



Journal Name

COMMUNICATION

Lithium and Boron as Interstitial Palladium Dopants for Catalytic Partial Hydrogenation of Acetylene

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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It is demonstrated that light elements, including lithium and boron atoms, can take residence in the octahedral (interstitial) site of the Pd lattice by modifying the electronic properties of the metal nanoparticle, and hence the adsorptive strength of a reactant. The blocking of the sub-surface sites to H in the modified materials results in significantly higher selectivity for the partial catalytic hydrogenation of acetylene to ethylene.

Ethylene polymerisation is an important industrial process for the synthesis of valuable polyethylene. The process requires as low as possible acetylene concentration in the feedstream, as traces of C₂H₂ and higher alkynes and C₂H₆ contaminants from the ethylene source can poison the catalyst used. Selective partial acetylene hydrogenation is therefore vital to increase ethylene concentration at the expense of acetylene.^{1,2} This is commonly conducted through the use of supported palladium based catalysts. However, they require modification to minimize the total hydrogenation to ethane. Typically, the Pd metal modifications can be achieved in three main ways, a controlled poisoning of the Pd surface with dopants such as Pb (cf. Lindlar's catalyst), P or S containing ligands,^{3,4} alloying with other metal (i.e. PdGa, PdSn)^{5,6} or the use of a core-shell structure.⁷ However, as far as we are aware, there is no work to use sub-surface modification of Pd lattice for this reaction, which may offer catalysis without the coverage of promotor species thereby reducing available active surface sites.

Palladium hydride is perhaps the most common and wildly known interstitial (or subsurface) species.^{8–10} In a hydrogen rich atmosphere at ambient pressure, up to 70–75% of the octahedral lattice holes of palladium are occupied by hydrogen.^{11,12} Teschner *et al.*¹⁰ reported that under gas-phase hydrogenation conditions over unmodified palladium, reactive

surface carbon fragments could penetrate into the Pd lattice, forming transient interstitial carbon (Pd^{-int}C). Previous work published by Tsang and co-workers has detailed a method for the synthesis of a stable interstitial carbon atom in Pd *via* glucose encapsulation of a palladium nanoparticle, followed by carbon atom penetration into Pd lattice at elevated temperature.^{13,14} Palladium interstitially modified with boron atoms (Pd^{-int}B) can also be synthesised through a number of approaches. Pd foil can be modified with boron by arc welding, and supported Pd nanoparticles can be modified *via* a borane compound treatment.^{15,16} In contrast, there is no reported method for the synthesis of palladium interstitially modified with lithium (Pd^{-int}Li) in literature. On the other hand, bulk palladium-lithium substitutional (i.e. not interstitial) alloys (e.g. Pd₇Li) have been reported as a hydrogen absorption material. It has been reported that bulk Pd substituted with small amounts of Li exhibits a small metal lattice contraction, as can be accounted by their difference in atomic size according to Vegard's law.¹⁷ These alloys have only been prepared on a bulk scale through high temperature annealing.^{18–20}

Here, we report a simple solid phase synthesis of carbon supported Pd^{-int}Li nanoparticles, and also explore the use of this subsurface modification technique by small atoms (Pd^{-int}Li and Pd^{-int}B) as a new approach towards altering the catalytic properties of Pd in the partial hydrogenation of acetylene. This is a first communication note focusing mainly on the fundamental subsurface modification of Pd by Li and B for this reaction without catalyst/condition optimizations or comparison to commercial catalysts.

Similar to our previously reported method for Pd^{-int}B synthesis using a reactive soluble boron compound such as BH₃.THF,¹⁶ treating Pd/C with reactive soluble lithium compound, BuLi in THF was found to be effective to prepare Pd^{-int}Li. However, we devised a more simple solvent-free route for the preparation of Pd^{-int}Li. The method required the physical grinding of 5% Pd/C with an excess of lithium acetate. This powder mixture was then heated to 250°C under nitrogen for 1 hour to form the supported Pd^{-int}Li material before

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† Electronic Supplementary Information (ESI) is available: See DOI: 10.1039/x0xx00000x

washing with copious water and ethanol to remove surface impurities (e.g. LiOH, Li₂CO₃).

