Carbidisation of Pd Nanoparticles by Ethene Decomposition with Methane Production

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In the presence of oxygenated organic molecules pure Pd, which is widely used in chemical processing and the pharmaceutical industry, tends to defunctionalise and dehydrogenate such molecules to \( \text{H}_2 \), \( \text{CO} \) and surface/bulk carbon, in the form of a palladium carbide. We have investigated the formation of this carbide by ethene adsorption using a variety of techniques, including pulsed flow reaction measurements, XAS and DFT calculations of the lattice expansion during carbidisation. These experiments show that two main reactions take place above 500 K, that is, both total dehydrogenation, but also disproportionation to methane and the carbide, after which the activity of the Pd is completely lost. We estimate the value of \( x \) in PdC\( x \) to be 0.28 (± 0.03), and show by computer modelling that this fits the lattice expansion observed by XAFS, and that there is charge transfer to C from Pd of around 0.2–0.4 e.

Introduction

Pd is an important catalytic metal and it is used in a variety of processes, for instance, in the Wacker process for the selective oxidation of ethane to acetaldehyde, in vinyl acetate synthesis and in a wide range of fine chemicals hydrogenation reactions.

In our work we have observed that there are different processes occurring during the formation of PdC\( x \). Surprisingly, together with dehydrogenation, and in contrast with the behaviour of single crystal Pd\( x \), we find that disproportionation of ethene to carbide and methane is a major reaction pathway. The stoichiometry of the carbide phase has been variously reported from a value of PdC\( 0.05 \) to PdC\( 0.16 \) (though...
higher levels are reported in the surface regions\(^{(6)}\), but here we find the loading of the carbid to be much higher at \(\sim 28\) atom\%C.

**Results and Discussion**

As we have shown earlier carbide can be formed in pure Pd crystals\(^{[1,2,4]}\) and Pd nanoparticles\(^{[5]}\) by treatment in a wide variety of organic molecules. In this work we have used ethene as carbidizing agent, a process which is, in principle, very simple. This was certainly shown to be the case by us on well-defined single crystal surfaces, both Pd(110)\(^{[4]}\) and (111)\(^{[3]}\). However, when we study this reaction carefully in a pulsed flow micro-reactor at much higher pressures, using a supported catalyst, we find something rather different, as shown in Figure 1. Here the main reaction is a kind of disproportionation reaction in which the products are methane and carbide (reaction 2), [Eq. (1) and (2)].

\[
\begin{align*}
\text{Eq. (1)}: & \quad \frac{x}{2} \text{C}_2\text{H}_4 + \text{Pd} \rightarrow \text{PdC}_x + x\text{H}_2 \\
\text{Eq. (2)}: & \quad \text{C}_2\text{H}_4 + \text{Pd} \rightarrow \text{PdC}_x + x\text{CH}_4
\end{align*}
\]

For clarity Figure 1 shows just the methane evolution at 300°C, but the other product, hydrogen is also shown in Figure S1. It can be seen though that the evolution is rather complicated, with initial hydrogen production, followed by a decrease and coincidently increasing methane. Ethene begins to break through the end of the reactor after about 10 pulses and none is converted after about 120 mins, at which point hydrogen and methane evolution have ceased. More detailed discussion is given in the supplementary information.

Immediately following this experiment, another titration was carried out, this time removing the C using oxygen pulses and the results are shown in Figure S1. Here the titration is clearly much more precise with only CO\(_2\) being evolved for the first 64 pulses, with all the oxygen in the pulse being consumed, followed by a sharp breakthrough of O\(_2\), and dramatic decline in CO\(_2\), which gives us an accurate measure of the carbon deposited into the sample under these conditions, since each pulse contains \(4 \times 10^{-7}\) mol and so the uptake was \(2.7 \times 10^{-5}\) mol of O\(_2\). The total molecular oxygen uptake is equal to the CO\(_2\) evolved, indicating the simple clean-off (C + O\(_2\) \(\rightarrow\) CO\(_2\)). The same is seen on single crystals, with all adsorbed oxygen being evolved as CO\(_2\) until the C is used up.\(^{[6]}\) We estimate the value of \(x\) in PdC\(_x\) to be 0.25 (\(\pm 0.03\)) the calculation of this number is shown in the supplementary material.

