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Dual-Site Mediated Hydrogenation Catalysis on Pd/NiO: Selective Biomass Transformation and Maintaining Catalytic Activity at Low Pd Loading.

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ABSTRACT: Creating a new chemical ecosystem based on platform chemicals derived from waste biomass has significant challenges; catalysts need to be able to convert these highly functionalised molecules to specific target chemicals, economical – not relying on large quantities of precious metals – and maintain activity over many cycles. Herein, we demonstrate how Pd/NiO is able to direct the selectivity of furfural hydrogenation and maintain performance at low Pd loading by a unique dual-site mechanism. Sol-immobilization was used to prepare 1 wt% Pd nanoparticles supported on NiO and TiO₂, with the Pd/NiO catalyst showing enhanced activity with a significantly different selectivity profile; Pd/NiO favours tetrahydrofurfuryl alcohol (72%), whereas Pd/TiO₂ produces furfuryl alcohol as the major product (68%). Density functional theory studies evidenced significant differences on the adsorption of furfural on both NiO and Pd surfaces. Based on this observation we hypothesised that the role of Pd was to dissociate hydrogen, with the NiO surface adsorbing furfural. This dual-site hydrogenation mechanism was supported by comparing the performance of 0.1 wt% Pd/NiO and 0.1 wt% Pd/TiO₂. In this study, the 0.1 and 1 wt% Pd/NiO catalysts had a comparable activity, whereas there was a 10-fold reduction in performance for 0.1 wt% Pd/TiO₂. When using TiO₂ as the support the Pd nanoparticles are responsible for both hydrogen dissociation and furfural adsorption, and the activity is strongly correlated with the effective metal surface area. This work has significant implications for the upgrading of bio-derived feedstocks, suggesting alternative ways for promoting selective transformations and reducing the reliance on precious metals.

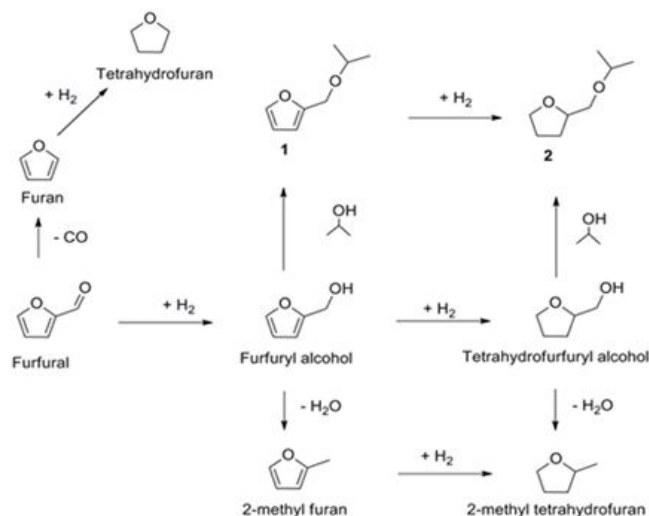
INTRODUCTION

To expedite the transition from a chemical ecosystem based on petroleum to one based on those derived from sustainable bio-derived platform chemicals requires a concerted effort: catalysts need to be (i) highly active at mild conditions, (ii) be atom efficient and achieve a high selectivity to a desired product, (iii) maintain performance over many cycles, and (iv) be economical by not relying on large amounts of scarce and expensive metals. This

objective necessitates detailed catalytic studies that probes the performance on an atomistic level and are able to describe how specific materials promote these complex transformations.

In this regard, there have been significant efforts to understand the transformation of lignocellulosic biomass to fine chemicals and fuels.¹⁻³ Furfural, derived from the hydrolysis of the hemicellulosic fraction of lignocellulose, is considered as a viable platform molecule to many value-added products (Scheme 1).^{4,5} Furfuryl alcohol (FA),

obtained via hydrogenation of the furfural carbonyl group, is widely used for producing resins, lubricants, plasticizers and fibers.^{6,7} The hydrogenation of both carbonyl group and furanic ring produces tetrahydrofurfuryl alcohol (THFA), a green solvent used in printer inks and agriculture applications.⁸ In spite of the relevance of these compounds, furfural hydrogenation presents a complex pathway, requiring tailored catalysts to direct the selectivity towards desired products.



Scheme 1. Chemical routes for furfural valorization.

