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# Aqueous phase hydrogenation of substituted phenyls over carbon nanofibre and activated carbon supported Pd

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ABSTRACT

The hydrogenation of aromatic acids and other substituted phenyls has been studied for two palladium-based catalysts; one supported on carbon nanofibres (CNFs) and the other on a steam-activated carbon. The reactions were conducted in both aqueous solution and aprotic organic solvents. The major product over both catalysts was the same irrespective of the substrate indicating that support characteristics and Pd dispersion play at most only a minor role in defining the reaction pathway. The key factor in determining the major reaction product resulting from either preferential hydrogenation of the aromatic ring, or reaction of the external functional group, was the extent to which the external group interacted with water molecules which acted in some cases to protect the external function from interaction with the metal surface and induced selective reduction of the aromatic ring.

## 1. Introduction

The need to produce more environmentally acceptable chemical processes has led to increased interest in replacing stoichiometric reagents with reusable heterogeneous catalysts. The replacement of volatile organic compounds (VOCs) by solvents with lower vapour pressures or by liquids which are deemed to be environmentally benign is also desirable. The use of water as a solvent has received attention [1–3] and there are numerous cases in which additional benefits, such as increased reaction rates have been found when water replaces organic solvents particularly in Diels Alder and coupling reactions [4,5]. A less well-documented case is where the addition of water to hexahydrobenzoic acid as a solvent, lead to enhanced rates of benzoic acid hydrogenation over Pd, Rh and Ru catalysts [6]. Henry's constant for hydrogen in water ($7.8 \times 10^{-4}$ mol $L^{-1}$ $atm^{-1}$ at 298 K) permits hydrogenation reactions to proceed at moderate hydrogen partial pressures. However, the rates of reaction may be relatively slow and, potentially, strongly influenced by gas–liquid mass transfer [7].

Palladium is often the metal of choice in selective hydrogenation reactions and this is often partnered by carbon as a support due to its high surface area and low relative cost along with the ease by which the supported metal may be recovered. Although the relative hydrophilicity of a carbon may be increased by treatment of the surface by reagents such as nitric acid and hydrogen peroxide which lead to increased density of surface oxygen containing functionalities, complete miscibility with water is seldom achieved [8] thus limiting these types of catalyst for water-based hydrogenation and other reactions. Oxidation of carbon nanofibres allows the active phase of the precursor salt to be applied from an aqueous solution [9]. There are different views as to the potential impact of such functionalities in selective hydrogenation reactions on activated carbons [10–12] whereas in the case of carbon nanofibres, these oxygen functionalities have been shown to play a key role in influencing activity and selectivity in the liquid phase hydrogenation of cinnamaldehyde [9]. In an earlier communication [13], we reported on the use of nitric acid treated carbon nanofibres (CNFs) as a support for Pd which lead to the formation of a material which showed high miscibility with water, and permitted the hydrogenation of water-soluble aromatic acids to proceed with high selectivity to the corresponding cyclohexane carboxylic acid. Pd is generally regarded as a poor catalyst for the hydrogenation of most aromatic rings at low temperatures [14], and, in general, aromatic ring hydrogenation requires more severe conditions than those required to hydrogenate other functional groups [6,15]. Carboxylic acid groups are difficult to reduce [16,17] but may be converted to aldehydes over oxides at high temperatures and pressures [16–18]. Current methods for ring hydrogenation of phenyl carboxylic acids include the use of Na–K alloys [19]. Alternatives involve the use of higher temperatures which enable the reaction of molten phase benzoic acid [20] and there are indications that this reaction may also be performed over carbon-supported precious metals in supercritical $CO_2$ [21]. In this paper, Pd supported on carbon nanofibres are compared with catalysts based on an acid treated activated carbon to determine whether the high

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yields to cyclohexane carboxylic acids in an aqueous phase hydrogenation [13] were specific to the nanofibre-supported material and also whether preferential ring hydrogenation occurred when substrate molecules containing more readily reducible external polar functional groups were employed.