Structural measurements were also made on the catalyst. TEM measurements indicate that the average size of particles is 7 nm, with a median of 5 nm (Figure S2). We have used XRD and XAS to investigate changes in the structure during reaction. We find that the Pd diffraction peak shifts after carbidization from 40.2 and 67.9° (Pd (111) and (220) respectively) to 39, and 66.3°, a surprisingly small shift showing a small lattice expansion with no real change in symmetry. This lattice expansion has been followed in more detail using TPXAS, temperature-programmed X-ray absorption spectroscopy. As shown in Figure 2 the lattice expansion overall correlates well with the XRD result, with an expansion of 0.07 (\(\pm 0.005\)) nm. However, it appears to proceed in two stages, with an expansion of \(\sim 0.015\) nm up to about 100°C, after which it expands much more up to completion at 180°C. The small expansion at low temperature may be associated with the formation of adsorbed layers, which generally cause surface lattice expansions of up to \(\sim 10\%\).\(^{[20]}\) This would lead to an average lattice expansion of \(\sim 0.001\) nm, which is not far from what we observe. As the temperature increases, so the full lattice expansion is achieved as the bulk becomes saturated with C. Note that some sintering has occurred after many runs,
with the average particle size in TEM increasing to \( \sim 9 \) nm (Figure S2b).

The exact cause of the lattice expansion can be determined by investigating the XANES region of the XAFS data (Figure 3). Pd hydride and Pd carbide have clear differences in their XANES spectra; both cause a negative shift in energy for the second XANES feature (\( \sim 24390 \) eV), however, only the carbide gives rise to a broadening and a shift in energy (\( \sim 1 \) eV) of the main edge transition.\(^7,17\) When assessing the difference spectra (compared to metallic Pd) of the hydridic and carbidic forms of Pd there are clear features that allow us to easily distinguish between these interstitial structures; the Pd hydride difference spectrum has an intense peak at \( \sim 24360 \) eV, whereas the Pd carbide difference spectrum has a distinguishing peak at \( \sim 24374 \) eV (Figure 3a). By assessing the XANES difference spectra during our time-resolved XAFS studies (Figure 3b) we can assign the interstitial structure types at both stages of lattice expansion. XANES difference spectra at 69°C and 224°C both have an observable feature at 24374 eV, which allows us to assign that the lattice expansion in both cases is caused by Pd carbide formation. Indeed, this is consistent with the proposed hypothesis that the carbide phase is initially formed at the surface before diffusing into the bulk lattice.\(^8\)

Turning to adsorption measurements, there is a significant change in the CO adsorption mode before and after such C dosing experiments seen by using in situ DRIFTS. As shown in Figure 4, the clean nanoparticles of Pd show the kind of CO spectrum seen by others,\(^21–23\) with a major band at \( \sim 1990 \) cm\(^{-1}\), proposed to be due to bridge-bonded CO, together with a lower intensity band at 2080 cm\(^{-1}\) (on-top) and broad shoulder on the high intensity band at \( \sim 1950 \) cm\(^{-1}\), possibly due to bridge sites at the edge of particles.\(^24\) Note that there appear to be no multiple bridge sites, which would be seen at much lower wavenumber (e.g. hollow 3-fold (111)

![Figure 2](image-url)  
*Figure 2.* In situ measurements of the average lattice expansion of the Pd nanoparticles exposed to ethene as a function temperature of the sample.

![Figure 3](image-url)  
*Figure 3.* (a) Normalised Pd K edge XANES spectra of Pd\(^0\), Pd hydride and Pd carbide. The difference spectra (Pd\(^0\) reference) of Pd carbide and Pd hydride are also shown. (b) Normalised Pd K edge XANES spectra during time resolved ethene decomposition (temperatures of 69°C, 142°C, 224°C) alongside associated difference spectra.

![Figure 4](image-url)  
*Figure 4.* DRIFT spectra collected after CO adsorption at RT after each treatment stage, (Green-after reduction, Blue-after carbidisation on ethene exposure, Red-after re-oxidation).
type sites). After carbidisation the main, clearly identifiable change is the loss of the 1990 cm\(^{-1}\) band, while the others remain, and after oxygen cleaning and removal, the original spectrum is largely restored, with some additional intensity in the 2130–60 cm\(^{-1}\) region due to CO–Pd\(^{+}\) species.\(^{[20]}\) Evidently then, carbidisation has significantly altered the surface layers and blocked the bridge site adsorption.