To optimise the hydrogenation reaction of furfural many noble metal catalysts have been studied.⁹ Pd and Ir lead to the formation of FA as the main product^{10,11} whereas Ni promotes selectivity to THFA.¹² The product distribution depends on the affinity of the reactant to the metal, as well as the preferential mode of adsorption on specific sites (e.g. steps, edges, corners and terraces) of the catalyst.^{9,13} A perpendicular adsorption, through the carbonyl group, results in the formation of furfuryl alcohol and 2-methyl furan.^{6,14} A flat adsorption, through the furanic ring and carbonyl functionality, produces THFA.¹⁵ At high temperature, a flat orientation results in the decarbonylation of furfural, producing furan and tetrahydrofuran.^{7,16} A strategy for tuning the selectivity is to selectively block these specific active sites on the metal surface using thiolates or polymers such as polyvinyl alcohol (PVA);¹⁷⁻¹⁹ the latter of these has a dual purpose as it is commonly used to limit the growth of colloidal Pd nanoparticles during sol-immobilization.¹⁸ However, the effects of the metal sites on directing the transformation of highly functionalized bio-derived substrates to specific products cannot be assessed in isolation; the support material is not benign and has a significant influence on the catalytic properties.²⁰⁻²² The 'so-called' strong metal-support interactions (SMSI) at the interface is responsible for electron transfer, charge redistribution, morphological changes, metal decoration or encapsulation, metal-support borderline site creation, and spillover phenomena.²³⁻²⁵ Furthermore, the supports themselves are involved in catalytic transformations either in isolation or

in tandem with supported metal nanoparticles.²⁶ Indeed, sea urchin-like NiO, was recently demonstrated to possess excellent catalytic activity in the selective hydrogenation of furfural to FA.²⁷ The mechanism for the enhancement enabled by the metal support interaction is very specific – both for the metal/metal oxide combination and the reaction under study. For furfural hydrogenation, Somorjai et al. used sum frequency generation (SFG) vibrational spectroscopy to reveal the role of O-vacancies at the metal support perimeter in determining the distribution of products over Pt/TiO₂ catalysts.²⁸ Elsewhere, Seemala et al. demonstrated that different supports (Al₂O₃ and TiO₂) induce a different surface composition of bimetallic Cu-Ni, and therefore a different activity in the furfural hydrogenation.¹⁴

It is clear that tailoring the properties of both the metal nanoparticles and the support has profound consequences for the resultant performance towards the hydrogenation of furfural. In this study, our combined experimental and theoretical approach demonstrates how Pd/NiO not only directs the selectivity of furfural hydrogenation but operates through a unique dual-site hydrogenation mechanism that allows for high catalytic activity to be maintained at low (0.1 wt%) Pd loading.

EXPERIMENTAL

Catalyst synthesis: NiO preparation: Nickel(II) nitrate hexahydrate (0.134 M, Ni(NO₃)₂•6H₂O, Sigma-Aldrich, purity > 99.9%) and urea (Sigma-Aldrich, purity > 99.5%) (Ni/urea molar ratio 1:12 mol/mol) were solubilized and mixed in 0.2 L of water with magnetic stirring for 240 min. at 80 °C. The suspension was filtered to separate the precipitated nickel hydroxide, Ni(OH)₂, from the solution. The powder was washed with 2 L of water, dried at 100 °C for 120 min. and finally calcined at 300 °C for 60 min.

Pd catalyst: Pd(II) salt (0.051 mmol of Na₂PdCl₄ Sigma-Aldrich, purity > 99.9%) was dissolved in 0.1 L of water and sequentially 1 mL of 1 wt% polyvinyl alcohol solution (Pd/PVA mass ratio 1:0.5 wt/wt) was introduced. As-obtained yellow solution was maintained under vigorous magnetic stirring for 3 min, then a precise volume of 0.1 M NaBH₄ solution (Pd/NaBH₄ molar ratio 1:8 mol/mol) was injected. Immediately, the solution assumed a brown coloration, indicating the formation of Pd(o) colloid. After few minutes, sulphuric acid was added to adjust the pH to 2 and then the solid support was dispersed in the vigorously stirring colloid. The amount of the support was selected in order to achieve a final palladium loading of 1 and 0.1 wt% (on the assumption of a quantitative metal uptake on the support). After filtration and washing, the catalysts were dried at 100 °C for 120 min.

