFS data, the high activity of the Pt material 413 can be attributed to the complete extrusion of the  $[PtCl_4]^{2-414}$ precursor, to yield stabilized discrete nanoparticles that are 415 amenable for catalysis, in stark contrast with the Au and Pd 416 materials (Figures 2 and 4). 417

The catalytic oxidation is composed of three main steps, 418 namely: (i) the adsorption of the alcohol on the surface with 419 the formation of a metal-alcoholate species; (ii) the  $\beta$ -hydride 420 elimination that results in the formation of the metal-hydride 421 intermediate and the carbonyl compound, which subsequently 422 desorbs; and (iii) the oxidation of the metal hydride 423 intermediate with concomitant formation of water and 424 subsequent regeneration of the metallic active site, which is 425 now available for further catalytic turnover.<sup>1,19,57</sup> The resulting 426 product selectivity from the catalytic reaction is outlined in 427 Figure 7b, from where it is possible to distinguish different 428 trends, in relation to the specific examined catalyst. The 429 reduced Pt catalyst affords the highest vanillin selectivity 430 (>80%), which is relatively consistent, except for the formation 431 of a small quantities of vanillic acid after prolonged contact 432 times. The vanillin selectivity for the reduced Pd material 433 increases steadily over time, but the corresponding reduced Au 434 catalyst displays a distinctly different behavior compared to the 435 others, with the selectivity toward vanillin decreasing 436 monotonically with reaction time. The formation of the 437 byproduct 4-hydroxy-3-methoxybenzyl tert-butyl ether was 438

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**Figure 7.** Kinetic plots outlining the catalytic activity for the Au (red triangles), Pt (blue squares), and Pd (green circles) reduced (a) and calcined catalysts (c). Corresponding selectivity profiles of Au (red), Pt (blue), and Pd (green) reduced (b) and calcined catalysts (d) toward vanillin (squares), 4-hydroxy-3-methoxybenzyl *tert*-butyl ether (triangles), and vanillic acid (circles). Reaction conditions: vanillyl alcohol (1 g), *tert*-butanol (30 mL), diglyme (0.85 g), catalyst (50 mg), T = 170 °C,  $P_{air}$  (20 °C) = 20 bar.



**Figure 8.** Comparison of catalytic turnover for Au (red), Pt (blue), and Pd (green) reduced (solid) and calcined (patterned) catalysts. See Figure 7 for reaction conditions.

439 confirmed using gas chromatography-mass spectrometry (GC-440 MS) analysis, and it was noted that the selectivity for this 441 particular product increases over time for the Au catalyst. The 442 origin of the 4-hydroxy-3-methoxybenzyl *tert*-butyl ether can be 443 readily rationalized on the basis of the generation of a hydride 444 species, <sup>57,58</sup> that induces local acidity in the nanoparticle, thus 445 facilitating the etherification between the stabilized vanillyl 446 alcoholate and the adsorbed *tert*-butanol solvent molecules 447 (Scheme 4). It is well-known that *p*-hydroxybenzylic alcohols 448 can undergo an etherification reaction in presence of another 449 alcohol under acidic or harsh oxidative conditions.<sup>59</sup> Although

Scheme 4. Etherification of Vanillin with *t*-Butanol To Form Byproduct



this is known for Au systems,<sup>57,58</sup> it is highly likely that similar 450 mechanisms are also facilitating the formation of this product 451 (4-hydroxy-3-methoxybenzyl *tert*-butyl ether) for the Pt and Pd 452 catalysts, though with varying kinetics of hydride formation, 453 which accounts for the different selectivities observed with 454 these catalysts, when compared to the Au analogue. Detailed 455 kinetic analyses are currently ongoing, and these will be 456 published separately.

In order to investigate the effect of temperature on the 458 catalytic activity of the materials, analogous reactions were 459 performed at 150 °C. In line with our expectations, the lower 460 temperatures afforded reduced activity but more importantly 461 resulted in a comparatively higher selectivity toward the ether 462 product (Table 2). It was indeed revealing that lower reaction 463 t2 temperatures facilitated the stabilization of the metal–alcohol- 464 ate complex, thereby inducing a higher propensity for 465 etherification. In addition to this, the adsorption stability of 466 the formed aldehyde was higher at lower reaction temperatures, 467 leading to longer induction periods in the catalysis. However, 468 the reduced Pt catalyst again affords the highest selectivity 469 toward the target product (vanillin), when compared to the Au 470 and Pd analogues, despite its activity being drastically inferior 471 when compared to the catalytic tests at 170 °C (Figure 7a). 472

Table 2. Kinetic Data for the Aerobic Oxidation of Vanillyl Alcohol at 150  $^{\circ}C^{a}$ 

metal	time (h)	conv. (%)	vanillin	ether <sup>b</sup>	acid <sup>c</sup>	TON <sup>d</sup>
Pt	8	14.35	74.15	25.85	0	133
	10	32.25	76.00	24.00	0	298
Au	8	35.79	54.06	45.94	0	140
	10	42.03	55.61	44.39	0	164
Pd	8	24.11	51.41	48.59	0	99
	10	32.38	52.83	47.17	0	133

<sup>*a*</sup>For reaction conditions (excluding temperature), see Figure 7. <sup>*b*</sup>4hydroxy-3-methoxybenzyl *tert*-butyl ether. <sup>*c*</sup>Vanillic acid. <sup>*d*</sup>TON based on conversion of vanillyl alcohol.

