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Versatile dual hydrogenation-oxidation nanocatalysts for the aqueous transformation of biomass-derived platform molecules[†]

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Carbon-supported Pd nanoparticles have been proved to be efficient dual hydrogenation—oxidation nanocatalysts in both the selective aqueous oxidation of benzyl alcohol and the hydrogenation of furfural in water under microwave irradiation. Nanocatalysts based on trioctylphosphine and triphenylphosphinestabilized-Pd NPs on oxidized carbon support were found to be the most active. The presence of oxygen groups on the surface of the carbon support, particularly those of acidic character, improve the Pd NPs immobilization as well as the water affinity, and consequently the catalytic performances of the system.

Introduction

Supported metal nanoparticles (SMNPs) have focused many research endeavours from the scientific community due to their inherent advantages compared to non supported nanoparticles.¹ The stabilisation and control (in terms of nanoparticle size and distribution), recoverability and robustness as well as preventing agglomeration of the particles that can be achieved via deposition in a porous framework predates all alternative methodologies reported to date (e.g. capping agents such as surfactants or ligands, ionic liquids, etc.).² The decoration of supports with metal nanoparticles (MNPs) has been achieved by a number of different methodologies (e.g. (photo)chemical, (sono)electrochemical, mechanochemical deposition, etc.)¹ over various solid supports including mesoporous silica,³ inorganic oxides,⁴ mol-ecular sieves,⁵ polymers,⁶ capsules,⁷ apatites⁸ or activated carbons.9 The use of mesoporous carbon materials as supports to stabilise MNPs is known as leading to highly dispersed and active materials (particularly for catalytic applications) due to their excellent mechanical properties as well as optimum pore size distributions, high stability and surface chemistry which can lead to functionalised materials.¹⁰ MNPs supported on carbon materials have been applied in different areas including medicine,¹¹ sensors and optics,¹² environmental remediation¹³ and catalysis.14

In terms of catalytic applications, supported metal nanoparticles ranging from noble (Pt, Pd, Au) to transition metals (Cu, Ni) have been widely employed in redox catalysed reactions including selective oxidation of alcohols,¹⁵ alkenes¹⁶ and alkynes¹⁷ as well as in hydrogenation of alkenes–alkynes¹⁸ and carbonyl compounds.¹⁹ However, few reports to date deal with catalysts able to perform either oxidation or hydrogenation reactions depending on the selected reaction conditions.²⁰ Supported-Pd nanoparticles are one example of such catalytic systems that can in principle be designed to display the dual redox activity due to excellent hydrogenation (under reducing atmosphere) and oxidation properties (both under air and oxidants including hydrogen peroxide).

Following our recent results in the development of environmentally sound methodologies for the design of catalytic (nano) materials for the synthesis of fine chemicals and biofuels via low impact chemical transformations,²¹ herein we report the dual use of Pd NPs supported on a variety of mesoporous carbon materials as both oxidation and hydrogenation catalysts. This work was encouraged by the preliminary activity observed for some of the described systems in the aerobic oxidation of benzyl alcohol in water.²² The selected chemical transformations, as proof of concept for catalytic activity, include the microwaveassisted selective oxidation of benzyl alcohol to benzaldehyde under mild conditions and the hydrogenation of a range of platform molecules such as furfural and organic acids (e.g. itaconic, pyruvic, levulinic acids) both under conventional heating and microwave irradiation. These biomass-derived compounds have attracted a great deal of interest due to their versatility and wide range of valuable derivative products they can lead.^{23,24}

Experimental

Chemical reagents and solvents

Tris(dibenzylideneacetone)dipalladium (0) complex $[Pd_2(dba)_3]$ (from Strem Chemicals), triphenylphosphine (TPP) and

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trioctylphosphine (TOP) (both from Sigma-Aldrich) were used without any further purification. THF and pentane solvents (from SDS) were distilled over sodium-benzophenone or P_2O_5 respectively or dried in a purification column, respectively. Reagents and solvents were degassed before use by means of three freeze–pump–thaw cycles.

Carbon supports

Mesoporous carbon beads (MB) of particle size in the range 0.5–1.0 mm with spherical shape were used as the starting support. They are commercially available phenolic resin-based activated carbon with a bi-modal pore texture.²⁵ MB carbon material was heated at 1500 °C for 1 h in a graphite electrical furnace, at a heating rate of 10 °C min⁻¹ in Ar flow. The new material prepared was denoted MB-1500. Oxidation of MB was carried out by treatment with hydrogen peroxide (30 wt% in water) at 50 °C for 16 h followed by washing with distilled water, thus obtaining a carbon material support denoted as MB-H₂O₂.

