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New environmentally friendly catalysts containing Pd–interstitial carbon made from Pd–glucose precursors for ultraselective hydrogenations in the liquid phase†

Chun Wong Aaron Chan,[a] Yaling Xie,[a] Nick Cailuo,[a] Kai Man Kerry Yu,[a] James Cookson,[b] Peter Bishop[b] and Shik Chi Tsang*[a]

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We report a novel preparation of a Pd nanocatalyst modified with subsurface C *via* blending a glucose precursor at the molecular level: the catalyst is demonstrated for the first time to be stereoselective in the hydrogenation of alkynes to *cis*-alkenes in the liquid phase.

Selective conversion of organic compounds is a key transformation in industrial organic synthesis.[1] The use of stoichiometric chemical reagents such as $LiAlH_4$ and $NaBH_4$ generates a lot of inorganic wastes. This poses limitations from both economical and environmental viewpoints regarding product purification and waste management. The use of more efficient protocols employing non-toxic and non-waste producing reagents, for example, molecular hydrogen for chemical reduction is more preferable. The employment of easily separable heterogeneous catalytic systems must also be considered in the development of novel environmentally aware protocols.[2]

Catalytic hydrogenation of alkynes to alkenes represents one of the most important steps in chemical manufacture. It is established that solid catalysts containing Pd in the presence of hydrogen are suitable candidates, affording high alkene selectivity in the gas phase.[3] Recent work by Teschner *et al.* demonstrated that the formation of subsurface C in Pd during catalysis greatly promotes alkene selectivity.[4] However, interstitial subsurface carbon atoms were only formed under transient conditions at elevated temperatures under an atmosphere of reactive gas.[5] We sought to develop a stable Pd analogue, modified with subsurface carbon atoms for liquid phase hydrogenations, where the conversion of alkynes to alkenes is one of the key steps in fine chemicals catalysis. Here we show that glucose can act as a reducing and capping agent as well as the supporting matrix to stabilise small Pd nanoparticles. Upon heat treatment, the glucose derived carbon atoms encapsulating Pd particles can also take residence on the octahedral interstitial sites of the metal, hence blocking the formation of β-hydride under hydrogen. We show that the alkyne reductions are stereoselective, occurring *via syn* addition to give mainly *cis*-alkenes by this new class of stable 'Pd–C' catalysts.

The aforementioned synthesis of the final Pd catalyst is described in the experimental section (ESI†). Fig. 1 shows the transmission electron micrographs (TEM) used to verify the carbon encapsulation on Pd at pH 10. The Pd particles are clearly seen inside the amorphous carbon derived from glucose. Furthermore, they appear to be dense and form clusters. The mean particle size was found to be 6.0 nm (±1.9 nm, number of particles = 37) with the mode at 5 nm. Energy dispersive X-ray analysis (EDX) confirmed that the dense clusters are rich in Pd.

Calculation of ⟨111⟩ peak broadening from powder X-ray diffraction (PXRD) confirms with the size obtained from TEM. Analysis of higher angle peaks for samples treated at 400 °C in N_2 appears to shift to lower values compared to pure Pd of comparable size as well as our as-synthesised sample without heat treatment (Table 1). This is consistent with previous reports by Zlemecki and Jones that the lattice parameter, a_0, of bulk Pd with carbon occupying interstitial octahedral sites has increased to 0.3995 nm.[5] This represents carbon modified palladium with the formula $Pd_{0.85}C_{0.15}$ (independent of size) where carbon saturation is reached at 15%. However, when treated with

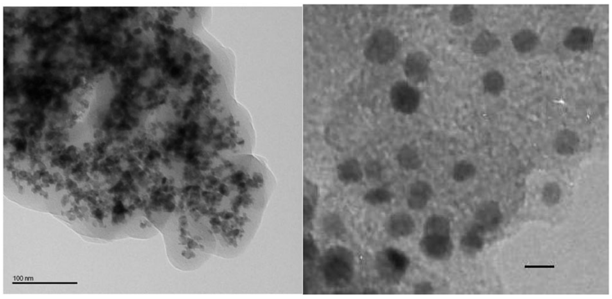

Fig. 1 TEM of (a) glucose derived carbon embedding 5–6 nm Pd nanoparticles after treatment at 400 °C, scale bar 100 nm (left), (b) HRTEM of the same sample (right), scale bar 5 nm.