## 2. Experimental

Carbon nanofibres (CNFs) were prepared by Grupo Antolin using the floating catalyst technique. Pretreatment of the as-received nanofibres involved treating each gram in 100 $cm^3$ of 65 wt% $HNO_3$ at 343 K in a round-bottomed flask fitted with a reflux condenser. The resultant material was washed with distilled water until the washings gave a pH of 5–6. The sample was then dried overnight at 373 K. The resultant material had an elemental oxygen content of 6.55%. Pd/CNF catalyst was prepared by combining the nitric acid pretreated nanofibres with a volume of an aqueous solution of $Pd(NO_3)_2$ equivalent of the adsorption capacity of the support and containing a predetermined quantity of salt to prepare a 5% loading of Pd on reduction. The resultant slurry was dried in air at 373 K for 24 h and then stored. Some tests experiments were also conducted on a 5% Rh/CNF catalyst which had been prepared from $Rh(NO_3)_3$ solution but otherwise was prepared in an identical fashion to the Pd/CNF.

The activated carbon-based catalyst was prepared as 5% palladium (Pd/AC) loaded on the carbon support (Johnson Matthey, Acid Treated Carbon) by the wet impregnation method. A pre-weighed amount of carbon (9.5 g) was wetted by slow addition of ca. 100 ml of water followed by dropwise addition of 249 ml of 0.018 M $Pd(NO_3)_2$ solution. After complete addition of solution, the whole mixture was stirred for a further 16 h followed by rotary evaporation and drying at 110 °C. The sample was then treated at 523 K in $N_2$ for 1 h to decompose the precursor. A number of experiments were also conducted over a commercial 5% Pt/charcoal (Pt/AC) sample (Johnson Matthey, Ref. 99905).

Prior to use in reaction or characterisation, all the catalysts were activated by exposure to a 1:1 $H_2/N_2$ mixture (50 $cm^3\ min^{-1}$) at 423 K for 1 h followed by cooling to 298 K under nitrogen.

Catalytic reactions using 50, 100 or 200 mg of catalyst were carried out using a 0.01 M aqueous solution of the aromatic acid except in the case of cinnamic (0.003 M) acids. High pressure reactions were performed at 15 Bar $H_2$ pressure in a 270 $cm^3$ stainless steel autoclave over 24 h at 358 K with temperature maintained constant by mounting the autoclave in a pre-heated silicone oil bath. A head assembly (Ken Kimble) fitted with pressure gauges, relief valve and magnetically driven stirrer was employed. Reactions at 1 Bar pressure were performed by continuously bubbling hydrogen through the solution in a three-necked flask with a stirrer arrangement. The reaction temperature was maintained at 358 K using an oil bath with a provision for heating and stirring. A series of reactions were also conducted using cyclohexane as a solvent but otherwise retaining all the other parameters. In the case of the mixed solvent reaction, which involved various compositions of dioxane and water, these were conducted at 333 K but using otherwise equivalent conditions. Products of reaction were identified by GC–MS and concentrations were determined by the use of calibration standards using either GC or HPLC.

## 3. Results

### 3.1. Characterisation

Table 1 contains the relevant surface area and pore characteristics of the two, as-prepared Pd-containing samples. Consistent with the expectations based on the data for the original starting support materials, the surface area of the Pd/AC sample was ca. six times greater than the Pd/CNF sample and the former contained a proportion (ca. 16%) of the surface area in micropores. TPR profiles showed that Pd precursor in the Pd/CNF was reduced upon contact with hydrogen at room temperature as indicated by a single, negative feature at ca. 353 K resulting from Pd hydride decomposition [22]. Pd/CNF prepared from $Na_2PdCl_4$ on the other hand, gave a TPR profile with a peak at ca. 400 K due to the reduction of $Pd^{2+}$ to $Pd^0$ [23]. TEM and CO chemisorption measurements indicate that a particle size of ca. 9 nm (12.7% dispersion) was prevalent. Dried Pd/AC gave a TPD in nitrogen plot which displayed an intense signal at 523 K indicative of decomposition of the precursor salt and hence the sample was pretreated at 523 K in $N_2$ for 1 h before use. Subsequent TPR profiles displayed a negative feature due to Pd hydride decomposition [22] along with positive features above 623 K which can be attributed to the release of methane following hydrogenation of the support material. Pd/AC catalyst reduced at 423 K gave a CO uptake of 16.82 $\mu mol\ g^{-1}$ which, assuming a Pd:CO ratio of 2:1 [24], corresponds with a dispersion of 7.15% and an average particle size of 16 nm.