Synthesis of isolated Pd NPs

Pd nanoparticles were prepared by the organometallic approach²⁶ using either triphenylphosphine (TPP) or trioctylphosphine (TOP) as stabilizing ligands. Typically, 0.084 mmol of Pd precursor [Pd₂(dba)₃] were dissolved in 40 mL of THF in a Fisher– Porter reactor. Then, the corresponding ligand (TPP or TOP dissolved in 10 mL of THF) was added to the metal precursor solution in a ligand–metal molar ratio of 0.5 at -30 °C to avoid the formation of the molecular complex. The reaction mixture was pressurized up to 3 bar with H₂ and stirred overnight at room temperature. The Fisher–Porter reactor was then depressurized and the solvent evaporated to a volume of *ca.* 2 mL. Pd NPs were afterwards precipitated and washed with pentane and dried under vacuum overnight to obtain a black powder which was kept in a glove-box (Ar, H₂O₂ < 1 ppm; O₂ < 0.1 ppm) until use.

MNPs/Carbon material catalyst preparation

The carbon supported catalysts were prepared in two different ways.

1. Impregnation of the carbon supports with a colloidal suspension of purified Pd NPs. Previously isolated Pd NPs were dispersed in distilled THF (12 mL). The colloidal suspension was divided in two equal portions and each of them was added to a Schlenk flask containing 200 mg of MB-H₂O₂ or MB-1500 as carbon supports. The reaction mixtures were stirred for 3 h at room temperature followed by a careful evaporation of the solvent. Pd NPs/carbon materials catalysts were then dried under vacuum overnight. The catalysts were denoted as Pd(TPP)/MB-1500 and Pd(TPP)/MB-H₂O₂ or Pd(TOP)/MB-1500 and Pd(TOP)/MB-H₂O₂. These names stand for the metal (Pd), the ligand (TPP or TOP) and the carbon support (MB-1500 or MB-H₂O₂) used.

2. Impregnation of the carbon supports with a solution of the palladium zero precursor followed by hydrogenation. 0.2 mmol

of $([Pd_2(dba)_3])$ was dissolved in 12 mL of distilled and degassed THF in a Fisher–Porter reactor. 200 mg of the carbon support (MB-H₂O₂ or MB-1500) were subsequently added to the solution and the mixture was stirred for 3 h. The solvent was then evaporated and the impregnated carbon material dried under vacuum for 1 h. The Fisher–Porter reactor was afterwards pressurized up to 3 bar with H₂ and the solid stirred overnight. After pressure releasing, the resulting catalysts were stored in a glovebox prior to their characterisation and use. The catalysts were denoted as Pd/MB-H₂O₂ and Pd/MB-1500.

Characterisation techniques

The surface area and pore size distribution of the carbon supports were derived from the N₂ adsorption–desorption isotherms performed at -196 °C in a Micromeritics ASAP 2420 volumetric adsorption system. Prior to measurement, samples were degassed overnight by heating at 250 °C under vacuum. Specific surface areas (S_{BET}) were calculated using the Brunauer–Emmett–Tellet (BET) method, taking 16.2 nm² for the cross-sectional area of the nitrogen-adsorbed molecule. Total pore volumes (V_t) were determined by the amount of N₂ adsorbed at $p/p^\circ = 0.99$. Pore size distributions were obtained by applying the DFT (density functional theory) method to the N₂ adsorption isotherms and they are given as ESI (ESI S1[†]).

HRTEM images of the MNPs/carbon material catalysts were obtained at the Service de Microscopie Electronique de l'Université Paul Sabatier Toulouse (TEMSCAN) with a JEOL JEM 2010 microscope working at 200 kV with a resolution point of 0.235 nm. The samples were prepared using ultramicrotomy technique. Thin slices were obtained by cutting down the middle of catalyst carbon spheres. They were deposited on carbon copper grids for the analysis. Statistical size distributions and mean diameter sizes of Pd NPs supported on the carbon materials were carried out manually by measuring *ca.* 300 particles when possible on enlarged TEM micrographs.

Pd contents of the MNPs/carbon material catalysts were determined by Atomic Absorption Spectroscopy (AAS) in an AA-6300 Shimadzu spectrophotometer. All samples were treated with H_2O_2 , HNO₃ and HCl before analyses.