We have also used density functional theory (DFT) to explore the expansion of Pd–Pd interatomic distances due to the presence of interstitial C atoms. For this study we included 0.357–3.124 wt % of interstitial carbon atoms in a 3 × 3 Pd model with 7 atomic layers (Figure 5). The calculated interatomic distances due to the presence of various concentration of interstitial C have been summarised in Tables 1–3. Our calculations show that in close proximity to the interstitial C-atom the Pd–Pd interatomic distance increases in the range of 0.007–0.042 Å, which show reasonable agreement with the experimental data. Additionally, we also calculate the charge transfer between the Pd and the interstitial C-atoms. There is an average

![Figure 5. Pd(111) surface with (a) 2 C-atom (0.357 wt%), (b) 4 (0.711 wt%), (c) 6 (1.063 wt%), (d) 12 (2.105 wt%), and (e) 18 (3.124 wt%).](image)

| Table 1. Layer by layer Pd–Pd bond distances with increasing percentage of C atom intercalation. |
|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|
| C [wt %] Pd–Pd bond distances Average | Layer | 1st | 2nd | 3rd | 4th |
|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|
| 0.357 2.763 2.771 – – 2.767 | Layer | 1st | 2nd | 3rd | 4th |
| 0.711 2.789 2.786 – – 2.787 | Layer | 1st | 2nd | 3rd | 4th |
| 1.063 2.818 2.787 – – 2.803 | Layer | 1st | 2nd | 3rd | 4th |
| 2.105 2.786 2.829 2.804 – 2.807 | Layer | 1st | 2nd | 3rd | 4th |
| 3.125 2.795 2.793 2.8238 2.797 2.802 | Layer | 1st | 2nd | 3rd | 4th |

| Table 2. Pd–Pd distance around the intercalated C atoms. |
|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|
| C [wt %] Nearest Neighbour Av. Pd–Pd bond distance [Å] Difference with bulk Pd–Pd bond distance [Å] Av. Pd–C [Å] | Layer | 1st | 2nd | 3rd | 4th |
|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|
| 0.357 2.816 0.056 1.909 | Layer | 1st | 2nd | 3rd | 4th |
| 0.711 2.823 0.063 1.911 | Layer | 1st | 2nd | 3rd | 4th |
| 1.063 2.825 0.065 1.936 | Layer | 1st | 2nd | 3rd | 4th |
| 2.105 2.828 0.068 1.985 | Layer | 1st | 2nd | 3rd | 4th |
| 3.125 2.830 0.070 2.007 | Layer | 1st | 2nd | 3rd | 4th |

| Table 3. Average Bader charge on Pd and C atoms with increase in the number of interstitial C atoms. |
|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|
| Atoms | Average Charges | 2 | 4 | 6 | 12 | 18 |
|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|
| Pd | 0.007 0.014 0.021 0.071 0.115 | Layer | 1st | 2nd | 3rd | 4th |
| C | –0.210 –0.225 –0.224 –0.370 –0.402 | Layer | 1st | 2nd | 3rd | 4th |
change in Bader charge on the Pd of \(+0.007\ e\) to \(+0.115\ e\), and on C between \((-0.210\ e\) to \(-0.402\ e\) (see Table S3). Effectively the radius of the Pd is decreased and the C increased, which may help to accommodate the C with relatively little overall expansion.

Conclusions

We have discovered that ethene not only dehydrogenates on nanoparticulate Pd supported on silica at above 200°C, but concurrently it disproporionates to also produce palladium carbide and methane. We have found a higher level of carbidisation than previously reported by using chemical titration of the carbide with oxygen. The carbide formed is probably \(\text{PdC}_x\), but with minimal expansion of the Pd lattice, which we propose to be due to interstitial formation plus some charge transfer between Pd and C.

Experimental Section

Catalyst Synthesis

Pd catalysts supported on SiO\(_2\) (Fumed 320–410 m\(^2\)g\(^{-1}\)) were prepared using a sol-immobilisation method. An aequous solution of \(\text{K}_2\text{PdCl}_4\), of the desired concentration (9.39×10\(^{-4}\) M) was prepared in MilliQ water. To this solution polyvinyl alcohol (PVA) (1 wt% solution, Aldrich, averaged molecular weight \(M_w=9000–10000\) g mol\(^{-1}\), 80% hydrolysed) was added (PVA/Pd (wt/wt) = 0.65). Subsequently, a 0.1 M freshly prepared solution of NaBH\(_4\) (\(>96\%\), Aldrich, NaBH\(_4\)/Au (mol/mol) = 5) was then added to form a dark/brown sol. After 30 min of sol generation, the colloid was immobilised by adding SiO\(_2\) (acidified to pH 1 by sulfuric acid) under vigorous stirring conditions. The amount of support material required was calculated so as to have a total final metal loading of 5% wt, but analysis of the filtrate indicated a loading of 4.4%. After 24 hours the slurry was filtered, the catalyst washed thoroughly with distilled water (1.5 L) and dried at 120°C for 8 hours. Finally, a calcination step was performed at 350°C for 3 hours to remove the PVA.