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[a] *Wolfson Catalysis Centre, Department of Chemistry, University of Oxford, Oxford, OX1 3QR, UK. E-mail: edman.tsang@chem.ox.ac.uk*
[b] *Johnson Matthey Technology Centre, Blount's Court Road, Sonning Common, Reading, RG4 7NH, UK*

† Electronic supplementary information (ESI) available: Synthesis of glucose encapsulated Pd, effect of pH, FTIR, TGA, PXRD, ICP, catalyst testing and reaction modelling. See DOI: 10.1039/c1cc12681d

Table 1 Lattice parameter of Pd nanoparticles

Pd glucose catalyst	Lattice a_0	Approx. C atom %
As-synthesised	0.3923(4)	4.7
Treatment at 400 °C N_2	0.3994(3)	15.1
Treatment at 400 °C 5% H_2/N_2	0.3892(3)	0.3

H_2 at 400 °C the interstitial carbon atoms are more unstable than other surface carbons, which are then expelled from the metal lattice, also consistent with previous observations.[6]

Carbon diffusion into a metal lattice has been previously carried out by passing hydrocarbons (acetylene, ethylene) or CO over supported or unsupported metal particles at elevated temperatures in the gas phase. This process involves the deposition of a carbonaceous overlayer, followed by an activated diffusion of carbon atoms through the metal lattice.[7] A major drawback of this strategy is that the Pd–C phase only exists under the transient reaction conditions[4] and it is challenging to control the degree of carbon saturation (rate of carbon diffusion is size dependent) while maintaining the particle size without sintering at high temperature. In addition, coke or graphitic carbon can be formed on the metal surface which is difficult to remove thus reducing the rate of carbon diffusion and usefulness of the material for catalysis.[8] The fundamental difference of our synthesis is the blending of precursors at the molecular level before Pd–C is gradually reduced and assembled, thus facilitating the saturation of interstitial carbons. Fig. 2 shows the temperature programmed reduction (TPR) of a sample after treatment with and without interstitial carbon atoms. The evolution of H_2 (negative peak) at 70 °C represents the decomposition of β-hydride species from the Pd lattice where there are no interstitial carbon atoms. The carbon atoms clearly inhibit the formation of β-hydride species by competing for the same octahedral interstices.[5]

Stereoselective hydrogenations of 3-hexyn-1-ol and 2-butyn-1,4-diol were tested at Johnson Matthey Laboratory on the glucose carbonised catalyst and compared to a commercial Pd/C to explore their activity in low temperature, liquid phase conditions. The former catalyst was pretreated with a mixture of H_2O_2/NH_4OH as a mild oxidation step, as it was found necessary to partially remove the amorphous carbon on the surface to increase the rate of reaction. Fig. 3 shows typical H_2 uptakes of the two catalysts for 3-hexyn-1-ol. The glucose derived catalyst was markedly different from Pd/C, which maintained an impressive selectivity to alkene (91.9% to 3-hexen-1-ol). Only one equivalent of H_2 was taken up even after prolonged exposure to excess H_2 with complete alkyne conversion while two equivalents of H_2 were used over Pd/C which led to 100% alkane formation (Table 2). The new catalyst also showed high stability with no apparent deactivation or loss in selectivity upon repeated testing.

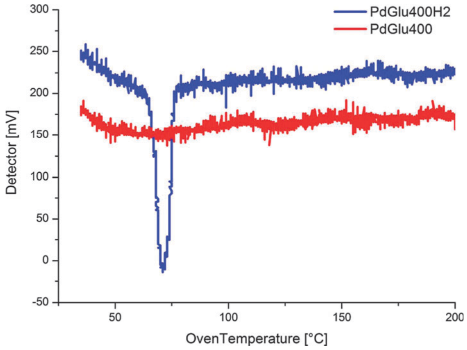

Fig. 2 TPR shows decomposition of the β-Pd–H phase on the catalyst with the interstitial carbon selectively removed (blue) and the blockage of β-hydride by the catalyst with the interstitial carbon (red).