Catalytic experiments

Microwave-assisted oxidation of benzyl alcohol. In a typical reaction, a mixture containing 2 mmol of benzyl alcohol, 0.4 mL of H_2O_2 (50 wt%), 2 mL of water and 0.05 g of catalyst was microwaved in a CEM-DISCOVER reactor for 3 min at maximum power output (300 W), reaching a maximum temperature between 100–110 °C (average temperature 90 °C). The microwave method was power-controlled and reactions were carried out in closed vessel mode (pressure 120–200 psi developed in the system).

Microwave-assisted hydrogenation of furfural. In a typical reaction, a mixture containing 2 mmol of furfural, 1.5 mL of formic acid, 1.5 mL of water and 0.1 g of catalyst was microwaved in a CEM-DISCOVER reactor for 30–45 min at 100 °C (power output 100–150 W). In this case, the microwave method was temperature-controlled (which was measured by a fiber optic

 V_t^{b} $S_{\rm BET}^{a}$ Pd^{c} Pd NPs mean $(m^2 g^{-1})$ $(cm^3 g^{-1})$ (wt%) size^d (nm) MB 1294 1.14 MB-H₂O₂ 1211 1.10 MB-1500 909 0.99 Pd(TOP)/MB-H₂O₂ 1.9 ± 0.3 1020 1.01 2.58 Pd(TOP)/MB-1500 2.01 1.9 ± 0.3 798 0.86 Pd(TPP)/MB-H₂O₂ 995 2.2 ± 0.5 0.93 1.34 Pd(TPP)/MB-1500 815 0.90 1.38 1.8 ± 0.3 Pd/MB-H₂O₂ 1055 0.99 1.8 ± 0.4 2.21 Pd/MB-1500 755 0.87 1.68 2.8 ± 0.5

 Table 1
 Textural properties of the carbon material supports and catalysts, Pd contents and Pd NPs mean size in the catalysts

^{*a*} BET surface area. ^{*b*} Total pore volume. ^{*c*} Determined by Atomic Absorption Spectroscopy. ^{*d*} Measured by HRTEM.

probe) and reactions were carried out in closed vessel mode (pressure 150–250 psi developed in the system) as formic acid efficiently decomposes under the investigated microwave irradiation conditions into CO_2 and H_2 and leads to over-pressure in the systems under power-controlled conditions.

Upon reaction completion (in both cases), samples were collected, extracted with an organic solvent (typically toluene) and subsequently analysed by GC and GC/MS in an Agilent 6890N fitted with an HP-5 capillary column (30 m \times 0.32 mm \times 0.25 µm) and a flame ionization detector (FID).

Results and discussion

The textural properties of the starting MB, oxidized MB-H₂O₂ and high temperature treated MB-1500 carbon materials investigated in this work are summarised in Table 1. The chemical oxidation with H₂O₂ of MB does not affect significantly the textural parameters. BET surface areas of 1294 and 1211 m² g⁻¹ were calculated for MB and MB-H₂O₂, respectively. However, the heat treatment of MB causes a significant decrease of the surface area as expected. DFT calculations on the nitrogen adsorption isotherms showed bi-modal pore size distributions for the carbon supports, with a mesopore distribution centred at approx 34 nm (ESI S1[†]).

The support surface oxygen functional groups available to interact with MNPs was reported to increase as follows MB-1500 < MB < MB-H₂O₂. It was thus expected that the hydrophilicity of the supports rises in a parallel. This trend was confirmed by the oxygen distribution in the different functional groups as calculated from XPS data (ESI S2 and S3⁺).²²

The Pd content in the MNPs/carbon materials catalysts is reported in Table 1. Higher Pd loadings were obtained with the MB-H₂O₂ carbon support. Considering the above mentioned surface properties of the carbon supports, this difference can be attributed to the higher surface area (an increase of the support surface area is expected to improve MNPs immobilization) and/ or the higher amount of surface oxygen (MNPs are expected to interact with the surface oxygen groups which could also improve their immobilization) of MB-H₂O₂ carbon material (Table 1).²²

HRTEM images of Pd/MB- H_2O_2 and Pd/MB-1500 catalysts are presented in Fig. 1 and 2. Spherical and homogeneously



Fig. 1 HRTEM images of Pd/MB- H_2O_2 (a) and Pd/MB-1500 (c) catalysts, and their corresponding size histograms (b) and (d).