**Table 1**
Characteristics of the prepared catalysts.

| Sample | BET ($m^2\ g^{-1}$) | Micropore area ($m^2\ g^{-1}$) | Micropore volume ($cm^3\ g^{-1}$) | Metal dispersion (%) |
|---|---|---|---|---|
| Pd/AC | 1187 | 189 | 0.06738 | 7.15 |
| Pd/CNF | 185 | – | – | 12.7 |
| Rh/CNF | 187 | – | – | 29.9 |

The Rh/CNF gave a single reduction feature in the TPR profile with an integrated intensity which accounted for a complete reduction. Sample which had been reduced at 423 K gave a CO uptake which equated to a dispersion of 29.9% assuming a 2:1 Rh:CO stoichiometry and which leads to an estimated particle size of 3.8 nm. The much smaller estimated particle size for Rh/CNF compared with Pd/CNF of similar loading was supported by the ease by which metal crystallites were observed by TEM of the latter but not of the former.

### 3.2. Catalytic tests

Pd-based samples were firstly compared in the hydrogenation of benzoic acid. Cyclohexane carboxylic acid was the only product detected for both Pd-based samples (Table 2) although neither sample completely converted all the starting acid after 24 h using 15 Bar hydrogen at 358 K. The conversions equate to average turnover frequencies (TOFs) of 2.83 and 5.70 $h^{-1}$ for Pd/CNF and Pd/AC, respectively. Under otherwise identical conditions, the Pd/AC sample converted only 34% benzoic acid when the hydrogen pressure was reduced to 1 atm (equivalent to an average TOF of 2.1 $h^{-1}$) although the high selectivity to cyclohexane carboxylic acid was maintained (Table 2).

The conversion of benzoic acid in an aqueous solution at 333 K over the Pt/AC was 83% (Fig. 1). However, when the reaction was

**Table 2**
Conversion of benzoic acid to cyclohexane carboxylic acid over 24 h over the two catalysts at 358 K.

| Catalyst | 15 Bar hydrogen | | 1 Bar hydrogen | |
|---|---|---|---|---|
| | Conversion | Selectivity | Conversion | Selectivity |
| Pd/AC[a] | 92 | 100 | 34 | 100 |
| Pd/CNF[b] | 80 | 100 | | |

[a] Catalyst (100 mg) using 50 $cm^3$ benzoic acid solution.

[b] Catalysts (50 mg) using 25 $cm^3$ benzoic acid solution.

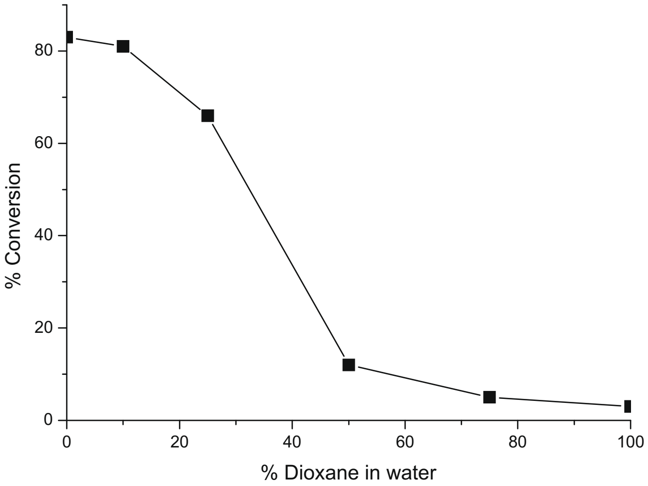


**Fig. 1.** Conversion of benzoic acid as a function of solvent composition over Pt/AC at 333 K.

performed in dioxane under similar conditions, conversion was only 3%. In both cases, cyclohexane carboxylic acid was the only reaction product. As the proportions of dioxane and water were varied, the extent of reaction was modified with water-rich solutions showing the higher levels of conversion (Fig. 1).

To determine whether the high selectivity to the hydrogenated ring was specific to substrates which included an acid functional group, a number of other functionalised phenyls were studied (Table 3). All molecules, as with the benzoic acid, contained an external carbonyl functional group. In the case of the Pd/CNF, all substrates were more reactive than the benzoic acid with benzaldehyde and acetophenone being 100% converted during the 24-h reaction period. The least reactive of the three, the benzamide, was still converted to a greater extent (92%) than the benzoic acid (80%). As observed for the acid, the main product of benzamide reaction involved hydrogenation of the aromatic ring, although with a selectivity of 96.1% in the case of the amide as opposed to 100% for the acid. Recycle experiments using Pd/CNF gave 91.3% conversion and 96.1% selectivity to the cyclohexane carboxamide. Both the benzaldehyde and acetophenone underwent hydrogenation of the carbonyl functional groups which was not observed in cases of the acid or amide. However, products originating from ring hydrogenation were still the dominant feature with 59.7% of the products of acetophenone, and 83.2% in the case of benzaldehyde resulting from ring hydrogenation.