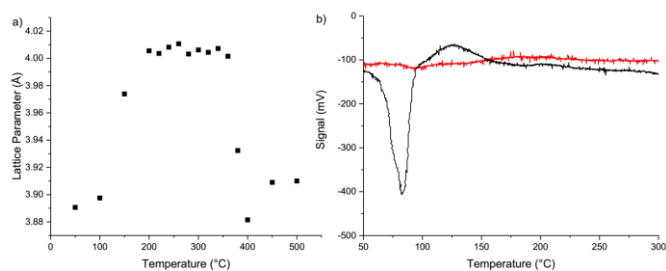


Figure 1: a) temperature dependent lattice expansion of palladium with Li under He evaluated by in-situ XRD; b) TPR of Pd/C (black) and Pd-intLi/C (red) with and without decomposition peak of Pd hydride at ~80°C in H₂.

Pd-intB was prepared as previously reported.¹⁶ All prepared catalysts in this paper were set at a nominal 5% Pd loading. Full details of the syntheses can be found in the experimental section (ESI†). At present, it is a significant challenge to estimate the content of the interstitial(s) (percent of octahedral holes filling) in our supported Pd nanoparticle system. First, without using support, the Pd nanoparticles can subject to rapid aggregation. Different particle sizes used may have different uptake values of the interstitial atoms. Secondly, the high surface carbon support is shown to take up the interstitials (by EDX). Thirdly, the surface of Pd nanoparticles will also be covered with the doper atoms. The samples are washed as part of the synthesis, otherwise boron oxide, lithium oxide/carbonate and other species are shown to be present in XRD. However, extensive washing is avoided due to the risk of leaching of the interstitial dopant out of the lattice. ICP/EDX or other analysis cannot give a clear indication on the degree of Li, B, or C content.

As a result, a fixed but large excess of the dopant was used to ensure some degree of octahedral holes filling of the palladium nanoparticles. Initial verification of the successful insertion of Li came from powder X-ray diffraction (PXRD) which showed a significant expansion of the Pd lattice from $a_0 = 3.89 \text{ Å}$ to 4.01 Å . This lattice expansion was not seen from the formation of a substitutional PdLi alloy, nor was it attributable to thermal expansion.²¹ This expansion was also taken as verification of light element (H, C, B) insertion in the literature.^{12–16,22,23} In order to estimate the degree of lithium filling of the interstitial sites within the palladium lattice, synchrotron X-rays were utilized for Pair Distribution Function method (PDF) analysis at the I15 Beamline, Diamond Light Source. According to our structural model, built using the PDFgui software, the best fit was found to be 13.7% of the octahedral sites filled with lithium (Fig. S1). There may have a degree of error in estimation of the filling by PDF however, it is in good agreement with a theoretical study by Gelatt Jr. *et al.* who proposed that there would be a 0.1 electron transfer from Li to Pd in Pd-intLi, which would equivalent to approximately 10% filling.²⁴ In addition, this is similar to the degree of interstitial octahedral hole filling seen for Pd-intB (15%)¹³ and Pd-intC (20%).¹⁶

Tracking the heating step of the synthesis of Pd-intLi by *in-situ* XRD (Fig. 1a), it is clear that lattice parameter changes with temperature

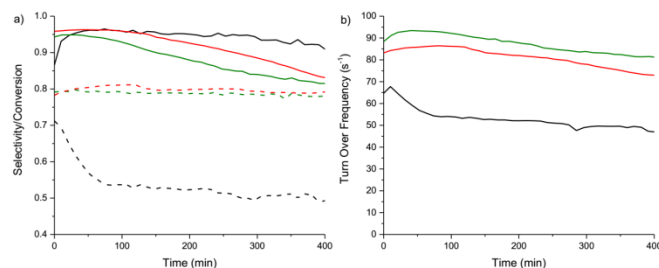


Figure 2: a) The relative conversion of acetylene (bolded lines) and selectivity towards ethylene (dashed lines) for Pd/C (black), Pd-intB/C (green) and Pd-intLi/C (red) for 1:1 C₂H₂: H₂ at 75°C over 5 mg catalyst; b) The turnover frequency (TOF) in terms of atoms of acetylene converted to ethylene per second, corrected for metal surface areas (measured by CO chemisorption).

in helium. The Pd lattice expansion appears to be a thermally activated process, where an elevated temperature is required to decompose lithium acetate and drive Li into the Pd lattice. However, the meta-stable Pd-intLi/C will decompose at above 350°C, leading to a return of the Pd lattice parameter to 3.89 Å. Under a flow of air, the lattice of Pd-intLi contracted from 3.99 Å to 3.90 Å at lower temperature range of 150 - 200°C, suggesting a favourable oxidative decomposition of Pd-intLi. The Li inclusion apparently shows a higher thermal stability in air than Pd-intC (approx. 150°C)^{13,14} but lower than Pd-intB (250°C).¹⁶ However, the material is still kinetically stable, and can be handled in air at room temperature (Fig. S2). Further verification for the successful filling of Li into interstitial Pd sites is to observe the absence of the typical β -hydride desorption peak from temperature programmed reduction (Fig. 1b). This peak arises at 75°C in Pd when H intercalated into the lattice at room temperature in an atmosphere of H₂ diffuses out from the lattice.¹⁴ The lack of this β -hydride peak indicates that the interstitial site is already occupied by the light element due to stronger interaction (i.e. Li), denying access by hydrogen.