Fig. 2 High magnification HRTEM micrographs of (a) $Pd/MB-H_2O_2$ and (b) a Pd nanoparticle on MB-1500.

dispersed Pd NPs without aggregation were obtained on both carbon materials. Larger nanoparticles with a mean diameter of 2.8 nm were measured in Pd/MB-1500 against a value of 1.8 nm in Pd/MB-H₂O₂ (Table 1). This difference in size can be explained on the basis of the higher amount of oxygen groups, particularly those of acidic character, on the surface of MB-H₂O₂ carbon support²² which can act as NPs stabilizers, thus limiting their growth.

Pd NPs stabilized with TPP and TOP were described in a recent report.²² Spherical Pd NPs with a mean size of 2.2 nm showing aggregation in some areas were observed by HRTEM for Pd(TPP)/MB-H₂O₂ catalyst (ESI S4†). Since this tendency to agglomerate was not observed at all for Pd(TPP)/MB-1500 sample (ESI S5†), it was related to the presence of a higher amount of oxygen groups, on the surface of MB-H₂O₂. Homogeneous in shape and well-dispersed supported Pd NPs with a mean diameter of 1.9 nm were in contrast observed when TOP was used as stabilizer ligand (ESI S4 and S5†). In this case, the steric hindrance due to the long aliphatic chains of TOP limits the approach and therefore the interaction between the Pd NPs and the carbon support surface oxygen groups, thus preventing their agglomeration.²²

The catalytic activity of the different carbon-supported Pd nanoparticles was investigated in a series of chemical transformations including oxidation and hydrogenation reactions. From previous work, the hydrophilicity of the carbon support was known to significantly influence the activity of these catalysts in the aerobic oxidation of benzyl alcohol in water.²² Quantitative conversion to benzaldehyde was obtained after 3.5 h reaction at 80 °C with all of the carbon-supported Pd NPs catalysts.

The catalytic activity of the carbon-supported Pd NPs was first evaluated in the microwave-assisted selective oxidation of benzyl alcohol to benzaldehyde using aqueous hydrogen peroxide as oxidant (Table 2 and Fig. 3). The catalysts showed good to excellent activities, with almost complete selectivity (90-95%) to benzaldehyde in all cases. The most remarkable feature is the high activities achieved after short reaction times (typically 3–5 min) under comparable conditions (90 °C, water). Particularly, excellent results were obtained with Pd(TPP)/MB-H₂O₂ and Pd(TOP)/MB-H₂O₂ after 3 min reaction. This

Table 2 Microwave-assisted selective aqueous oxidation of benzylalcohol catalyzed by carbon-supported Pd NPs^a

ОН	Pd catalyst MW, H ₂ O ₂ /wat	er C		
Catalyst	Reaction time (min)	Conversion (mol%)	Selectivity to benzaldehyde (mol%)	
Blank (no catalyst)	30	<20	>99	
MB-H ₂ O ₂	30	<30	>99	
MB-1500	30	<20	>99	
Pd(TOP)/MB-H ₂ O ₂	3	>95	90	
Pd(TOP)/MB-1500	3	70	92	
Pd(TPP)/MB-H ₂ O ₂	3	90	95	
Pd(TPP)/MB-1500	3	60	87	
Pd/MB-H ₂ O ₂	5	60	>95	
Pd/MB-1500	5	50	>95	

^{*a*} Reaction conditions: 2 mmol benzyl alcohol, 2 mL H₂O, 0.3 mL H₂O₂ (50% v/v), 0.05 g catalyst, microwaves, 300 W, 90 °C (100–110 °C maximum temperature reached), 100–200 psi (pressure developed in the systems).



Fig. 3 Selectivity switch to benzoic acid (over-oxidation) for Pd(TOP)/ MB-H₂O₂ at different reaction times. Reaction conditions: 0.2 mL benzyl alcohol, 2 mL H₂O, 0.3 mL H₂O₂ (50% v/v), 0.1 g catalyst, microwaves, 300 W, 90 °C (100–110 °C maximum temperature reached), 150–200 psi (pressure developed in the systems).

correlates well with the stronger water affinity of MB-H₂O₂ support (due to its higher oxygen content), being in good agreement with previous results.²² In any case, the best results were achieved with Pd(TOP)/MB-H2O2 catalyst with larger Pd content (2.58 wt%) as well as smaller Pd NPs size (1.9 nm). Therefore, both Pd NPs amount and size appear to be keyfactors for the optimum performance of this catalyst. Interestingly, blank runs performed without catalyst in similar reaction conditions led to low conversion of benzyl alcohol to benzaldehyde (10-30%) (similar to those obtained with the nonimpregnated carbon supports, blank experiments, Table 2) after longer times of reaction. This indicates that the oxidation of benzyl alcohol proceeds under microwave irradiation even without any added catalyst. Longer reaction times (≥ 5 min) led to increasing quantities of benzoic acid upon over-oxidation of benzaldehyde. Other catalysts including Pd/MB-H2O2 and Pd/ MB-1500 provided significantly lower yields of products, probably due to the additional stability and activity given by the combination of ligand-NPs and oxidised support,²² as well as to the lower Pd content observed for these catalytic systems (Table 1, last two entries).