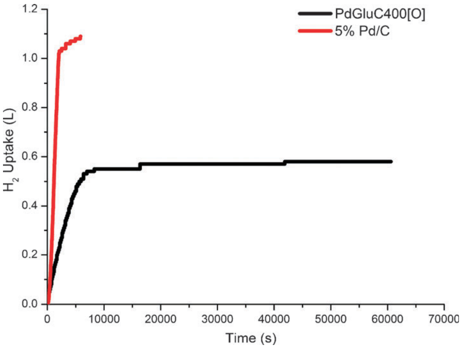

Fig. 3 H_2 uptakes of a glucose carbonised Pd catalyst modified with interstitial carbon (black) and commercial 5% Pd/C (red).

This result suggests that the adsorption strength of alkene on the metal surface over this new type of catalysts is relatively attenuated, thus allowing for high alkene selectivity in the liquid phase. Hydrogenation of the more polar 2-butyn-1,4-diol in a polar solvent can reduce the corresponding polar alkene diol adsorption from the surface as shown in the case of Pd/C. Nevertheless, this was still evident in enhancing the alkene diol selectivity from 72.5 to 97.2% (Table 2) using the glucose derived catalyst without a significant drop in alkene selectivity as the conversion increased along with the reaction time (ESI†). Stereoselective *syn* addition to unsaturated multiple bonds is well known to occur on the metal surface. However, excessive adsorption of alkenes or intermediates in the liquid phase can allow time for their isomerisation on surface to give *trans*-alkenes. It is noted from Table 2 that the reduction in alkene adsorption from alkyne hydrogenation over the glucose derived catalyst diminishes bond rearrangements, thus giving high selectivity to *cis*-alkenes.

Investigation of which carbon atom (surface, sub-surface interstitial or both) causes the attenuation of alkene adsorption was conducted. Stereoselective hydrogenation of 4-octyne was tested on the glucose carbonised catalysts with ($C_{Surface}$) and without H_2 pretreatment ($C_{Surface} + C_{Subsurface}$) and compared to commercial JM 5% Pd/C (Type 39). Kinetic reaction profiles were fitted based on the Langmuir–Hinshelwood kinetic model. The model assumes equilibrium establishment of hydrocarbons and weak H_2 adsorption.[9] Kinetic fittings to the experimental data were excellent with good reproducibility, reinforcing the validity of the model (Fig. 4 and ESI†). As seen from Fig. 4, there is strong adsorption of 4-octyne over alkene species (supported by the *K* constants derived from the model), resulting in almost exclusively 4-octene production until the 4-octyne is completely consumed in both cases when Pd contains $C_{Surface}$ or $C_{Surface} + C_{Subsurface}$. This is due to lower adsorption energy of the weaker adsorbate, in this case

Table 2 3-Hexyn-1-ol and 2 butyn-1,4-diol hydrogenations

Substrate	Catalyst	Conv./%	Sel/% alkene	*cis*/*trans*
3-Hexyn-1-ol[a]	5% Pd/C (Johnson Matthey)	100	0	0
3-Hexyn-1-ol[a]	PdGluC400[O]H_2O_2/NH_4OH[b]	100	91.9	10.8
2-Butyn-1,4-diol[c]	5% Pd/C (Johnson Matthey)	19.1	72.5	5.83
2-Butyn-1,4-diol[c]	PdGluC800[O]HNO_3[d]	35.4	97.2	18.45

[a] 100 mg catalyst, 50 mL, 0.5 M of 3-hexyn-1-ol in IPA, 3 bar H_2, 30 °C with stirring at 450 rpm, 20 h, 1,4-dioxane as standard, *cis* and *trans*-hexen-1-ol as alkene and 1-hexanol as alkane product. [b] Catalyst pretreated with an oxidant to increase activity. [c] 0.3 mg 5% Pd/C or 2 mg PdGluC800[O]HNO_3, 5 mL, 0.46 M of 2-butyn-1,4-diol in IPA, 10 bar H_2, 30 °C with stirring at 450 rpm, 1 h. *cis* and *trans* 2-butene-1,4-diol as alkene and butane-1,4-diol as alkane product with traces of 1-butanol, butyraldehyde, *E*,*Z*-butene-1,4-diol, crotyl alcohol and 2-hydroxytetrahydrofuran. [d] Catalyst pretreated with acid to increase activity.