The Reactor

Reaction measurements were carried out in a Hiden Catlab using its pulsed flow reactor capability.[27] 0.22 g of catalyst was loaded into the quartz reactor tube and heated in-situ prior to reaction to 250°C in 10% H\(_2\) in He, followed a pure He flow for one hour prior to the pulsing experiments. 10% Ethene in He was then regularly pulsed over the catalyst every 2 mins and products analysed by on-line mass spectrometry. O\(_2\) (10% in He) could then be pulsed over the catalyst to remove the adsorbed/absorbed C.

XAFS-DRIFTS Measurements

XAFS measurements were performed at the Pd K-edge on the B18 beamline at the Diamond Light Source, Didcot, UK. Measurements were performed in transmission mode using a QEXAFS setup with fast-scanning Si (311) and (111) double crystal monochromators for the Pd edge. The time resolution of the spectra reported herein was 90/spectrum (kmax = 12.5). A DaVinci arm fitted with Praying Mantis Optics was used to refocus the IR beam outside the FTIR spectrometer so that the X-ray beam could be transmitted through the DRIFTS cell. The samples were placed in the Harrick X-ray transmission DRIFTS cell attached to the end of the DaVinci arm. The arm has motorized stages able to move vertically and horizontally by 48 mm, enabling ease of alignment of the DRIFTS cell in the X-ray beam. The cell is fitted with glassy carbon windows for exit and entry of the X-ray beam and ZnSe windows for collection of DRIFTS spectra. The XAFS/DRIFTS cell which has been described in detail elsewhere,[19] has an X-ray path length of 3.17 mm placed 1.04 mm below the surface of the catalyst. DRIFTS spectra were collected with an Agilent Carey 680 FTIR spectrometer taking 64 scans with a resolution of 4 cm\(^{-1}\) using the liquid nitrogen cooled MCT detector.

EXAFS (Extended X-ray Absorption Fine Structure) Analysis

All XAFS spectra were acquired concurrently with a Pd foil placed between It and Iref. XAFS data processing was performed using IFEFFIT[27] with the Horae package[28] (Athena and Artemis). Athena was used to calibrate, align, and normalize the spectra with respect to the Pd foil, for which \(E_0\) was set at 24358 eV. EXAFS data processing of k2 data used an appropriate k range for the data (3.2–12.5 Å\(^{-1}\)). Analysis of the Fourier transformed data was limited to fitting with the first coordination shells using cif files of Pd. The amplitude reduction factor, S\(^2\), was derived from EXAFS data analysis of the Pd foil reference spectra, (with known coordination numbers which were fixed during analysis). The value obtained was 0.85 for Pd, this value was used as fixed input parameters in the fits. The increase with temperature of the \(\sigma^2\) value, the mean-square relative displacement of absorber and backscatter atoms, was estimated based on the method described elsewhere for the change in the \(\sigma^2\) value with increasing temperature.[29] While the EXAFS measurements showed an increase in Pd–Pd bond distance that is consistent with carbon absorption, it cannot directly measure the amount of carbon within the sample. Other X-ray techniques such as diffraction are also similarly hampered due to the strong scattering from Pd with respect to carbon.

Computational Details

We employed the Vienna Ab-initio Simulation Package (VASP) to perform DFT based calculations.[30–33] The projector augmented wave (PAW) method was used and the cut-off energy for the expansion of the plane-wave basis sets was set to 550 eV, which gave bulk energies converged to within 10 eV. We chose a convergence criterion of 0.01 eV/Å for our structural optimisations. For all the preliminary calculations, the most commonly used Perdew-Burke-Ernzerhof (PBE) version of the generalized gradient approximation (GGA) was used to carry out total energy calculations and perform geometry optimization.[34] The ideal Pd(111) surface was modelled by a 3×3 supercell with 7 atomic layers with a theoretical lattice constant of 3.904 Å and a k-point grid of 3×3×1. During the optimization process, we relaxed the entire system, which consisted of interstitial carbon and the Pd(111) surface. In our models we placed the interstitial carbon atoms on the subsurfaces close to both sides of the exposed Pd(111) surface, which is to nullify the spurious dipole moments due to the presence of carbon atom on one side (Figure 1 (a–d). For all these calculations we also used Grimme’s D3 corrections as dispersive effects in these systems may play a crucial role.[35] The charges on various atoms were obtained using the Bader charge analysis as implemented by Henkelman and co-workers.[36]
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Conflict of Interest

The authors declare no conflict of interest.

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