Peer-reviewed version available at *Catalysts* **2019**, *9*, 134; doi:10.3390/catal9020134

Article

Nanoparticles and Single Atoms in Commercial Carbon-Supported Platinum-Group Metal Catalysts

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Abstract: Nanoparticles of platinum-group metals (PGM) on carbon supports are widely used as catalysts for a number of chemical and electrochemical conversions on laboratory and industrial scale. The newly emerging field of single atom catalysis focuses on the ultimate level of metal dispersion, i.e. atomically dispersed metal species anchored on the substrate surface. However, the presence of single atoms in traditional nanoparticle-based catalysts remains largely overlooked. In this work we use aberration-corrected scanning transmission electron microscope to investigate four commercially available nanoparticle-based PGM/C catalysts (PGM = Ru, Rh, Pd, Pt). We show that in addition to nanoparticles, single atoms are also present on the surface of carbon substrates. These observations raise questions about the role that single atoms play in conventional nanoparticle PGM/C catalysts. We critically discuss the observations with regard to the quickly developing field of single atom catalysis.

Keywords: single atom catalysis; carbon-supported catalysts; platinum-group metals; aberration-corrected scanning transmission electron microscopy

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1. Introduction

Catalysts that consist of metal nanoparticles dispersed on a supporting carbon material (M/C) are very commonly used in various fields of catalysis and electrocatalysis. Materials containing dispersed platinum-group metals (PGM) such as Ru, Rh, Pd and Pt are often used as heterogeneous catalysts in many reactions for chemical production [1, 2]. Pt/C is also an important electrocatalyst for oxygen reduction and hydrogen oxidation reaction in low-temperature fuel cells [3]. Due to their widespread use there are many commercial PGM/C catalysts available on laboratory and industrial scales.

In the past decade, a new research field of heterogeneous catalysis has emerged, namely single atom catalysis (SAC). While atomically dispersed species of non-noble metals such as Fe, Co and Ni on carbon supports have long been studied as an alternative to Pt-based materials in fuel cells [4, 5], the idea of single atoms of noble metals as counterparts to traditional nanoparticle-based catalysis is relatively recent [6-8]. This line of investigation has become strongly promoted with the increasing availability of sub-ångström resolution aberration-corrected transmission electron microscopy [9, 10] which has made it possible to visualize single atoms dispersed on support. In terms of visual detection, carbon materials have an advantage over some other support materials (such as oxides) because of the large difference in atomic numbers (Z) between the support and the dispersed transition metal. That enables an easier visualization of the dispersed metal with Z-contrast images compared to the supports that themselves contain atoms of other metals with similar Z number.

SAC was initially regarded as a new frontier of nanoparticle-based heterogeneous catalysis. The properties and expected catalytic behaviours of single atoms were predicted by simply extrapolating size-dependent trends observed in nanoparticles to the ultimate limit of size reduction, i.e. atomic dispersion [6, 7]. It was suggested that by achieving atomic dispersion the efficiency of the metal use could be maximized since all of the metal atoms would be on the surface of the support and thus accessible to the reactants. At the same time, single atoms were expected to maintain or increase their activity as compared to active sites on the metal. Thus SAC promised to offer a significant improvement in cost efficiency over traditional supported PGM catalysts where part of the atoms within the nanoparticles are not exposed to the surface and thus cannot serve as active sites. This strong motivation coupled with increasingly accessible technique for detection and visualization lead to single atom catalysis becoming an established and growing research field within heterogeneous catalysis and electrocatalysis. The surge of interest in atomically dispersed metals has significantly diversified the field by investigating many different transition metals, supporting materials and catalysed reactions [8, 11-14].