On the other hand, Rh/CNF catalyst converted 100% of the acetophenone and produced two major products, which resulted from hydrogenation of the aromatic ring (Table 3). Cyclohexylethanol was the principal product with a selectivity of 85.4% while cyclohexylethanone was present at 10.3% of the total products. Other minor products were detected. The results suggest that Rh preferentially hydrogenated the aromatic ring of acetophenone initially followed by partial hydrogenation of the external carbonyl function.

To determine the extent to which additional reducible functional groups influenced the balance between ring *versus* external functional group hydrogenation, and other factors such as the length of carbon chain between the ring and the acid functionality were important, a number of substrates were selected and compared with the data for benzoic acid (Table 4). Increasing the length of the carbon chain separating the acid functionality from the phenyl group by the use of phenylacetic acid did not diminish the excellent selectivity to ring hydrogenated product although the conversion for both the Pd/AC and Pd/CNF samples was diminished with respect to benzoic acid. The impact of increasing the chain

**Table 3**
Conversion and selectivity to major products of the aqueous phase hydrogenation at 15 Bar $H_2$ and 358 K of several carbonyl containing substituted aromatic compounds.

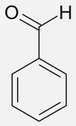
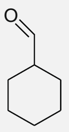
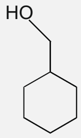
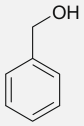
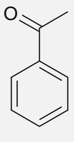
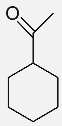
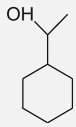
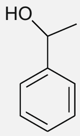
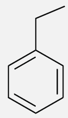
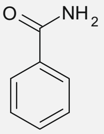
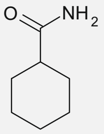
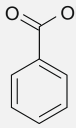
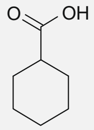
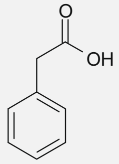
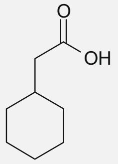
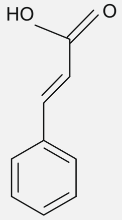
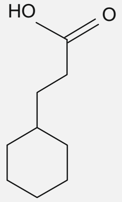
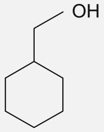
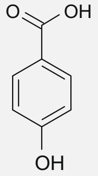
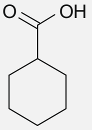
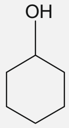
| Catalyst | Substrate (conversion) | Ring hydrogenated product (selectivity) | Functional group hydrogenated product (selectivity) |
|---|---|---|---|
| | <br>Benzaldehyde | <br>Cyclohexyl methanal<br>+<br><br>Cyclohexyl methanol | <br>Benzyl alcohol |
| Pd/AC (%) | 100 | 85.0 | 15.0 |
| Pd/CNF (%) | 100 | 83.2 | 16.8 |
| | <br>Acetophenone | <br>Cyclohexyl ethanone<br><br>Cyclohexyl ethanol | <br>Phenyl-1-ethanol<br>+<br><br>Ethylbenzene |
| Pd/AC (%) | 100 | 65 | 35.0 |
| Pd/CNF (%) | 100 | 59.7 | 40.3 |
| Rh/CNF (%) | 100 | 95.4 | 4.6 |
| | <br>Benzamide | <br>Cyclohexane carboxamide | |
| Pd/AC (%) | 100 | 100 | |
| Pd/CNF (%) | 92 | 96.1 | |

**Table 4**
Conversion and selectivity of the hydrogenation at 15 Bar $H_2$ and 358 K of several aromatic acids containing additional functional groups.