Due to the interesting Pd redox properties, the aforementioned Pd catalytic systems were also applied in hydrogenation processes. Hydrogenation of biomass-derived platform molecules including C4 organic acids with Ru and Pd nanoparticles supported on carbonaceous materials as catalysts was recently reported in the literature.²⁷ For that purpose, the redox bifunctional activity of the carbon-supported Pd catalysts was tested in the microwave-assisted transfer hydrogenation of furfural (Scheme 1).

Hydrogenation is generally the most common route to upgrade furfural, from which the high yield preparation of numerous high added value chemicals can be attained, depending on the extension of the reduction step. Furfuryl alcohol can be generally obtained under mild reduction conditions using Cubased catalysts.²⁸ The use of noble metal supported catalysts (*e.g.* Pt, Ir NPs on different supports) combined with more severe hydrogenation conditions including higher temperatures



Scheme 1 Products distribution in the hydrogenation of furfural.

Table 3 Microwave-assisted hydrogenation of furfural catalyzed by
carbon-supported Pd NPs^a

H C	Cat. O onylation)		Cat. H ₂ hydrogenation	→ \
Catalyst	Reaction time (min)	Conversion (mol%)	Selectivity to furan (mol%)	Selectivity to THF (mol%)
Blank (no catalyst) MB-H ₂ O ₂ MB-1500 Pd(TOP)/MB-H ₂ O ₂ Pd(TOP)/MB-1500 Pd(TPP)/MB-H ₂ O ₂ Pd(TPP)/MB-1500 Pd/MB-H ₂ O ₂ Pd/MB-1500	60 60 30 30 30 30 30 45 45		 15 20 10 <10 30 35	80 72 85 80 70 65

^{*a*} Reaction conditions: 2 mmol furfural, 1.5 mL formic acid, 1.5 mL water, 0.1 g catalyst, microwaves, 100 °C, 100–150 W (average power), 150–200 psi (pressure developed in the systems).

and pressures can lead to complete hydrogenation of the furanic ring, yielding 2-methyltetrahydrofuran (MTHF), which has been recently highlighted as an interesting fuel blender compound²⁴ as well as a green solvent with improved extraction characteristics for polar compounds and a relatively high boiling point (80 °C).²⁹ Last, but not less importantly, decarbonylation of the aldehyde moiety of furfural, followed by ring hydrogenation leads to furan and further to tetrahydrofuran.³⁰ Furan derivatives find interesting applications as fuel blenders while THF is a well known and widely utilised organic solvent and polymer precursor, with an annual production in excess of 0.2 million tonnes per year.²⁴

The transfer hydrogenation reaction was carried out under microwave irradiation using a formic acid–water 1:1 mixture both as solvent and hydrogen donor. Optimised results in Table 3 show that THF is efficiently produced from furfural in high selectivities (>90%) after short reaction times, typically 30–45 min. The other major product obtained is furan (Scheme 1) while only traces of tetrahydrofurfuryl alcohol are observed. Furfuryl alcohol, 2-MTHF and related compounds were not found under the reaction conditions used. These results are in good agreement with previous work reporting the ability of Pd-based catalysts in promoting decarbonylation over hydrogenation in the first step.^{30,31} Upon decarbonylation, furan is readily hydrogenated to THF at relatively high hydrogen pressure (pressure in the microwave vessel was in all cases above 200 psi).

