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Use of Water as a Solvent in Directing Hydrogenation Reactions of Aromatic Acids over Pd/carbon Nanofibre Catalysts

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Abstract By conducting the catalytic hydrogenation over water miscible Pd/carbon nanofibre catalysts, selective ring hydrogenation of aromatic acids can be performed in aqueous solution without the need to provide protection for the external acid function.

Keywords Selective reduction · Aqueous hydrogenation · Aromatic acids · Pd/nanofibres

1 Introduction

The desire to produce more environmentally acceptable chemical processes has led to increased interest in replacing stoichiometric reagents with reusable heterogeneous catalysts which are capable of producing high selectivities to a desired product. Further improvements are possible where commonly used volatile organic compounds (VOC) are replaced by solvents with lower vapour pressures or with liquids which are deemed to be environmentally benign. The use of water as a solvent has received some attention [1, 2] and there are cases in which additional benefits, such as increased reaction rates have been found when this replaces organic solvents [3, 4]. The use of water in biphasic solvent systems is also of interest, in particular where improved selectivities may be obtained as a result of the high partition coefficient of a desired product in water relative to the hydrocarbon partner solvent.

Water may be used in hydrogenation reactions since its Henry's constant (7.8×10^{-4} mol L^{-1} atm^{-1} at 298 K [5]) permits reactions to proceed at moderate hydrogen partial pressures.

Palladium is commonly the metal of choice in selective hydrogenation reaction 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, hydrogen peroxide etc. which lead to increased density of surface oxygen containing functionalities, complete miscibility with water is seldom achieved [6], thus limiting these types of catalyst for water-based hydrogenation and other reactions. In this communication we report on the use of nitric acid treated carbon nanofibres (CNF), which leads to the formation of a material which shows high miscibility with water, allowing us to perform hydrogenation of water-soluble aromatic acids with high selectivity to the corresponding cyclohexane carboxylic acid. In general, aromatic ring hydrogenation requires more severe conditions than those required to hydrogenate other functional groups [7] which would normally lead to preferential reaction of the latter relative to the former. Current alternatives include the use of Na-K alloys for ring hydrogenation of phenyl carboxylic acids [8] and Pd/C [9], Raney Ni [9] or cinchonidine modified Pd/Al_2O_3 [10] for furan and benzofuran carboxylic acids.

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2 Experimental

Carbon nanofibres (CNF) were prepared by Grupo Antolin using the floating catalyst technique [11]. Nanofibre pretreatment was performed by 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.

Pd/CNF catalyst was attained 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. Prior to use, 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. TPR profiles showed that Pd precursor 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. TEM and CO chemisorption experiments indicate that a particle size of *ca*. 9 nm (12.7% dispersion) was prevalent.

Catalytic reactions using 50 mg of catalyst were carried out using 25 cm^3 of a 0.01 M aqueous solution of the aromatic acid except in cases of naphthoic (0.001 M) and cinnamic (0.003 M) acids. All 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. Sample analysis was performed using a HP6890 Series GC with an integrated mass selective detector HP5973. A Varian Factor Four (VF-1 ms) low bleed capillary column (15 m × 250 μm × 0.25 μm) with 100% polydimethyl siloxane (non-polar) as stationary phase was used to separate reagents/products of reaction. The equipment was configured with a splitless inlet set at 200 °C, and a flow rate of 9.0 ml min^{-1}. FID ccalibration was carried out for each of the intended reagents using hydrocinnamaldehyde and decane as internal standards.

3 Results

Table 1 shows details of the elemental composition before and after nitric acid treatment. Results confirm that acid treatment was successful in increasing the concentration of oxygen containing groups in addition to removing a proportion of S and N containing impurities.

Table 1 Elemental analysis of nanofibre composition before and after treatment in nitric acid

Sample	Composition (%)					Ash
	C	H	N	S	O	
Original	84.18	0.47	0.87	0.92	3.04	10.52
HNO_3 treated	92.82	0.28	0.36	0.00	6.55	0.00

To determine the extent to which nitric acid treatment influenced the textural characteristics of the nanofibres, analysis of nitrogen (77 K) and carbon dioxide (273 K) adsorption isotherms was undertaken. Results are summarised in Table 2 and show that only minor changes to pore volumes and total surface area resulted from the oxidative treatment.