Indeed many atomic species on carbon and other hosts have been synthesized and shown to possess high catalytic activity for various reactions [15, 16]. However with growing number of experimental and theoretical results those initial assumptions regarding the role of SAC is being investigated in more detail and, occasionally, partly reinterpreted. Publications reporting atomic dispersion on carbon supports show ionic nature of the single atoms and direct attachment of metal to atoms that are part of the carbon framework [15-17]. This shows that single atoms are fundamentally different chemical species than metallic atoms on nanoparticle surface. Any trends observed for nanoparticle size-dependent behaviour cannot be expected to be generally valid when the particle size is reduced from nanoparticles to clusters and finally single atoms. This is of course also true for catalytic activity. Even though it has been shown that in some cases single atoms can catalyse the same reaction as nanoparticles, this behaviour cannot be expected as a general rule. Instead, it has recently been suggested that atomically dispersed metals may have more similarities with analogous homogeneous catalysts than with supported nanoparticles [13]. Of course, any properties of a given supported metal atom are defined by the exact nature of the single atom specie(s) present in the catalytic material (oxidation state, type of bonding with the support, bonding symmetry) and the nature of the support. Yet as a rough generalization, the comparison of single atoms to homogeneous complexes seems more rational than comparison with metallic surfaces.

Understanding similarities and – more importantly – differences between supported single atoms and nanoparticles and how they behave towards the same reaction is especially important when both species coexist in the same catalyst material. In SAC community, a lot of effort is being put towards synthesizing catalysts with exclusively atomic distribution without additional nanoparticles. This becomes challenging when trying to increase the loading of atomically dispersed atoms. Typically, catalysts with only individually dispersed metals are prepared on carbon materials with high specific surface area and heteroatom doping – predominantly with N [15, 17, 18], but also S [16]. When allowing clusters and nanoparticles to be present alongside single atoms, however, preparation of single atoms seems trivial and can be achieved with different deposition techniques. Heteroatom doping appears beneficial but not necessary for occurrence of atomically isolated species [19]. Predominantly it has been shown that metal atoms bond with atoms (N, S or C) at the edges of graphene sheets or are inserted within the plane of graphite sheet [15, 16, 18, 20].

In this work we bring into attention the coexistence of single atoms alongside nanoparticles in commercial PGM/C catalysts for four materials (PGM = Ru, Rh, Pd, Pt,). By demonstrating that the presence of single atoms is common even in widely used commercial PGM/C catalysts we wish to contribute towards more comprehensive understanding of the nature and behaviour of atomically dispersed metal species on carbon and their role in already established catalytic materials.

2. Results and Discussion

Commercial PGM/C catalysts have various different applications and therefore vary in their properties (e.g. carbon substrate, metal loading and average nanoparticle size) according to their intended use. For this work four different commercial catalysts with varying metal loading were chosen, namely Ru/C, Rh/C, Pd/C (in all cases the content was 5 wt.%,) and Pt/C (46 wt.%). The Pt/C

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catalyst is produced for electrocatalysis in low-temperature fuel cell where typical metal loadings on carbon are between 20 and 50 wt.%. The other three materials are commonly used in organic synthesis where loadings in the range of 0.5–10 wt.% are common among commercially available catalysts [2]. Producers of commercial PGM/C materials typically do not disclose structural details about the materials other than the total metal loading. In order to understand the basic morphological properties of the materials they were analysed by scanning-electron microscopy (SEM) and X-ray diffraction (XRD).

Figure 1 shows SEM images of the PGM/C materials and their X-ray diffractograms. All four diffractograms results show distinct carbon peaks related to the hexagonal carbon (graphite) at 2θ = 26° and 44° angles (their positions are marked with grey lines) [21], however the carbon signal in the Pt/C sample is significantly lower. This can be explained by SEM images which show a markedly different morphology of the carbon substrate. While Pt is dispersed on a high-surface area carbon with small primary particle size, all three fifth row PGM metals are deposited on a highly polydisperse carbon support with particles ranging in size up to several micrometres (Ru/C, Rh/C) or tens of micrometres (Pd/C).