Catalytic tests: Catalytic performances in the furfural (F) (Sigma-Aldrich, purity 99%) hydrogenation reaction were evaluated at 25 °C, carrying-out batch experiments in a stainless steel reactor (0.03 L capacity), equipped with heater, mechanical stirrer, gas supply system and thermocouple for temperature control. The reactor was

filled with 0.015 L of furfural solution (0.3 M in 2-propanol) and the proper amount of catalyst (F/metal ratio=500 mol/mol) was suspended in the solution. The reactor was pressurized with 5 bar of pure hydrogen. The mixture was kept at room temperature (25°C) under mechanical stirring (1250 rpm). At the end of the test, gas flow switched from H₂ to N₂ for purging the autoclave with flowing nitrogen. Periodical sampling (200 µL) allowed for monitoring the progress of the reaction by chromatographic analysis, using a HP 7820A gas chromatograph equipped with a capillary column HP-5 30m x 0.32mm, 0.25 µm Film, by Agilent Technologies. Compound identification was performed on the basis of retention times obtained from the analysis of authentic samples. External standard method (n-octanol) was used for the quantitative analysis.

Transmission Electron Microscopy (TEM). Holey copper grids were used for performing TEM studies, where small quantities of powdered catalysts were deposited onto the grids prior to analysis. The TEM studies – both for producing images and elemental analysis through X-ray energy dispersive spectroscopy (XEDS) – were conducted in High Annular Dark Field mode using a FEI Titan3 80-300 microscope. The acceleration voltage was 200 kV. All data was analyzed using the software packages: Digital Micrograph, TIA, and INCA. Information on particles size distribution (PSD) assumed a truncated cubooctahedron particle shape and was assessed using Gauss software.

X-ray Photoelectron Spectroscopy (XPS). The acquisition of X-ray photoelectron spectra (XPS) was performed on a PHI 3056 XPS with an Al anode source operated at 15kV and an applied power of 0.35 kW. A sputter cleaned silver foil was used for checking the energy scale calibration. Powders were hand-pressed between two clean slices of indium foil; the indium foil, in which the powders were embedded, was then placed in the sample holder with a fragment of carbon tape (Nisshin E.M. Co. LTD). The lowest C1s binding energy species were shifted about 0.1 eV to 284.8 eV for comparison purposes with literature values. The XPS analyses did not require any pretreatments (i.e. cleaning, heating, processing). High resolution scans were acquired with a 23.5 eV pass energy and 0.05 eV steps a minimum of 50 times; survey scans were measured with a 93.9 eV pass energy and 0.5 eV energy steps a minimum of 25 times. Peak area integration provided surface concentrations, considering the proper standard atomic sensitivity factors provided by the instrument producer. Gaussian-Lorentzian functions and a Shirley-type background were used for spectra deconvolution.

X-ray Absorption Fine Structure (XAFS). Measurements were conducted at the UK national synchrotron Diamond Light Source, using the core-XAFS beamline, B18. XAFS data at the Pd K edge were acquired simultaneously with a Pd foil reference positioned between I_t and I_{ref}. Samples were prepared as self-supporting pellets and were assessed using fluorescence acquisition using a QEXAFS set-up with a fast-scanning Si(311) double crystal monochromator and a 36 element Ge detector. Each

spectrum was measured for 4 min and on average 6 scans were measured to improve the data quality of the final summed spectrum. Data were measured in *K* space to a maximum value of 16. Data processing was performed using IFEFFIT²⁹ with the Horae³⁰ packages (Athena and Artemis). The amplitude reduction factor, *S*₀² was determined by analyzing a Pd foil and determined to be 0.88 and used as a fixed input parameter.

Infrared CO Chemisorption Studies. A Nicolet iso spectrometer was used for all Fourier transform infrared (FTIR) spectroscopy measurements. The spectral resolution was 2 cm⁻¹ and the total number of scans of the sample and the background was 64. All samples were measured in transmission as ultra-thin self-supporting discs; approximately 25 mg of sample was used to form a disc of 13 mm diameter. A Harrick Dewar cell was used for the environmental studies. The sample environment was flushed with He for 30 min to obtain a background spectrum before CO was introduced using a 10% CO/He mixture at 70 mL min over a 30 s period. There were 3 doses of CO for each experiment. Before obtaining a final spectrum the gas was switched to helium for 30 min at 70 mL min⁻¹, in order to remove gaseous and physisorbed CO.

Atomic Absorption Spectroscopy (AAS). The palladium concentration on solid catalysts was determined by AAS analysis of the post-synthesis filtrate using a Perkin Elmer 3100 instrument. For each catalyst, 0.01 L of the filtered solution was withdrawn and analyzed.

Powder X-ray diffraction (XRD). X-ray diffraction patterns were collected on a PANalytical X'PertPRO X-ray diffractometer utilizing a Cu-K_α radiation source (40 kV and 30 mA). XRD patterns were recorded in the 10-80° 2θ range over a scan time of 1 h.