SEM images confirm (Fig. 1) that the basic morphology of the nanofibres was retained after treatment, although the expanded scale of the micrograph for the treated samples shows some indication of fibre agglomeration. However a sample which was washed and filtered without nitric acid treatment, also showed a similar aspect, showing that this was not the result of the oxidative treatment.

In order to determine the catalysts performance in selective hydrogenation reactions, benzoic acid was used as a test substrate. Results show (Table 3) that at high conversion, 100% selectivity to the hydrogenated ring product (cyclohexane carboxylic acid) was obtained.

To focus and determine the influence of the external functional group on the ring, the reaction was repeated using phenylacetic acid. Although the reaction rate was less for this substrate, leading to lower conversion for the same reaction time, the system continued to show 100% selectivity to the saturated acid (Table 3). Cinammic acid, containing both external acid and alkene units was studied under identical conditions. On this occasion, although the acid function remained intact, both aromatic ring and alkene functionalities were hydrogenated under conditions where high substrate conversion was attained. Selectivity to cyclohexylpropanoic acid was very high (97%) with the remainder of the converted substrate resulting from hydrogenation of all 3 functional groups to give cyclohexylpropanol. Experiments at reduced conversion are

Table 2 Surface area and pore volume measurements for nanofibres before and after nitric acid treatment

Sample	BET (m^2 g^{-1})	[a]Vol. N_2 (cm^3 g^{-1})	[a]Vol. CO_2 (cm^3 g^{-1})
Original	178	0.09	0.05
HNO_3 treated	185	0.08	0.05

[a] Using Dubenin Raduskevich method

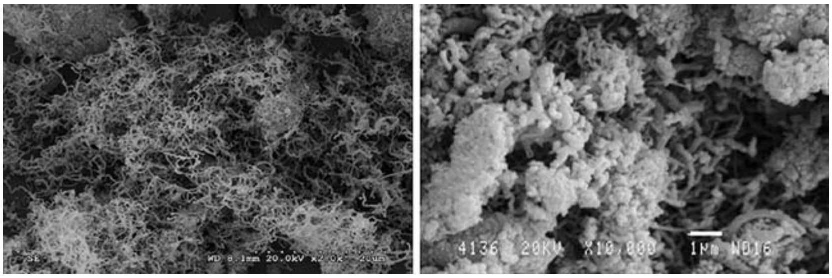
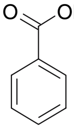
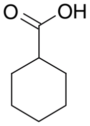
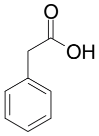
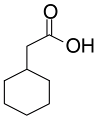
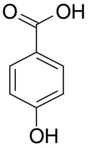
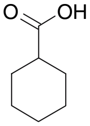
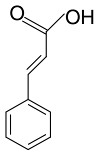
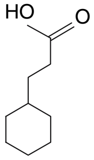
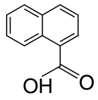
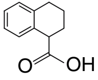


Fig. 1 Scanning electron micrographs (SEM) of (left × 2000) original untreated carbon nanofibres and (right × 10000) following nitric acid treatment

being performed which will assist in determining whether conditions for preferential hydrogenation of the ring, without hydrogenation of the external C = C can be attained.

Addition of a second substituent to the ring, for example an OH group as in *p*-salicylic acid (Table 3) did not affect the preferential hydrogenation of the aromatic ring relative to the acid function. However, both ring and OH groups were hydrogenated at high conversion. A further test involved studying the influence of a second aromatic ring as exemplified by naphthoic acid (Table 3). In this case, again the carboxylic acid unit remained intact while the ring directly attached was preferentially hydrogenated, leaving the secondary ring intact. The only other detected product was the consequence of over hydrogenation, resulting in the full saturation of both rings and reduction of the acid to the corresponding alcohol.