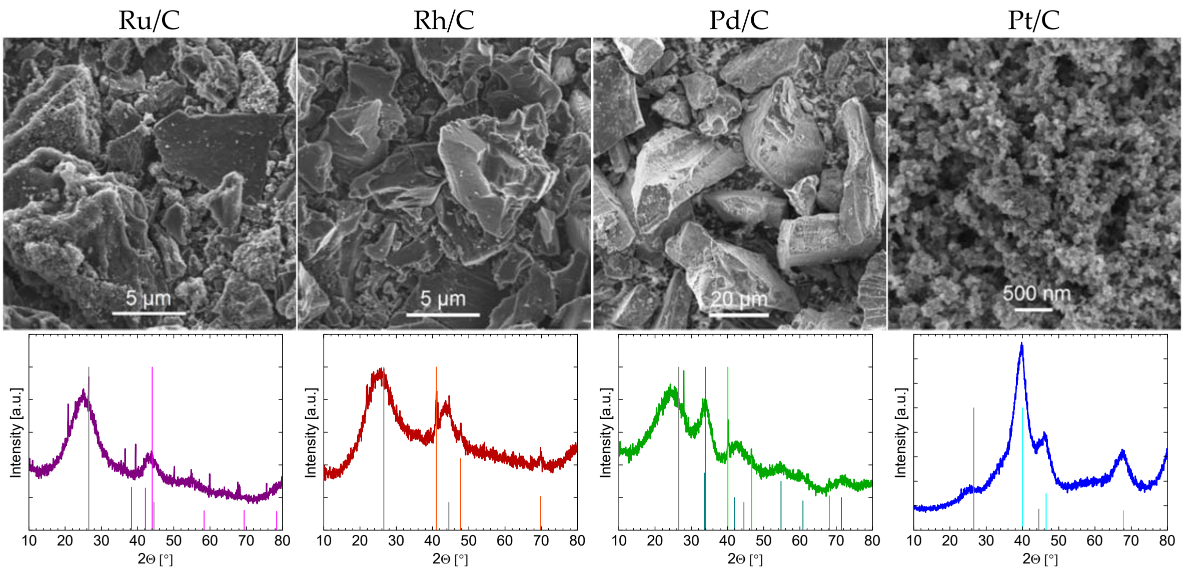

Figure 1. Characterization of commercial samples PGM/C samples; SEM images (top row) and XRD patterns (bottom row). Note that the scales in SEM micrographs vary. In addition to hexagonal carbon [21] each XRDs also display characteristic peak positions for the corresponding metal and metal oxide (Ru – pink [21], Rh – orange [21], Pd – light green [22], PdO – dark green [23] and Pt – light blue [21]).

The main role of carbon support in PGM/C catalysts is to enable high dispersion of the metal and prevent nanoparticle aggregation. The size and distribution in the PGM/C materials was analysed by a scanning transmission electron microscope microscopy (STEM). The annular dark-field (ADF) images and bright field images in Figure 2 illustrate the typical particle distribution in the carbon support. The size distribution analysis obtained from a number of recorded images is also shown. It can be observed that both Ru/C and Rh/C materials consist of active metal phase that is dispersed in the form of nanoparticles with the average size of 1.3 and 1.2 nm, respectively. Crystalline particle of this size cannot be detected on XRD patterns. Narrow peaks observed on the Rh/C diffractogram corresponding to cubic Rh suggest that there is a small amount of larger nanoparticles present in the material that were not observed under STEM analysis. The Pd/C catalyst on the other hand consists of nanoparticles with an average size of 2.2 nm. They are not evenly dispersed across the carbon support – instead they form large aggregates. XRD pattern reveals that in addition to metallic Pd phase, PdO is also present in the material. Pt/C contains nanoparticles with a similar average particle size (2.3 nm, close to the 2.6 nm value reported by the supplier) and are evenly dispersed in the high-surface area substrate. SEM, STEM and XRD results illustrate the differences between the chosen commercial materials – that is various types of carbon support morphologies, different particle sizes and distribution.