In this work, dilute acetylene (5% v/v) and hydrogen (5% v/v) in N₂ with a total flow rate of 50 ml min⁻¹ was initial used in a fixed-bed reactor at 75°C over Pd-intLi/C in comparison with Pd-intB/C and Pd/C. Industrial more relevant gas mixture i.e. acetylene/H₂ in excess ethylene was also studied for comparison (ESI). According to the lattice parameters boron and lithium dopants measured above, the low reaction temperature used for acetylene hydrogenation should not cause their extrusions from the Pd lattice. The gaseous products (only ethylene and ethane were detected) were analysed by GC. Fig. 2(a) shows the relative selectivity to ethylene (dashed lines) and conversion of acetylene (solid lines) for the three catalysts over six and a half hours of continuous flow. All of them exhibit some degree of deactivation over this time period due to the build-up of small quantity of polymeric materials within carbon porous structure, which can be reduced at a higher operational temperature.^{10,25} The time-acetylene conversion profile over Pd/C shows a short induction before reaching the stable >90% conversion plateau, followed by a gradual decline in conversion, while Pd-intLi/C and Pd-intB/C do not show induction but are associated with a more rapid decline in conversion. It is thought

that a greater surface area of Pd/C catalyst with a higher degree of Pd metal exposure (Table S1) would require longer time for surface PdO reduction and for the build-up of equivalent 'carbon' coverage on the porous structure.

It is very interesting to note that both interstitially modified catalysts give consistently higher and stable ethylene selectivity of over 80%, but the unmodified Pd maintains an ethylene selectivity of only 50% during the steady period. It may not be possible however, to conclude with certainty that the difference in selectivity between the Pd^{int}B/C and Pd^{int}Li/C catalysts is significant. However, the prime reason for the large increase in selectivity towards ethylene at the expense of ethane (the total hydrogenation product) during this catalytic reaction over the two interstitial filled Pd catalysts, as compared to unmodified Pd, is probably due to the blocking of the unselective sub-surface hydrogen^{10,16} from the Pd interstitial sites, which otherwise causes over-hydrogenation.^{1,14,26}

Similarly, when the three catalysts were tested under industrially relevant conditions (ESI) of 1% acetylene and 1.1% hydrogen balanced with ethylene (97.9%), the obtained ethane concentration at the equivalent acetylene conversion over Pd was also significantly higher than the two interstitial samples (Fig. S3). This is economically inefficient and clearly suggests the blockage of unselective H from interstitial site by the dopant (B and Li) is the main cause of the reduction of over-hydrogenation observed in this reaction.

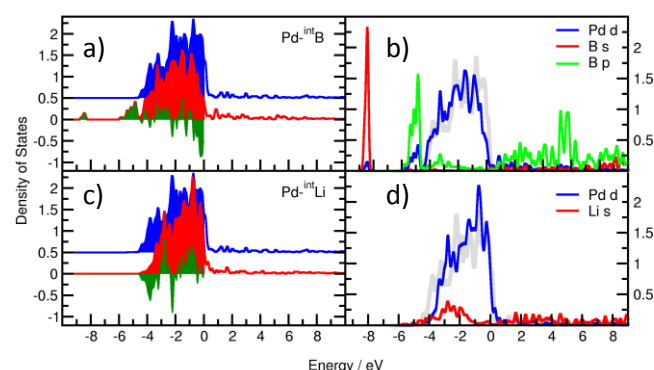


Figure 3: Density of states plots for the a) Pd^{int}B and c) Pd^{int}Li. The blue curve is the DOS of unmodified palladium, red is the DOS of the doped system, green is the Δ between the two at various energies. b) and d) show the relative positions of the Pd 3d, B sp and Li s orbitals for both systems. Grey here represents the Pd d band for the clean surface.

By normalizing the rate of each three catalysts for acetylene conversion to ethylene per Pd metal site (evaluated by CO chemisorption in Table S1) it can be seen that the unmodified Pd/C indeed gives the lowest TOF for C₂H₂ to C₂H₄ despite the highest C₂H₂ conversion (Fig. 2b). This is presumably due to a significantly larger amount of over-hydrogenation of C₂H₄ to C₂H₆.