| Catalyst | Substrate (conversion) | Primary product (selectivity) | Other product(s) |
|---|---|---|---|
| | <br>Benzoic acid | <br>Cyclohexanecarboxylic acid | None |
| Pd/AC (%) | 92 | 100 | |
| Pd/CNF (%) | 80 | 100 | |
| | <br>Phenyl acetic acid | <br>Cyclohexaneacetic acid | None |
| Pd/AC (%) | 81 | 100 | |
| Pd/CNF (%) | 65 | 100 | |
| | <br>Cinnamic acid | <br>Cyclohexylpropanoic acid | <br>Cyclohexylethanol |
| Pd/AC (%) | 100 | 100 | 0 |
| Pd/CNF (%) | 100 | 97 | 3 |
| | <br>4-hydroxy benzoic acid | <br>Cyclohexanecarboxylic acid | <br>Cyclohexanol |
| Pd/AC (%) | 100 | 75 | 0 |
| Pd/CNF (%) | 93 | 51 | 3 |

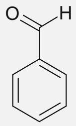
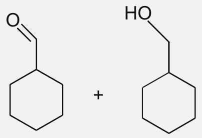
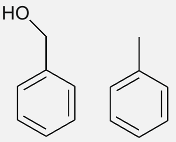
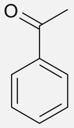
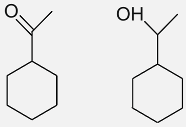
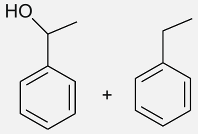
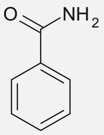
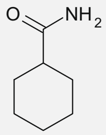
length further, but also adding an olefinic functionality to the chain separating the acid group and the aromatic ring was tested by the use of cinnamic acid (Table 4). The results indicate high activity of the catalysts for this substrate (with respect to benzoic acid) where the starting concentration was three times that of the benzoic acid. However, the olefinic double bond was also hydrogenated in the principal product obtained. The high conversion level obtained lead to high selectivity to cyclohexylpropanoic acid indicative that both olefinic and phenyl rings had undergone hydrogenation. Experiments conducted for various time periods less that 24 h showed that 65% of the starting cinnamic acid had undergone reaction in the first 4 h and that the principal intermediate formed (towards the formation of cyclohexylpropanoic acid) still retained the aromatic ring. This indicates that the olefinic function of the cinnamic acid underwent initial, more rapid reaction, and that this was followed by ring hydrogenation showing that the acid group again was preserved at the expense of the ring, consistent with the findings for the other aromatic acids studied (Table 4). Aromatic acids, which also contained phenolic functions, were studied using 4-hydroxy benzoic acid as an example. The results at the high conversions obtained (Table 4) indicate that the phenyl unit had been reduced through to the corresponding cyclohexyl rather than cyclohexanone product but again, with retention of the acid functionality. Only in the case of the Pd/CNF catalysts was there indication of acid group hydrogenation to generate minor quantities of cyclohexanol.

In order to test the impact of solvent choice on selectivity for the substrates containing external functional groups, the hydrogenation of acetophenone and benzaldehyde and benzamide were studied using cyclohexane as a solvent. In the case of benzamide, the extent of hydrogenation was limited and only the product of ring hydrogenation was obtained. However, in the cases of the benzaldehyde and acetophenone, with readily reducible external carbonyl functional group [14], no ring hydrogenation products were detected (Table 5), despite the high conversion levels obtained and the only reaction products were the result of partial or full hydrogenation of the external carbonyl function.

## 4. Discussion

The use of carbon nanofibre-based catalysts has received significant attention in the recent years with one key advantage over

**Table 5**
Conversion and selectivity in the hydrogenation of several carbonyl containing substituted aromatic compounds at 15 Bar $H_2$ and 358 K using cyclohexane as a solvent.

| Catalyst | Substrate (conversion) | Ring hydrogenated products (selectivity) | Functional group hydrogenated products (selectivity) |
|---|---|---|---|
| | <br>Benzaldehyde | <br>Cyclohexyl methanal + Cyclohexyl methanol | <br>Benzyl alcohol Toluene |
| Pd/AC (%) | 100 | 0 | 100 |
| Pd/CNF (%) | 100 | 0 | 93 |
| | <br>Acetophenone | <br>Cyclohexyl ethanone Cyclohexyl ethanol | <br>Phenyl-1-ethanol + Ethylbenzene |
| Pd/AC (%) | 100 | 0 | 100 |
| Pd/CNF (%) | 100 | 0 | 100 |
| | <br>Benzamide | <br>Cyclohexane carboxamide | |
| Pd/AC (%) | 10 | 100 | |
| Pd/CNF (%) | 10 | 100 | |