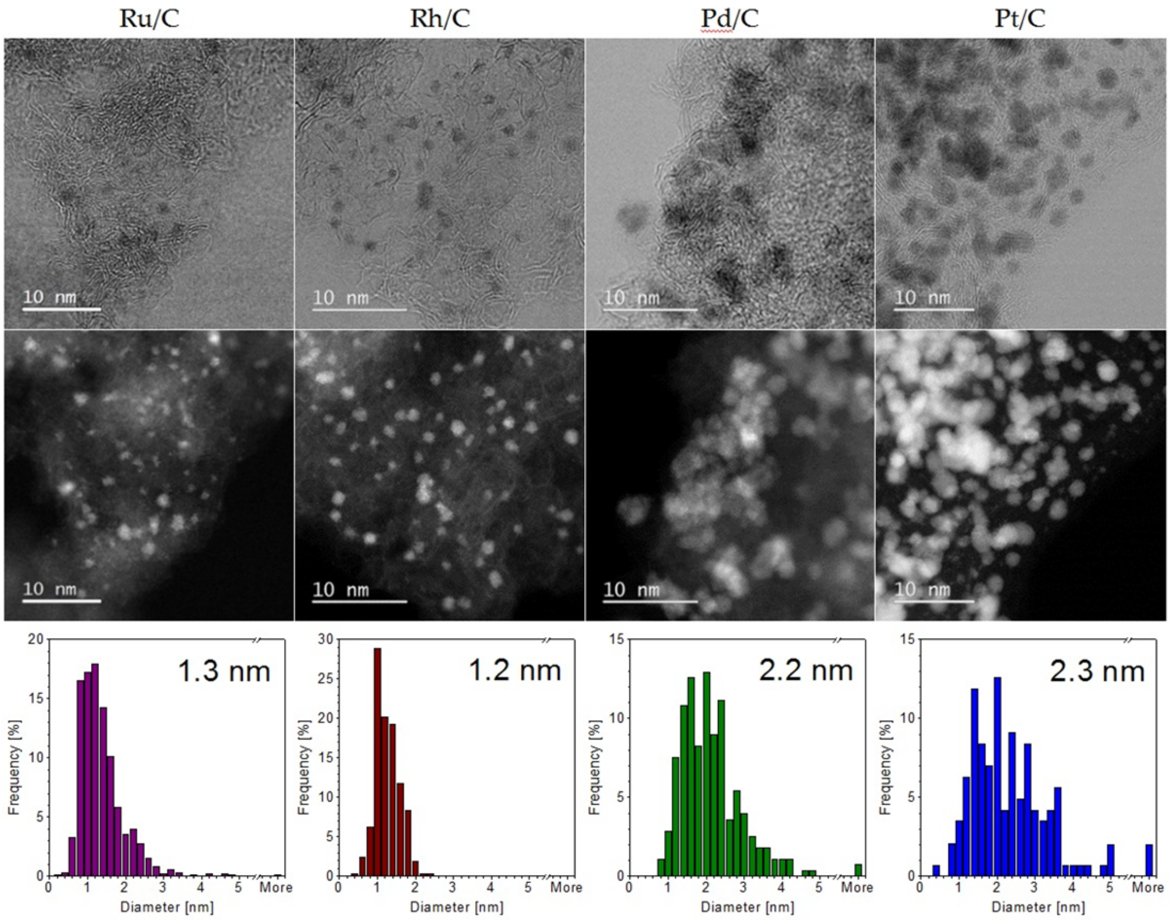

Figure 2. Representative images of the commercial PGM/C materials (PGM = Ru, Rh, Pd, Pt) acquired by STEM in bright-field (top row) and annular dark-field mode (middle row). Size distribution analyses obtained from STEM imaging (bottom row). The average sizes of the particles (diameters) are given in the size distribution diagrams.

One of the allures of single atom catalysis as an alternative to supported nanoparticles is increasing the dispersion of the expensive metal. Dispersion is the ratio between the number of surface atoms and the total amount of metal atoms and it represents the fraction of metal that is exposed to the reactants and may act catalytically. For Pt/C material, which is used as an electrocatalyst, the surface area can be determined electrochemically. Depending on the pre-treatment the electrochemical surface area (ESA) of this commercial sample varies from approximately 75 to 100 m^2 g^{-1}_{Pt} [24, 25] which corresponds to approximately 30 to 40 % dispersion. A commercial Pt/C with average particle size 4.8 nm and ESA 56 m^2 g^{-1}_{Pt} has only about 20 % of its atoms at the surface while by choosing a catalyst with smaller particles (1 nm, 116 m^2 g^{-1}_{Pt}) the dispersion increases to about 50 %. This illustrates that the smaller the nanoparticles, the larger the portion of surface exposed atoms. Although it may seem a good strategy to aim for 100 % dispersion when trying to reduce Pt use, increasing the dispersion by a factor of 2 by dispersing Pt atomically instead of as 1 nm-sized particles is completely irrelevant if the atomic species cannot catalyse the reaction. Increasing the dispersion by atomic dispersion should therefore not be the guiding principle in designing better catalysts. This of course does not preclude the possibility of some atomic Pt species acting as catalytically active centres for ORR or even achieving higher mass-specific activity. It merely illustrates that the logical argument that is so often used (namely of