Table 3 Results of catalytic hydrogenation tests

Reagent	Product(s)	Conversion/% and (Selectivity)/%
Benzoic acid 	Cyclohexanecarboxylic acid 	80 (100)
Phenyl acetic acid 	Cyclohexaneacetic acid 	65 (100)
p-Salicylic acid 	Cyclohexanecarboxylic acid 	93 (51)
Cinnamic acid 	Cyclohexylpropanoic acid 	100 (97)
Naphthoic acid 	1,2,3,4-tetrahydro-1-naphthoic acid 	80.5 (61.5)

Note that preferential hydrogenation of the ring and/or protection of the external functional group appeared to be highly dependent on the exact nature of the latter. When the same reaction conditions were applied to acetophenone and benzaldehyde, a mixture of both ring and side chain hydrogenation products were obtained. However, preliminary results obtained using other external, polar functional groups showed similar trends as those observed using the aromatic acids [12]. Benzamide could be hydrogenated with 91.8% conversion with 96.1% selectivity to cyclohexane carboxamide. On recycling, the catalysts showed 91.3% conversion and 95.8% selectivity. Liquid phase hydrogenation of nitroaromatics over Pd/C catalysts in the absence of water would be expected to show high selectivity to the corresponding aromatic amine [13]. Note that catalytic hydrogenation of molten dinitrotoluenes over Pd/charcoal in the presence of water gives selectively the aromatic amine as product [14], pointing to a unique property of the Pd/nanofibre catalysts described here. Note that the use of molten reagents in the present system is not essential. Even though some of the potential reagents may have limited solubilities in water, this need not be an issue as solid reagent may be loaded into the reactor to yield a concentration in solution as given by the equilibrium solubility product under reaction conditions.

4 Discussion

Selective hydrogenation of aromatic rings in the presence of external, reducible, functional groups is unusual and would normally require a protecting agent such as that provided for an acid function by esterification [15]. Similarly, although it is known that Pd is able to selectively hydrogenate aromatic rings containing heteroatoms in preference to phenyl rings [16] preferential activation of a ring in the presence of an acid function is not widely achieved and there are few, if any occasions of reports where this is achieved in water. This novel route permits selective reaction without accompanying solvent loss due to volatilisation or solvent hydrogenation.

It is known that the support-metal interface may be highly influential in governing product selectivity as exemplified in the case of catalysts which, upon entering a state of SMSI, exhibit improved selectivity to C = O over C = C hydrogenation for molecules such as crotanaldehyde [17, 18] and cinnemaldehyde [17]. Similar improvement in selectivity for the latter molecule has been reported following the introduction of oxygen surface groups for carbon nanofibre supported ruthenium catalysts [19]. An increased concentration of surface oxygen groups on carbon supports may improve Pd dispersion but with no corresponding improvement in hydrogenation activity for substituted aromatics [13]. An alternative argument to the role of the support surface groups in providing a desirable geometry for the adsorbed species for carbon nanofibre supported metal catalysts [19] would involve a role of this activated surface in inducing strong interaction between support and metal which would render the metal particle surface more amenable to a particular adsorption mode by the adsorbate. Such a scenario is supported by TEM observation of Pd on graphitic nanofibres where highly crystalline, faceted and relatively thin Pd structures are found [20]. Extended flat surfaces are desirable for ring hydrogenation as a parallel adsorption mode facilitates ring activation and hydrogen transfer. However, from results in Table 3, and the reactions performed with acetophenone and benzophenone, where a mixture of ring and external functional group hydrogenation took place, it is clear that the presence of an appropriately faceted metal surface alone is not sufficient to explain the selectivity effects observed. In the absence of more detailed studies, it is proposed that the role of solvent water, or more succinctly, the water-reagent-metal surface, is key. The polar O-H group of the acid or amide, given the option between being surrounded by water molecules or interacting with the Pd surface, selects the former option, resulting in increased probability of the aromatic ring interacting with the metal surface. Such a scenario is consistent with the interactions between Pt (111) and methanol where, although vapour phase reaction leads to preferred interaction *via* the oxygen, in the presence of water, maximisation of $CH_3OH–H_2O$ interactions leads to C-H bond weakening followed by dehydrogenation [21].

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