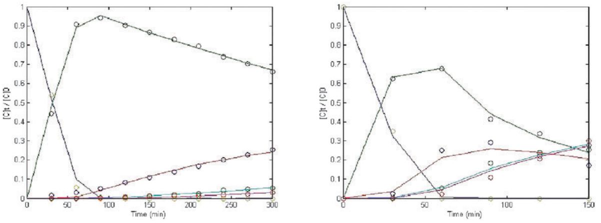

Fig. 4 Hydrogenation of 4-octyne in toluene over the glucose carbonised catalyst modified with interstitial carbon pretreated with H_2O_2/NH_4OH (left) and Pd/C (right). Conditions: 40 mg (left) and 10 mg (right) catalyst, 50 mL, 0.188 M 4-octyne in toluene, 1 bar H_2, 50 °C, *n*-heptane as standard (blue: 4-octyne; green: *cis*-4-octene, red: octane, brown: *trans*-4-octene, dark: 3-octene). Experimental data points with best fitted lines according to the model (ESI†) are given.

an alkene over an alkyne (see *K* values) such that the alkyne molecule forces the intermediate alkene molecule to desorb from the metal surface by taking up the adsorption site. The catalyst surface will favour re-adsorption of 4-octene after near complete alkyne consumption, only then will it catalyse isomerisation and over-hydrogenation (ESI†). On comparing the slopes of *cis*/*trans* isomerisation and over-hydrogenation between the two samples, the influence of subsurface carbon atoms was clearly evident in reducing these reaction rates, despite the fact that they have no contact with substrate molecules. Table 3 shows resolved rate ratios of *cis*-4-octene/full hydrogenations and *cis*-4-octene/isomerisations as compared to commercial Pd/C. It was found to be about 17.5 and 10.6 times less in full hydrogenations and isomerisations for the sample with $C_{Surface}$ + $C_{Subsurface}$ *cf.* 5% Pd/C, respectively. Selective removal of subsurface carbon atoms by H_2 giving only $C_{Surface}$ gave 8.9 and 3.2 times in reduction.

Thus, apart from surface carbon effects, this study shows that the interstitial carbon atoms in the subsurface of Pd play a significant role in reducing the rates of alkene intermediates from over-hydrogenation and isomerisation. They could be related to the inhibition of the β-Pd–H phase, which is known to alter the hydrogen atom equilibria. In addition, there is also electronic modification of Pd by the reduction of alkene adsorption energy. This is achieved by hybridisation of the Pd d-band with C s–p bands.[10,11] It is noted that despite the high ratios and atomic blending of carbon to Pd atoms, the octahedral occupancy is still limited to 15%, implying that the filling is driven by hybridisation.[5]

Our results are enforced by Teschner *et al.* who recently made a direct observation on the influence of subsurface carbon and hydrogen atoms in Pd for alkyne hydrogenation in the gas phase, by a new high pressure XPS technique.[4] As reported, the diffusion of C and H atoms from model reactions with the Pd lattice is dynamic, substrate dependent and transient. In contrast, at low temperatures in the liquid phase, the combination of kinetically stable trapped carbon atoms from our preparation, the solvent cage effect, stronger molecular adsorption, and molecule re-adsorption render the 'carbon effects' more significant than gas phase reactions. Here, we demonstrate that interstitial carbon atoms in the Pd subsurface created by our green synthesis route using glucose are indeed effective to catalyse the hydrogenation of alkynes to alkenes in the liquid phase. Nevertheless, this new class of catalysts could open up rational ways to tune adsorption with subsurface interstitials for ultraselective catalysis.

Table 3 Kinetic analysis of two catalysts for rate ratios

Rate ratio	PdGlu400[O][a]	PdGlu400[O]H_2[a]	JM Pd/C
k cis-4-Octene/ $\sum k$ Full hydrogenations	7.53(±0.49)	3.82(±0.53)	0.43(±0.14)
k cis-4-Octene/ $\sum k$ Isomerisations	2.66(±0.18)	0.79(±0.11)	0.25(±0.08)

[a] Catalyst was pretreated with a mixture of H_2O_2/NH_4OH to increase the rate of reaction.

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