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equating larger dispersion with better metal efficiency) is flawed since it inherently makes unjustified assumptions when comparing nanoparticles and supported atoms. It presumes unmodified (or increased) activity of active centres despite the change of the active centre structure and unmodified (or increased) number of active centres per number of surface-exposed atoms.

While the images in Figure 2 only show metallic nanoparticles, higher magnification images in Figure 3 reveal that all four investigated commercial catalysts contain significant numbers of atomically dispersed metal species. Several different areas of each material were investigated and single atoms were consistently found in the materials. For single atom imaging, the ADF detector is preferred over the bright field detector because it can accept large-angle scattered electrons [26-28], especially in carbon substrate because of the large Z-contrast between carbon (Z = 6) and PGM atoms (Z = 44, 45, 46 and 78 for Ru, Rh, Pd and Pt, respectively). However the observed contrast strongly depends on substrate thickness. To visualize atomic species, areas of the carbon substrates were chosen at the edges of carbon particles or at thin areas of the carbon particles.

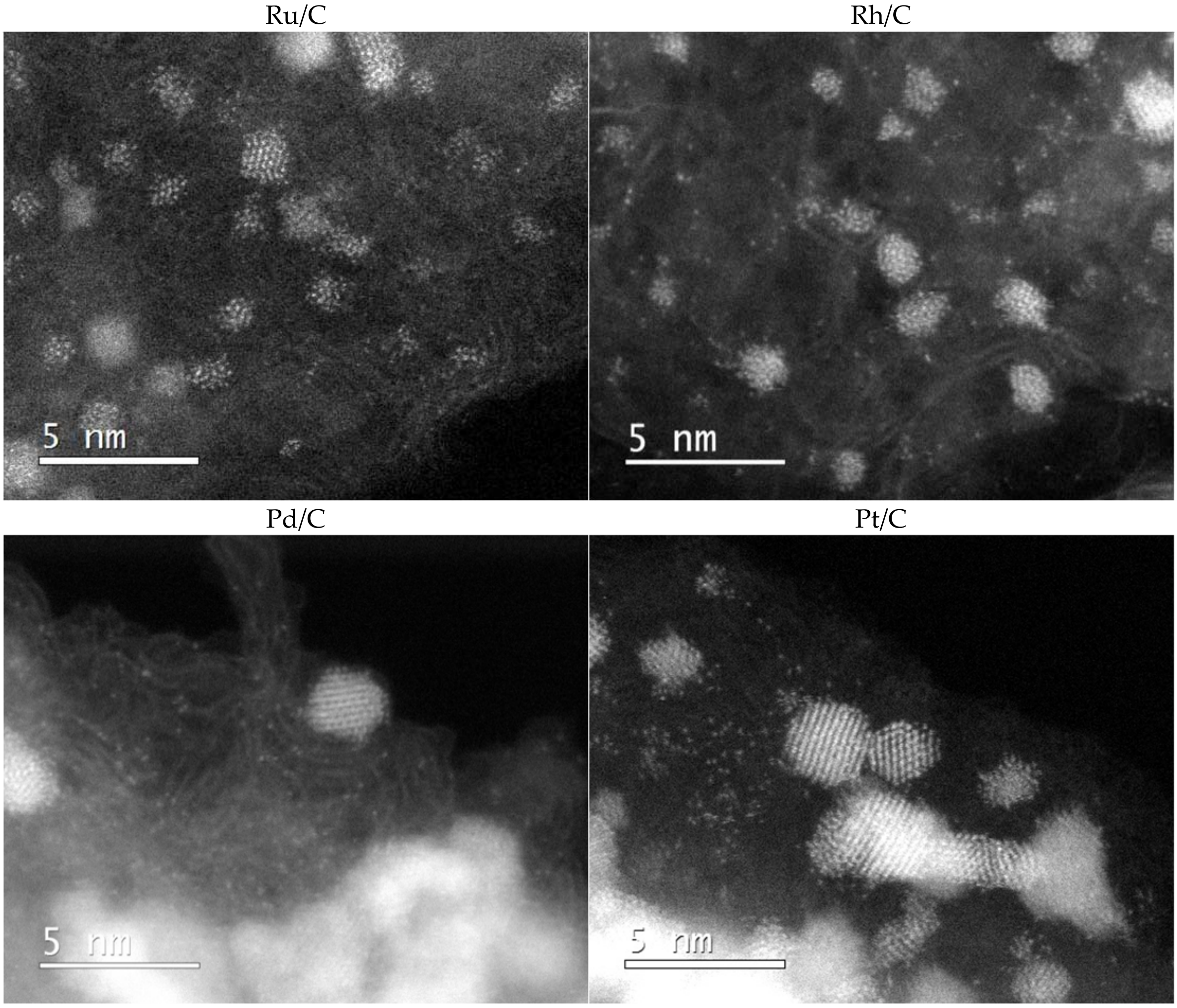

Figure 3. AC-STEM images of PGM/C catalysts (PGM = Ru, Rh, Pd, Pt) recorded in annular dark-field mode.

It is well known that irradiation by the electron beam in STEM can cause structural damage to clusters and nanoparticles due to electron dose accumulation [29]. This may result in sputtering of single atoms or even complete breakdown of smaller clusters into atomic species [29]. Several precautions were taken during imaging in order to avoid unintentional sputtering. A relatively low-voltage of 80 keV and a beam current of ~14.5 pA was used. Additionally, settings and focus were adjusted outside of the area intended for investigation before the image was recorded on that area that had previously not been exposed to the beam. Single atoms were observed even at

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relatively low magnification (around $5 \cdot 10^6$) where electron dosage per unit area was very low. Moreover, single atomic species were observed not only in the vicinity of nanoparticles (where they would be expected if they were caused by sputtering), but also in areas of the carbon material that were several nanometres away from the nearest metal clusters. All this confirms that the majority of the observed atoms were indeed characteristic for the material and were not sputtered from nanoparticles by electron beam irradiation.