activated carbons being the absence of micropores (Table 1) which removes the potential disadvantages resulting from diffusion limitations and secondary reactions [12] which often lead to poorer selectivity to the desired product. It is noted that the activated carbon selected for comparison here had a relatively low proportion of its total surface area (ca. 16%) in micropores and this value is often considerably higher. Other advantages of the CNF have been made regarding selectivity induced through functionalisation of the nanofibre surfaces by oxidation [9,13,25]. The results obtained here, by comparing selectivities in the hydrogenation of functionalised aromatics, provide no evidence (Tables 3–5) for modified behaviour over carbon nanofibres compared with the activated carbon when used to support the same metal (i.e. Pd). Differences in dispersion (Table 1) also led to minimal differences in selectivity although differences in turn-over frequencies were noted, with the poorer dispersed Pd on the activated carbon support (Table 1) giving the greater TOF for benzoic acid hydrogenation. As the only reaction product observed was cyclohexane carboxylic acid, which resulted from ring hydrogenation which may be assumed to require a flat (parallel) lying ring requiring an ensemble of metal atoms (Fig. 2), it can be assumed that smaller crystallites on higher dispersed samples contain arrangements of atoms at steps and edges which are unable to adsorb the aromatic ring in such a favourable orientation.

Replacement of palladium by rhodium as the active metal on the carbon nanofibres led (Table 3) to a predictable [6,12] enhanced selectivity to products involving hydrogenation of the aromatic ring with hydrogenation of the external carbonyl group of acetophenone occurring as a secondary (consecutive) reaction (Table 3). Palladium on the other hand, gave a mixture of products for reaction with acetophenone which resulted from either initial ring hydrogenation or carbonyl group hydrogenation when the reaction was conducted in water (Table 3). However, as will be discussed in detail below, this was a considerable shift in selectivity from when the reaction was conducted in cyclohexane where no ring hydrogenation products were observed (Table 5). A similar shift towards ring hydrogenation was observed using benzaldehyde as a substrate.

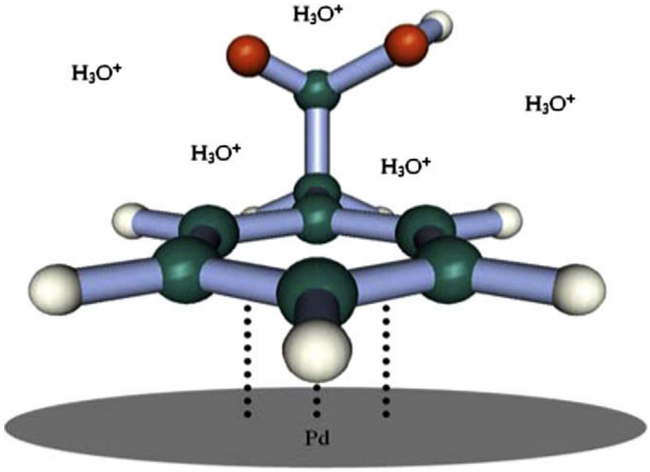


**Fig. 2.** Representation showing the role of the water in solvating the external, polar functional group and orientating the aromatic ring over the Pd surface in a manner which facilitates ring hydrogenation.

The use of solvents in liquid-phase hydrogenation reactions to influence selectivity in substrates with multiple functional groups has been reported. In molecules containing both olefinic and carbonyl groupings, polar solvents appear to activate hydrogenation of the C=O whereas non-polar solvents favoured C=C hydrogenation [26,27]. In the case of molecules containing both aromatic and carbonyl functions, choice of solvent with increasing dielectric constant, led to an increase in reaction rate (conversion) of acetophenone over Pt–Ni, and with reduced selectivity to the 1-phenyl ethanol. However, no ring hydrogenation was observed and the loss of selectivity was mainly a consequence of formation of ether and methylene groups at the external function [28]. Reactions in this study performed in aprotic solvents over Pd/CNF and Pd/AC (Table 5) gave only phenyl 1-ethanol and ethyl benzene consistent with the results using *n*-hexane as a solvent [28]. The results using water, with a dielectric constant of 80, higher than any solvent employed by Malyala in their studies of acetophenone [28], show that the selectivity towards products arising from the hydrogenation of external functional group dropped from 100% (Table 5) to 40.3% (Table 3) with the remaining products resulting from hydrogenation of the aromatic ring. Similarly, the hydrogenation of benzaldehyde which produced only benzyl alcohol and toluene in aprotic solvent (Table 5) produced mainly products arising from ring hydrogenation when the reaction was performed in water (Table 3).