DFT Studies. We used the Vienna Ab Initio Simulation Package (VASP) to perform all the spin polarized periodic density functional theory based calculations.³¹⁻³³ The projector augmented wave (PAW) method was used and a cut-off energy of 550 eV was employed for the expansion of the plane-wave basis sets, which gave bulk energies converged to within 10⁻⁵ eV.³⁴ For the structural optimization we chose a convergence criterion of 0.01 eV Å⁻¹ and a k-point grid of 3×3×1 was employed for all slab calculations. The Perdew-Burke-Ernzerhof (PBE) version of generalized gradient approximation (GGA) was used to carry out geometry optimizations and the total energy calculations.³⁵ As the dispersive effects may be significant for the systems under consideration we also used Grimme's dispersion correction (DFT+D₃).³⁶ The ideal surfaces of Pd(111) and NiO(110) and rutile TiO₂(111) were modelled by a 4×4 cell with 5 atomic layers. Of the five atomic layers, the bottom three layers were fixed to mimic the bulk of the material and in the direction perpendicular to the surface we used a vacuum gap of ~15 Å, which is sufficient to eliminate slab-slab interactions. The slabs were cut from bulk Pd, NiO and rutile TiO₂ with a calculated energy minimized lattice constant of 3.904 Å (Exp. 3.891 Å), 4.192 Å (Exp. 4.168 Å)

and 4.695 Å (Exp. 4.594 Å), respectively. In all the calculations, the adsorption of furfural was allowed on only one of the two exposed surfaces. The spurious dipole moment due to the adsorbed species, was taken into account by using the methods implemented in VASP according to the procedures of Markov et al. and Neugebauer et al.^{37,38} For the calculations on the interaction of furfural on the NiO(110) and TiO₂(111) surfaces we used DFT+U. Previous studies have shown that an U value of 5.77 eV, obtained by using linear response methods, for the d-orbital of Ni is suitable.³⁹ It has been also reported that an U value of 4.20 eV is suitable for the d-orbitals of Ti.⁴⁰

RESULTS

Pd nanoparticles were supported on TiO₂ (P25, 50 m² g⁻¹) and NiO through an established sol-immobilization method with a loading of 1 wt%. The metal loading was confirmed by Atomic Absorption Spectroscopy (AAS). The NiO support was prepared using an in-house method involving the precipitation of Ni(OH)₂ in aqueous solution, followed by subsequent calcination. The preparation resulted in a nanostructured NiO with a particle size of 6 nm and a surface area of 210 m²g⁻¹. The NiO phase was identified using XRD (Figure S1). X-ray photoelectron spectroscopy (XPS) analysis provided useful insight on the nature of Ni surface species (Figures S2). Ni2p_{3/2} data disclosed the presence of two main peaks corresponding to different Ni species on the surface; the first peak centered around 854.5 eV is due to Ni²⁺-O lattice species, while the second peak centered around 856.1 eV confirmed that Ni(OH)₂ was also formed at the surface (Figure S2). The oxidation state of surface species has been investigated by XPS. Comparison of Pd 3d XP spectra for Pd/TiO₂ and Pd/NiO (Figure S2) revealed that Pd is present in the metallic form in both cases with a similar percentage of Pd⁰ (85% and 88% for Pd/NiO and for Pd/TiO₂, respectively). The supported metal nanoparticle catalysts and bare supports were then evaluated for the hydrogenation of furfural under mild conditions (Table 1); furfural 0.3 M, furfural/Pd ratio 500 mol/mol, 5 bar H₂, 50 °C and 2-propanol as solvent. Prior to the catalytic evaluation the appropriate Pd/furfural molar ratio was established to ensure the catalytic performance was in the kinetic regime and not mass-transport limited (Table S1). The catalytic activity testing demonstrated that the 1 wt% Pd/NiO catalyst exhibited superior activity compare to the 1 wt% Pd/TiO₂ (470 (metal mol)⁻¹ h⁻¹ vs. 321 (metal mol)⁻¹ h⁻¹) - approximately a 50% increase in activity. Notably, not only was there a difference in activity, there was also a pronounced change in the selectivity profile. The Pd/NiO catalyst had a preferential selectivity towards THFA (72%), whereas Pd/TiO₂ favoured FA (67 %). Catalytic performance testing of the bare supports was also performed as a control experiment. Here, under analogous testing conditions there was no observable conversion of furfural on TiO₂. However, NiO showed a minor level of activity (39 (metal mol)⁻¹ h⁻¹) with THFA found as the major