These STEM observations clearly reveal that single atoms are present alongside nanoparticles in commercial PGM/C catalysts with different types of metals (Pt, Pd, Ru, Rh), loadings (5 wt.% or 46 wt.%), particle sizes (1.3 to 2.2 nm) and carbon supports (high-surface are carbon and large polydisperse carbon particles). If the investigated four materials can be thought of as typical and representative commercial catalysts, it can be presumed that single atoms may be ubiquitously present alongside nanoparticles in many other commercial and laboratory-synthesized carbon-supported metal catalysts. Surprisingly, such findings are not commonly reported. Some reports within the single-atoms community that show nanoparticles and single atoms in the same material relate the atomic distribution to positive effects on observed catalytic activity [19, 30, 31]. Simple wet chemical deposition techniques that have been proven successful for preparing single atoms [11] are also widely used for depositing nanoparticle-based catalysts. Therefore it stands to reason that substantial concentrations of single atoms may be present in many carbon-supported materials, especially when high-surface area carbons or heteroatom-doped carbons are used as substrates. However, even when such materials are investigated with sub-ångström resolution STEM, individual atoms may be overlooked if they are not investigated at high-enough magnifications or under optimal conditions (annular dark field mode instead of bright field). Large particles of carbon support may also cause a high background signal upon which individual atoms may not be notable. And most importantly – even when individual supported atoms are detected, they may be considered to be caused by beam irradiation damage or just simply not relevant for the conducted research and therefore not shown or remarked on in the publications [32].

In addition to the commercial materials discussed in this work, our experience with STEM analysis of carbon-supported catalysts has suggest that atomic species are indeed a common companion to metal nanoparticles. For example, we detected single atoms in a commercial PtRu/C catalyst [33] and commercial Pt–SnO_2/C catalyst [34], on a high-surface area nitrogen-doped carbon alongside Pt nanoparticles [25] and on a graphite rod after electrochemical deposition of Ag [35].