A full account on the various mechanisms of decarbonylation and ring hydrogenation in the formation of such compounds has been elegantly described in a recent report by Sitthisa and Resasco.³⁰ Decarbonylation seems to be related to the favourable formation of acyl surface species on Pd catalysts as compared to other metals (*e.g.* Ni, Cu) while ring hydrogenation occurs in Pd-based systems through a strong interaction of the furan ring with Pd (as opposed to Cu or Ni).³⁰ In the oxidation of benzyl alcohol (Table 2), the Pd(TOP)/MB-H₂O₂ system was found to be the most effective catalyst for the hydrogenation to THF. Besides the strong water affinity of the MB-H₂O₂ support (due to its high oxygen content), this catalyst has also the largest Pd content (2.58 wt%) and the smallest Pd NPs mean size (1.9 nm) which, as mentioned above, are most likely to be important parameters for the optimum performance of Pd(TOP)/MB-H₂O₂ in both selected redox reactions.

The extension of the hydrogenation in the microwave assisted reaction (and thus the selectivity to products) seems to be strongly influenced by two main parameters: temperature and reaction time. The power of microwave irradiation and the quantity of catalyst did not seem to have a major effect in a selectivity switch from THF to furan, although both improved the conversion in the systems at shorter times of microwave irradiation. However, a major selectivity to either furan or THF could be achieved playing with temperatures and reaction time. In this context, additional hydrogenation reactions were carried out using Pd(TOP)/MB-H₂O₂ as catalyst (Fig. 4 and 5). Higher temperatures (≥ 120 °C) or longer reaction times generally improved selectivities to THF. At high temperatures, formic acid decomposition into CO₂ + H₂ takes place to a larger extent (which was clearly noticed by a significant pressure increase, see



Fig. 4 Influence of the temperature on the selective hydrogenation of furfural to THF catalysed by $Pd(TOP)/MB-H_2O_2$. Inset corresponds to the temperature (red line) and pressure (blue line) profiles of one typical experiment. Reaction conditions: 2 mmol furfural, 1.5 mL formic acid, 1.5 mL water, 0.1 g catalyst, microwaves, 120–150 W (average power), 150–200 psi (pressure developed in the systems), 30 min reaction.



Fig. 5 Influence of the time of microwave irradiation on the selective hydrogenation of furfural to THF catalysed by $Pd(TOP)/MB-H_2O_2$. Reaction conditions: 2 mmol furfural, 1.5 mL formic acid, 1.5 mL water, microwaves, 120–150 W (average power), 150–200 psi (pressure developed in the systems), 100 °C.

- 13 B. Sunkara, J. Zhan, K. Jingjing, W. Igor, H. Yingging, H. Jibao,

(a) B. Wu, Y. Kuang, X. Zhang and J. Chen, *Nano Today*, 2011, 6, 75–90; (b) L. F. Mabena, S. Sinha Ray, S. D. Mhlanga and N. J. Coville, *Appl. Nanosci.*, 2011, 1, 67–77.