product (87 %). This observation is consistent with recent studies that have already proven that NiO is able to hydrogenate furfural in the absence of precious metals.²⁷ The time-on-line data for the catalytic testing (Figure S3 and S4) confirmed that Pd/NiO favors THFA over FA as the major product at all-time points. However, there is a sharp increase in THFA selectivity as the conversion of furfural progresses. This arises because of sequential hydrogenation reactions and the transformation of isopropyl tetrahydrofurfuryl ether to THFA. To understand the difference in catalytic properties a series of studies to establish the physicochemical properties of the Pd nanoparticles was performed; the intention was to establish whether the catalytic data could be accounted for solely by the changes to Pd or if there was a synergistic effect between the metal and support. The Pd nanoparticle size data was found using transmission electron microscopy (Table 1, Figure S5).

The Pd/TiO₂ and Pd/NiO catalysts were found to have comparable Pd particle sizes of 2.7 and 3.1 nm, respectively. Considering that smaller Pd nanoparticles have a larger available surface area the difference in catalytic activity cannot be rationalized by this effect. In this instance, the catalyst with larger particles, and therefore smaller surface area, has the greatest catalytic activity. To probe the properties of the supported nanoparticles in further detail a high-angle annular dark-field scanning TEM (HAADF-STEM) study was performed (Figure 1). The Pd/TiO₂ catalyst has been characterized previously by HAADF-STEM with the data reported elsewhere;¹⁸ to summarize, the Pd NPs were found to exhibit a significant number of sub-nanometer 'clusters', as was also found for Au NPs prepared using an analogous low-temperature sol-immobilization procedure.⁴⁰

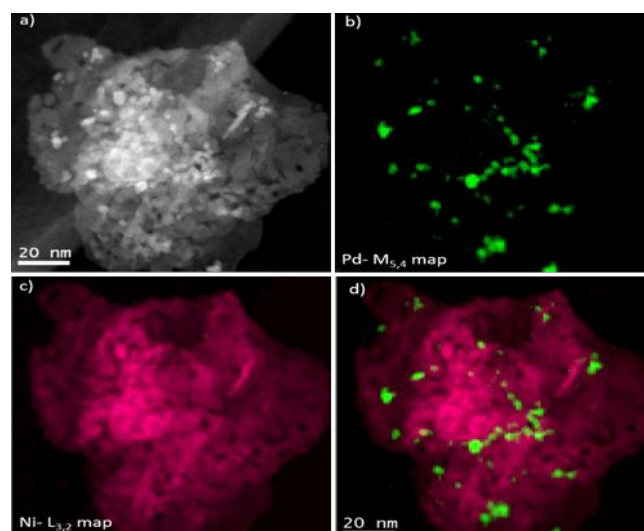


Figure 1. Representative low magnification STEM-HAADF images of Pd-NiO catalyst. (a–d) Montage of HAADF image of Pd particles showing the corresponding EELS elemental maps and RGB reconstructed overlay maps [Green–Pd: Pink–Ni].

Figure 1a, shows a representative HAADF-STEM image of the Pd/NiO catalyst. In HAADF imaging, the intensity is approximately proportional to the square of the atomic number of the scattering element and therefore provides information of the local composition. In Figure 1a, the Pd particles ($Z = 46$) are clearly revealed as bright features on the nickel oxide matrix ($Z \approx 36$). This interpretation was confirmed by using electron energy loss spectroscopy (EELS). The EELS maps, Figure 1b-d, illustrate the presence of well-dispersed Pd nanoparticles (Pd-M_{4,5} map in color green) on NiO (Ni-L_{3,2} map in color pink). The NiO appears as a collection of agglomerated platelets with diameters between 20 and 30 nm. Atomic resolution STEM images of a selected area (Figure 2a) reveals a highly crystalline particle with multi twinning planes and clearly resolved

lattice planes with a d spacing of 2.26 Å. This is in agreement with the expected spacing of the (111) planes of face centered cubic Pd metal. Additionally, high resolution HAADF-STEM (Figure 2b) provides evidence of the presence of a sub-nanometer species (marked by yellow circles). This is in agreement with previous HAADF-STEM studies on other supported nanoparticle catalysts prepared using low temperature sol-immobilization.^{18,41} Figure S6 show the deconvolution of the EELS data into three components originating from the supporting NiO material (pink), the background (not shown) and the pure Pd particle (green). The features present could be assigned to Pd-M_{4,5} edge (for Pd with onset at 335 eV), the oxygen K edge (onset at around 532 eV) and the Ni-L_{3,2} edge (at 855 eV).