In addition to solvation effects, limiting interaction between the hydrogenating Pd surface and the polar, reducible functional group, high selectivities towards ring hydrogenation partially arise due to enhance reaction rates of ring hydrogenation in water compared with aprotic solvents. The observation of enhanced reaction rates of benzoic acid over Ru/C and Rh/C by addition to water was made by Rylander [6] and is entirely consistent with observations made here (Fig. 1) where the conversion of benzoic acid in water, dioxane and mixtures of the two, showed reaction rates to be greater in water. Note that the differences cannot be attributed to hydrogen availability since the mole fraction of hydrogen in water is approximately an order of magnitude less than it is in dioxane. (Mole fraction in water at 15 Bar (assuming Henry's law holds) is $1.965 \times 10^{-4}$ whereas the value can be calculated as $3.585 \times 10^{-3}$ for dioxane. Value for water at 333 K quoted in [29] and calculated at 333 K for dioxane using the relationship, $\ln x = -5.7347 - 8.6743/(T/100\,\mathrm{K})$ [29].)

Increased rate of ring hydrogenation can be attributed to favourable orientation of the aromatic ring on the metal surface brought about by solvation of the polar functional group, and orientation of the ring due to the local structure of water in the proximity of the surface. The orientation of the molecule *via* solvation effects is known and may be exemplified by the case of methanol on Pt(1 1 1) where in the vapour phase, the methanol interacts with the surface though the oxygen atom, whereas on the introduction of water, methanol twists through 90° to allow the CH bond to interact with the surface [30]. This is driven by a desire of the molecule to maximise methanol–water interactions of the polar groups. Similar scenarios leading to preferential ring down adsorption (Fig. 2) would explain the selectivity effects observed leading to increased ring hydrogenation relative to function group hydrogenation in water (Table 3) in cases where the functional group undergoes facile hydrogenation in aprotic solvents (Table 5). However, the enhanced reaction rate (increased conversion) in water compared to aprotic solvent of molecules containing functional groups not readily hydrogenated such as benzamide (Tables 3 and 5) and benzoic acid (Fig. 1) suggests that additional factors are involved. On surfaces such as Pt, Pd and Rh employed here, water is known to form ordered overlayers as a consequence of the ability of water to wet the metal surfaces as predicted by the hydrophilicity or wettability parameter, *w*, as described by Meng et al. [31] $w = E_{\mathrm{HB}}/\Delta E_{\mathrm{ads}},$ where the numerator denotes the water–water hydrogen bond strengths and the denominator denotes the calculated adsorption energy for water on the different metals. Although such a semi-rigid layer at the metal surface may impose a barrier to the solute molecule in terms of transport, this layer may also enhance reactivity by localising (and orientating) the surface species close to the metal and stabilising partial charges in the transition or product states [32]. For example, the acetate anion is stabilised by an additional 57 kJ mol$^{-1}$ on Pd (1 1 1) when it is completely solvated by water [33]. It is not clear at this stage whether it is as benzoic acid or as the benzoate anion that the species undergoing hydrogenation is present.

Although the strong solvation of the external polar functional group in water was sufficient to orientate the molecule in such a manner that preferred adsorption mode was through the aromatic ring (Fig. 2), leading to reduced selectivities to the functional group hydrogenated product which had been favoured in aprotic solvent, external groups such as the olefinic unit in cinnamic acid, which are readily hydrogenated over Pd catalysts [14], did not appear to receive significant protection.

## 5. Conclusions

Aromatic compounds with highly polar functional groups such as acids and amides undergo preferred ring hydrogenation where the rate of ring hydrogenation is enhanced compared to reaction in aprotic solvents due to a combination of strong solvation of the polar side group and solvent-assisted orientation of the ring on the metal surface which favoured hydrogenation. The nature of the carbon support has little influence in this reaction. Less polar functional groups which were more prone to hydrogenation in aprotic solvents were less susceptible to reaction in water, which again enhanced the relative rate of hydrogenation of the aromatic ring, leading to considerable differences in selectivity in the two types of solvent.

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