E. Jennifer, G. L. McPherson and T. V. John, Langmuir, 2011, 27, 7854-

- 15 (a) T. Matsumoto, M. Ueno, N. Wang and S. Kobayashi, Chem.-Asian J., 2008, 3, 196-214; (b) J. Han, Y. Liu and R. Guo, Adv. Funct. Mater., 2009, 19, 1112-1117; (c) A. Villa, D. Wang, N. Dimitratos, D. Su, V. Trevisan and L. Prati, Catal. Today, 2010, 150, 8-15; (d) B. Feng, Z. Hou, H. Yang, X. Wang, Y. Hu, H. Li, Y. Qiao, X. Zhao and Q. Huang, Langmuir, 2010, 26, 2505-2513; (e) A. M. Balu, A. Pineda, K. Yoshida, J. M. Campelo, P. L. Gai, R. Luque and A. A. Romero, Chem. Commun., 2010, 46, 7825-7827; (f) M. Tristany, K. Philippot, Y. Guari, V. Collière, P. Lecante and B. Chaudret, J. Mater. Chem., 2010, 20, 9523-9530; (g) A. Chen, Z. M. Cui, F. Niu, L. Jiang and W. G. Dong, Chem. Commun., 2010, 46, 6524-6526; (h) C. Hao and X. Zhao, Adv. Mater. Res., 2010, 113-114; (i) J. Okal, M. Zawadzki and W. Tylus, Appl. Catal., B, 2011, 101, 548-557; (j) V. B. Komvakis, M. Marti, A. Delimitis, I. A. Vasalos and K. S. Triantafyllidis, Appl. Catal., B, 2011, 103, 62-71; (k) C. M. Cirtiu, A. F. Dunlop-Brière and A. Moores, Green Chem., 2011, 13, 288-291.
- 16 (a) G. G. Wildgoose, C. E. Banks and R. G. Compton, *Small*, 2006, 2, 182–193; (b) B. Li, P. He, G. Yi, H. Lin and Y. Yuan, *Catal. Lett.*, 2009, 133, 33–40; (c) N. Dimitratos, J. A. Lopez-Sanchez and G. J. Hutchings, *Chem. Sci.*, 2012, 3, 20–44; (d) J. M. Campelo, T. D. Conesa, M. J. Gracia, M. J. Jurado, R. Luque, J. M. Marinas and A. A. Romero, *Green Chem.*, 2008, 10, 853–858.
- 17 M. Yu, Y. Wang, W. Sun and X. Yao, Adv. Synth. Catal., 2012, 354, 71–76.
- (a) D. Astruc, F. Lu and J. R. Aranzaes, Angew. Chem., Int. Ed., 2005, 44, 7852–7872; (b) M. Haruta, Chem. Rec., 2003, 3, 75–87; (c) M. Jahjah, Y. Kihn, E. Teuma and M. Gomez, J. Mol. Catal. A: Chem., 2010, 332, 106–112; (d) E. V. Starodubtseva, M. G. Vinogradov, O. V. Turova, N. A. Bumagin, E. G. Rakov and V. I. Sokolov, Catal. Commun., 2009, 10, 1441–1442.
- 19 (a) Z. Yang, S. Guo, X. Pan, J. Wang and X. Bao, *Energy Environ. Sci.*, 2011, 4, 4500; (b) N. Neelakandeswari, G. Sangami, P. Emayavaramban, S. Ganesh Babu, R. Karvembu and N. Dharmaraj, *J. Mol. Catal. A: Chem.*, 2012, in press.
- 20 M. S. Kwon, N. Kim, C. M. Park, J. S. Lee, K. Y. Kang and J. Park, Org. Lett., 2005, 7, 1077–1079.
- 21 (a) H. Liu, Y. Li, R. Luque and H. Jiang, Adv. Synth. Catal., 2011, 353, 3107–3113; (b) R. A. Arancon, H. R. Barros, A. M. Balu, C. Vargas and R. Luque, Green Chem., 2011, 13, 3162–3167; (c) A. M. Balu, B. Baruwati, E. Serrano, J. Cot, J. Garcia–Martinez, R. S. Varma and R. Luque, Green Chem., 2011, 13, 2750–2758.
- 22 E. J. Garcia-Suarez, M. Tristany, A. B. Garcia, V. Collière and K. Philippot, *Microporous Mesoporous Mater.*, 2012, **153**, 155–162.
- 23 M. J. Climent, A. Corma and S. Iborra, Chem. Rev., 2011, 111, 1072– 1133.
- 24 J. C. Serrano, R. Luque and A. Sepulveda-Escribano, *Chem. Soc. Rev.*, 2011, 40, 5266–5281.
- 25 S. R. Tennison, O. P. Kozynchenko, V. V. Strelko and A. J. Blackburn, *Porous carbons, US pat.*, 0032092, 2008.
- 26 E. Ramirez, S. Jansat, K. Philippot, P. Lecante, M. Gómez, A. Masdeu and B. Chaudret, J. Organomet. Chem., 2004, 689, 4601–4610.
- (a) C. S. K. Lin, R. Luque, J. H. Clark and C. Du, *Biofuels, Bioprod. Biorefin.*, 2012, **6**, 88–104; (b) R. Luque, J. H. Clark, K. Yoshida and P. L. Gai, *Chem. Commun.*, 2009, 5305–5307; (c) D. Pham Minh, M. Besson, C. Pinel, P. Fuertes and C. Petitjean, *Top. Catal.*, 2010, **53**, 1270–1273; (d) C. Delhomme, D. Weuster-Botz and F. E. Kuehn, *Green Chem.*, 2009, **11**, 13–26; (e) J. C. Serrano-Ruiz and J. A. Dumesic, *Green Chem.*, 2010, **11**, 992–999.
- 28 K. J. Zeitsch, *The Chemistry and Technology of Furfural and its Many By-Products*, Elsevier, Amsterdam, 1st edn, 2000, Sugar Series, vol. 13, pp. 150–155.
- 29 V. Pace, P. Hoyos, M. Fernandez, J. V. Sinisterra and A. Alcantara, *Green Chem.*, 2010, **12**, 1380–1382.
- 30 S. Sitthisa and D. E. Resasco, Catal. Lett., 2011, 141, 784-791.
- 31 R. D. Srivastava and A. K. Guha, J. Catal., 1985, 91, 254-262.
- 32 (a) R. Luque and J. H. Clark, *Catal. Commun.*, 2010, 11, 928–931; (b) R.
 M. Deshpande, V. V. Buwa, C. V. Rode, R. V. Chaudhari and P. L. Mills, *Catal. Commun.*, 2002, 3, 269–274.
- 33 http://www.thalesnano.com/products/x-cube

Fig. 4 inset) and thus the more hydrogen produced drives the reaction towards the two step decarbonylation and subsequent hydrogenation to THF. Longer times of irradiation obviously favoured the second hydrogenation step also leading to high selectivities to THF (Fig. 5).