DFT was used in order to understand the theoretical contribution of the interstitial dopant to the electronics of a palladium nanoparticle. A palladium fcc (111) surface was constructed with a bulk lattice parameter of $a = 3.89$ Å, consisting of four atomic layers with a vacuum gap of 12 Å. The bottom two layers were frozen and

the top layers allowed to relax in position (see Fig. S4). Focusing on the electronic structure of this model, with a particular interest on the influence of our dopant and its interaction with the transition metal, the density of states for each system was projected (Fig. 3).

Fig. 3 a,c show that although the overall DOS integral shows ($\Sigma +ve$ and $-ve$ green area = 0) little or no alteration for both the model materials, the distribution of local electron density at different energies is the key difference. Boron modification has lowered the electron density near the Fermi level ($E_f = 0$) while lithium modification has clearly increased it. Interstitial B shows a marked broadening (the d-band width has increased by 0.1 eV) and lowering (d-band centre has dropped by 0.4 eV) of the average d-band centre, suggesting a strong overlap of the B sp and Pd d bands (Fig. 3). Most of the electron redistribution comes from the 'effective coordination' covalent overlap of the orbitals, rather than addition or subtraction of electrons from this dopant into the Pd d-band. The overlap with the tail of the d-band counteracts the energy cost of expanding the palladium lattice.⁶ In contrast, lithium (only s electrons) has no p-orbital to interact and stabilise the transition metal d-orbitals, but the charge transfer from Li to Pd causes a clear narrowing (d-band width -0.2 eV) and raising of the d-band (d-band centre $+0.2$ eV) (Table S2). The stabilisation of the lithium within the lattice is clearly not coming from an orbital overlap, but rather the charge-transfer from lithium to the palladium host.

Considering the lattice expansion and charge transfer in the case of Li separately, the majority of the narrowing and broadening of Pd d-band is a result of the increasing outermost Pd–Pd bond distances, not the electron transfer from Li (Fig. S5). This lattice expansion is caused by the interstitial location of Li; despite the overall contribution of lithium's orbitals being relatively minor. Indeed, it is possible to view the Pd^{int}Li system as having 'undercoordinated' lithium within the metal lattice.

It is thus believed that the interstitial boron pulls electron density from the Fermi level of palladium resulting in a lower and broader band due to the strong covalent interaction between the B sp band and Pd d band.¹⁶ Indeed, a computational study by Yang *et al.* also found boron modification significantly weakens acetylene adsorption onto a palladium surface, consistent with reduced electron density at the Fermi level.²⁷ For the lithium case, it is likely there is a small electron transfer to the palladium, as theorised by Gelatt Jr., having the effect of increasing electron density at the Fermi level (Fig. 3). This will give the opposite effect to the boron, by chemisorbing the acetylene/ethylene molecule more strongly to the surface by electron back donation. According to kinetic studies stronger adsorption of unsaturated alkynes and alkenes over modified Pd catalysts gives lower activity due to a degree of poisoning to active sites (Sabatier principle).^{14,16} This effect accounts for the reduction in hydrogenation TOF for Pd^{int}Li compared to the Pd^{int}B catalyst (Fig. 2b).²⁴

In summary, this is the first report on the synthesis of interstitial lithium in palladium nanoparticles, outside of hints from electrochemistry.^{28,29} The material appears to be air and moisture stable at room temperature. The subsurface modification of

palladium by lithium or boron shows a dramatic improvement in ethylene selectivity from the partial acetylene hydrogenation mainly due to blocking the H from accessing the interstitial sites for over-hydrogenation. Thus, this method of modification offers a clear alternative method to well-established surface poisoning or alloying approaches in the partial hydrogenation of acetylene.^{13,16} The apparent increase in electron density at the Pd surface promoted by the subsurface Li can enhance adsorption strength of acetylene due to electron back donation to π^* of the molecule, which lead to its longer residence time on the catalyst surface. However, the subsurface B appears to reduce the Fermi level electron density of the metal surface, which ~~gaveto give~~ weaker adsorption, but sustaining an overall faster hydrogenation rate. We propose the subtle difference in the influence of adsorption strength by using different interstitial atoms could be useful in catalytic hydrogenation reactions of more complex molecules in order to tune the activity and selectivity of the reactions.

Notes and References

We thank Johnson Matthey (JM) for funding this work and ITE acknowledges JM for the DPhil studentship. We are indebted to Dr Pilar Gomez-Jimenez of JM Technology Centre, Sonning Common for her catalyst testing under the industrial acetylene/ ethylene/ hydrogen regime.

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