473 Thus, in order to maximize both conversions and selectivities to 474 the desirable vanillin, higher reaction temperatures must be 475 employed in this particular system.

Analogous reactions were also carried out with the calcined 476 477 catalysts, in order to make reactivity/selectivity comparisons with those of the reduced counterparts described in Figure 7a,b. 478 479 As can be seen from Figure 7c,d, there is very little difference in 480 the reactivity and selectivity profiles for all three catalysts. It is 481 however significant that the latter (calcined catalysts) are 482 markedly inferior in catalytic performance when compared with 483 their reduced analogues, which further indicates the superior 484 performance of the reduced materials, and in particular the Pt 485 catalyst. The catalytic performance of these materials can 486 indeed be rationalized from the XPS data (Figure 4), which 487 reveals an enhancement in the metallic character of the reduced 488 Pt catalyst, which are clearly the desired active sites for this 489 aerobic oxidation reaction. Consistent with the above, the 490 pronounced increase in activity for the reduced Au catalyst, 491 when compared with its calcined analogue, can also be 492 corroborated from the detection of higher quantities of 493 nanoparticulate gold, as confirmed from the shift in the binding 494 energies in the XPS spectra (Figure 3). It was therefore 495 unsurprising to note that only a marginal difference was 496 observed in the catalytic activity of the reduced Pd catalyst, when compared with its calcined counterpart, as only a very 497 small proportion of metallic Pd was detected by XPS (and 498 499 TEM), with the EXAFS analysis predominantly revealing the 500 presence of the precursor  $([PdCl_4]^{2-})$  species, postreduction. There are very few reports on the use of NP catalysts for the 501 502 aerobic oxidation of vanillyl alcohol to vanillin. However, the so3 use of  $Pt/MOF-5^{60}$  and  $Pt/C^{61}$  were recently shown to have some activity, but with low TOFs of 4.9  $h^{-1}$  and 19  $h^{-1}$ 504 respectively, in comparison with 93  $h^{-1}$  achieved with our 505 506 reduced Pt/CuClP material. Other recent studies have explored the use of Co catalysts to catalyze the aerobic oxidation of 507 vanillyl alcohol,<sup>62,63</sup> although the use of a base was mandatory 508 in these systems. In these studies, <sup>62,63</sup> conversion and selectivity 509 toward vanillin appear promising; however, the low substrate to 510 catalyst ratios employed result in inferior TONs at complete 511 conversion. The superior TONs displayed by these extruded 512 catalysts and, in particular, the reduced Pt nanoparticles (Figure 513 514 8), which afford TON/TOFs that are at least 4 times higher 515 than existing Pt NP catalysts and almost two-orders of 516 magnitude greater than other transition metal systems (to the 517 best of our knowledge), offers adequate scope for the industrial 518 implementation of these catalysts for the production of vanillin 519 through benign, aerobic oxidation routes.

520

### SUMMARY AND FUTURE PROSPECTS

It has been shown that the  $[PtCl_4]^{2-}$  supported porous copper 521 chlorophosphate framework is highly susceptible to complete 522 extrusion by reduction, forming isolated, discrete nanoparticles, 523 which are the loci for aerobic oxidation reactions. The 524 propensity of the Pt NPs to readily extrude from within the 525 porous architecture offers a unique strategy for the design of 526 single-site heterogeneous catalysts, where the nature of the 527 active site can be dexterously manipulated and controlled 528 through judicious activation procedures. The design approach 529 has also facilitated the structural (XRD, EXAFS, TEM) and 530 spectroscopic (XPS, XAS) characterization of the active sites at 531 a molecular level, which have proved invaluable in facilitating 532 structure-property correlations for understanding the implica- 533 tions of the superior activity afforded by reduced Pt particles for 534 the aerobic oxidation of vanillyl alcohol to vanillin. 535

The study has further established that analogous precursors 536 for generating Au and Pd nanoparticles are sensitive to the 537 thermal activation procedures that are employed, which in turn 538 has a critical influence on the ensuing catalysis. It has been 539 found that reduction procedures under  $H_2$  are more effective 540 than calcinations for extruding the chlorometallate precursors 541 in all three catalysts, but with distinct and varying influences 542 that directly affect the catalytic turnover. While we have 543 identified an efficient route for generating Pt NPs by this route, 544 further studies (currently in progress) will pinpoint activation 545 methodologies that favor complete extrusion of the analogous 546 Au and Pd catalysts.

It is envisaged that this initial investigation will pave the way 548 for further exploring and exploiting the potential of this novel 549 extrusion strategy for generating new nanoparticle catalysts. By 550 using a combination of in situ and operando tools for directly 551 probing the nature of the active site during the activation 552 procedure will afford a greater understanding of how each metal 553 within the framework responds to thermal treatments. This 554 would help establish a detailed understanding of size/shape 555 distributions, compositional integrity, and, more importantly, 556 precise location of the extruded nanoparticles, which could, in 557 turn, facilitate a design-application approach for the controlled 558 engineering of superior catalysts for a wider-range of 559 industrially significant catalytic transformations.

ASSOCIATED CONTENT	56
S Supporting Information	50
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.5b00481.	50 50
Industrial process schemes, EXAFS spectra, XPS data, TEM particle size distribution (PDF)	50 50
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Notes	57
The authors declare no competing financial interest.	5
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