Thus, this approach offers a simple and straightforward pathway to THF from furfural in comparison with other reported alternatives from related biomass-derived platform molecules (e.g. succinic acid),³² featuring the *in situ* generation of hydrogen in the systems by using a renewable-derived solvent together with mild reaction conditions and short reaction times.

Finally, our protocol may also pave the way for the utilisation of designer redox-bifunctional nanoparticle catalytic systems for oxidation and hydrogenation of related platform molecules (*e.g.* γ -valerolactone). Further investigations in our group are ongoing to translate the optimised batch microwave chemistry into more scalable continuous flow processes by mimicking the moderate to high temperatures and pressures achieved in a sealed microwave vessel using the X-CubeTM flow reactor.³³

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References

- R. J. White, R. Luque, V. L. Budarin, J. H. Clark and D. J. Macquarrie, *Chem. Soc. Rev.*, 2009, **38**, 481–494; (b) J. M. Campelo, D. Luna, R. Luque, J. M. Marinas and A. A. Romero, *ChemSusChem*, 2009, **2**, 18–45.
- G. Salas, C. C. Santini, K. Philippot, V. Collière, B. Chaudret, B. Fenet and P. F. Fazzini, *Dalton Trans.*, 2011, 40, 4660–4668; (b) G. Salas, A. Podgorsek, P. S. Campbell, C. C. Santini, A. A. H. Padua, M. F. Costa Gomes, K. Philippot, B. Chaudret and M. Turmine, *Phys. Chem. Chem. Phys.*, 2011, 13, 13527–13536; (c) J. L. Pellegatta, C. Blandy, V. Collière, R. Choukroun, B. Chaudret, P. Cheng and K. Philippot, *J. Mol. Catal. A: Chem.*, 2002, 178, 55–61; (d) C. Pan, K. Pelzer, K. Philippot, B. Chaudret, F. Dassenoy, P. Lecante and M. J. Casanove, *J. Am. Chem. Soc.*, 2001, 123, 7584–7593; (e) J. Dupont and J. D. Scholten, *Chem. Soc. Rev.*, 2010, 39, 1780–1804.
 V. Polshettiwar and A. Molnar, *Tetrahedron*, 2007, 63, 6949.
- 4 S. S. Próckl, W. Kleist, M. A. Gruber and K. Köhler, Angew. Chem., Int.
- Ed. 2004, 43, 1881.
- 5 C. P. Mehnert, D. W. Weaver and J. Y. Ying, *J. Am. Chem. Soc.*, 1998, **120**, 12289–12296.
- 6 Z. K. Esumi, R. Isono and T. Yoshimura, *Langmuir*, 2004, **20**, 237–242.
- 7 S. V. Ley, C. Ramarao, R. S. Gordon, A. B. Holmes, A. J. Morrison, I. F. McConvey, I. M. Shirley and S. C. Smith, *Chem. Commun.*, 2002, 1134–1136.
- 8 E. Roduner, Nanoscopic Materials. Size-Dependent Phenomena, Royal Society of Chemistry, Cambridge, 2006, pp. 239–262.
- 9 M. Lakshmi Kantam, K. B. S. Kumar, P. Srinivas and B. Sreedhar, *Adv. Synth. Catal.*, 2007, **349**, 1141–1149.
- 10 P. Serp and J. L. Figueiredo, *Carbon Materials for Catalysis*, Wiley-VCH, Weinheim, Germany, 2009.
- 11 K. C. Hwang, J. Phys. D: Appl. Phys., 2010, 43, 1-13.
- 12 (a) R. Singh, T. Premkumar, S. Thathan, G. Ji-Young and E. Kurt, *Chem.-Eur. J.*, 2010, **16**, 1728–1743; (b) R. Baron, G. G. Wildgoose and R. G. Compton, *J. Nanosci. Nanotechnol.*, 2009, **9**, 2274–2282.