This visual confirmation of significant amounts of single atoms alongside nanoparticles in commercial PGM/C catalysts poses a number of questions regarding their nature and behaviour. An important information would be a quantitative estimation of the amount of single atoms with respect to the nanoparticles. For model catalysts with flat surface this estimation can be made on the basis of STEM images [36], but for materials with large three-dimensional carbon particles such quantifications would be extremely unreliable. Another dilemma would be what role these atomic species play in the overall catalytic behaviour of the material. Based on the number of reportedly active single atoms it is conceivable that in some cases, the atomic species may be catalytically active in addition to or instead of the active sites on the nanoparticles. However, as discussed above, due to fundamentally different natures of atomic and metallic species, in majority of cases atomic species cannot be expected to display similar activity for a given reaction than clusters or nanoparticles. They may, however, strongly influence the properties of the material in other ways. For example, one of the mechanisms of supported catalyst deactivation is Ostwald ripening, that is transport of metal from smaller to larger nanoparticles driven by higher thermodynamic stability of larger nanoparticles that can occur either through liquid or gas phase or across the surface of the substrate, i.e. as single atoms [37]. Concentration and type of anchoring sites for single atoms may have an important role during catalyst synthesis (nucleation, sintering during annealing) and under reaction conditions [36] or can re-adsorb metal atoms leached from the nanoparticles [25]. Another important issue is the stability of isolated metal species under reaction conditions. Questions like this about the role of single atoms in traditional nanoparticle-based materials have thus not yet been introduced into the growing field of single atom catalysis. It would however be highly beneficial to increase our

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understanding of their nature and behaviour under catalytic conditions. It may be imagined that atomic species are ubiquitously present also in other commercial M/C catalysts and laboratory-prepared materials that follow similar preparation methods (eg. wet deposition followed by annealing). While the concentration of single atoms most likely varies significantly with different supports, metals and preparation techniques, the largest amounts may be expected for metals with small particle size, dispersed on high-surface area carbons with heteroatom doping [15, 16].

The first step towards addressing all the raised questions is to understand the nature of the atomic species, i.e. is their electronic structure and type of bonding with the support. Figure 6 shows single atoms in a Pd/C material at high magnification on a very thin edge of carbon particles that only consist of several entangled graphene sheets. The image suggests possible anchoring sites for metal atoms in the carbon material. It can be observed that some Pd atoms tend to appear alongside bright lines that represent edges of graphene sheets (oval shapes in Figure 6) while it is also possible to find atoms that appear to be imbedded in the plane of graphene sheet (square in Figure 6). This is in accordance with literature that reports anchoring sites for metal atoms at defect sites (such as vacancies) and alongside graphene edges [31, 38].

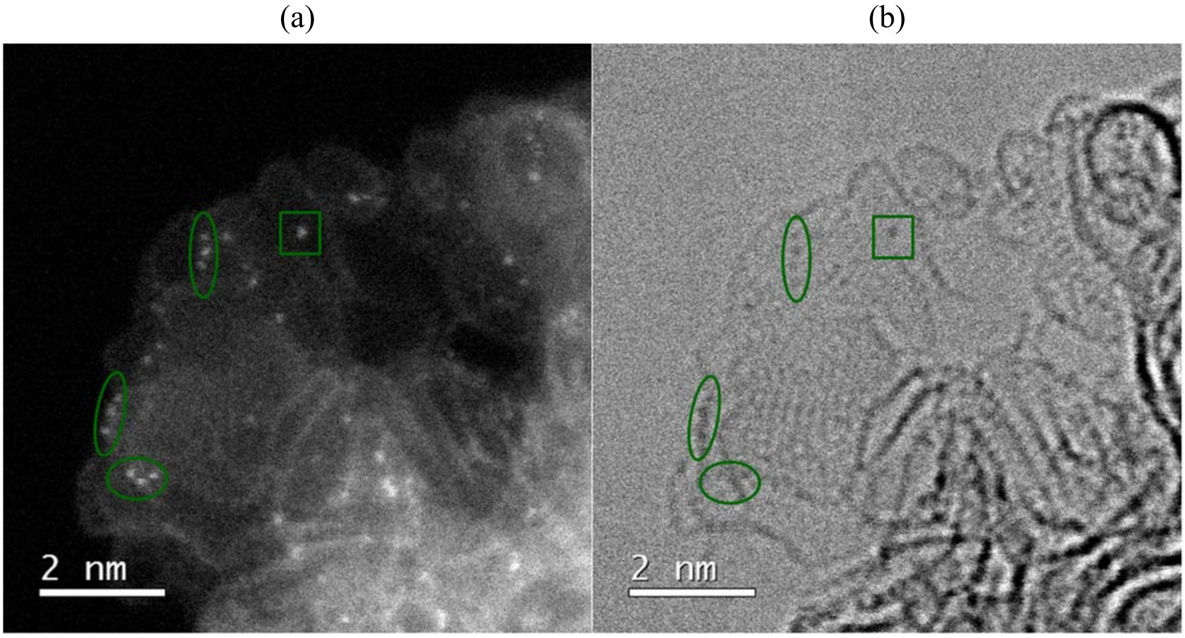

Figure 6. Single atoms of Pd in Pd/C catalyst in (a) annular dark-field and (b) bright-field mode.

3. Materials and Methods

Four commercially available PGM/C materials were investigated, namely Ru/C (5 wt.% Ru, Sigma-Aldrich, 206180, powder), Rh/C (5 wt% Rh, Riogen, 0127-CRhA05, pallets), Pd/C (Sigma-Aldrich, 5 wt.%, 520837, powder) and Pt/C (Tanaka Kikinzoku Kogyo, 46 wt.%, TEC10E50E, powder). The Rh/C material was supplied in the form of pellets and was milled and sieved before further characterization. The other catalysts were supplied in powder form. Their morphology was investigated under Zeiss field emission scanning electron microscope FE-SEM SUPRA 35 VP (Carl Zeiss). X-ray diffractogram (XRD) patterns of the catalysts were recorded on flat disc-like sample holder with a X-ray powder diffractometer PANalytical X'Pert PRO MPD with radiation wavelength CuKα1 = 1.5406. The diffractograms were recorded with 0.04° resolution and 1 s signal integration time in the 2Θ range from 10° to 70°. The materials were also characterized with an atomic resolution aberration corrected scanning transmission electron microscope ARM 200 CF (Jeol) working at 80 kV.

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4. Conclusions

Single atoms were observed in some commonly used commercial nanoparticle-based catalysts with PGM metals on carbon support. Although sub-ångström resolution AC-STEM is becoming progressively more accessible, the ubiquitous presence of single atoms alongside nanoparticles on carbon supports has not yet been widely recognized let alone taken into account in catalyst evaluation. We believe that the present results strongly suggest that any thorough study of catalytic activity of given materials needs to address the presence of single atoms. In that respect, the new understanding about atomically dispersed metals can contribute greatly not only to developing new types of active catalysts with low metal loadings, but also to the understanding of the traditional nanoparticle-based supported catalyst. Without that the possible (significant) contribution of the so-far "invisible" single atoms and atomic clusters will remain overlooked.

Author Contributions: U.P. conceptualized the idea for the manuscript and prepared the original draft. F.R.Z. recorded AC-STEM images, performed size-distribution analysis and reviewed the manuscript. M.B. supervised the project and revived the manuscript. M.G. supervised the project and reviewed the manuscript.

Funding: This research was funded by the Slovenian Research Agency through research programme P2-0393 and the young researcher programme (U. Petek). Part of the work was carried out within the NATO SfP Project EAP.SFPP 984925 – "DURAPEM".

Acknowledgments: XRDs were recorded by E. Kranjc (Department of Inorganic Chemistry and Technology, National Institute of Chemistry, Slovenia). The authors also thank A. Bjelić and M. Grilc (Laboratory of Catalysis and Chemical Reaction Engineering, National Institute of Chemistry, Slovenia) for providing some of the analysed materials.

Conflicts of Interest: The authors declare no conflict of interest.

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