Table 1 Catalytic activity testing for the hydrogenation of furfural at 50°C and TEM particle size data.

Catalyst ^a	Activity ^b	Selectivity (%) ^c						Pd particle size ^e		
		FA	THFA	2-MF	2-MTHF	Furan	Ethers	Median (nm)	Deviation (nm)	
										1
TiO ₂	-	-	-	-	-	-	-	-		
NiO	39	4 ^d	87 ^d	-	-	-	-	4 ^d		
1% Pd/NiO	470	14	72	1	5	1	-	3	3.1	0.5
1% Pd/TiO ₂	321	67	23	-	-	1	5	-	2.7	0.9

FA = furfuryl alcohol, THFA = tetrahydrofurfuryl alcohol, 2-MF = 2-methylfuran, 2-MTHF = 2-methyltetrahydrofuran. ^a Reaction conditions: Furfural = 0.3 M; F/metal ratio=500 mol/mol, 50°C, 5 bar H₂, solvent 2-propanol. ^b Mol of furfural converted per hour per mol of metal, calculated after 15 min reaction mol (metal mol)⁻¹ h⁻¹. ^c Selectivity at 60% conversion. ^d Selectivity at 10% conversion. ^e Calculated using 300 particles. Histograms shown in Figure S5.

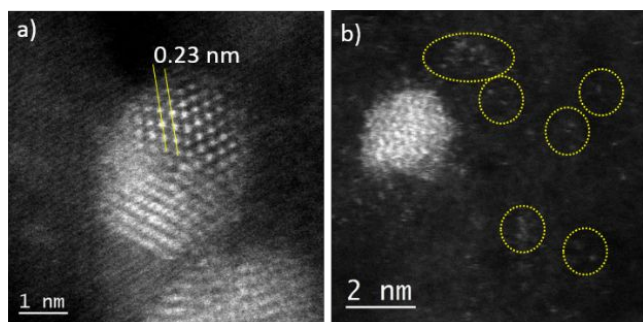


Figure 2. High-resolution STEM-HAADF images of 1 wt% Pd/NiO catalyst showing a crystalline particle (a) and sub-nanometer species of Pd distributed across the support (b).

Although particle size is a valuable descriptor for catalytic activity there are other effects to consider. Notably, the distribution of discrete sites on metal nanoparticle surfaces and their inherent ability to promote catalytic transformations is also of significant importance. The surface characteristics of the Pd/TiO₂ and Pd/NiO catalysts were assessed by a combination of CO adsorption and Fourier transform infrared (FTIR) spectroscopy (Figure 3).

Before assigning the vibrational absorption bands on both catalysts there is a clear difference between the

intensity of the absorption spectra; the data is normalized to mass of Pd and the reduced intensity for the Pd/NiO data is indicative of a smaller available Pd surface area in agreement with the TEM data. The signals at 2120 cm⁻¹ and 2086 cm⁻¹ are ascribed to CO linearly bound to Pd⁺ and Pd particle corners, respectively.⁴² The signal at 1985 cm⁻¹ is related to bridge-bonded CO on Pd facets, whereas that at 1945 cm⁻¹ is attributed to bridge-bonded CO on Pd edges.⁴² The shoulder at 1865 cm⁻¹ can be assigned to 3-fold sites.⁴³ The spectrum of 1 wt% Pd/NiO has additional bands at 2165, 2140, and 1927 cm⁻¹. The band at 2165 cm⁻¹ is attributable to CO adsorption on NiO,⁴⁴ with the band at 1927 cm⁻¹ assigned to bridge-bonded CO on Pd facets.⁴⁵ The FTIR spectra with CO probe molecule adsorption do not reveal profound differences in the surfaces of the Pd nanoparticles of both catalysts. Previously, the ratio of linear to bridge-bonded CO has been used to infer the likelihood of parallel or perpendicular furfural adsorption and then correlated to the selectivity of furfural hydrogenation. In the spectra presented in Figure 3, there are only minor differences in the linear/bridged ratio (0.28 and 0.32 for Pd/NiO and Pd/TiO₂, respectively), which confirms that the observed difference in selectivity for the hydrogenation of furfural is not linked to the surface characteristics of the Pd nanoparticles. This observation led to the hypothesis that there are distinct mechanistic

pathways for both catalysts that are directed by differences in the metal-support interaction.

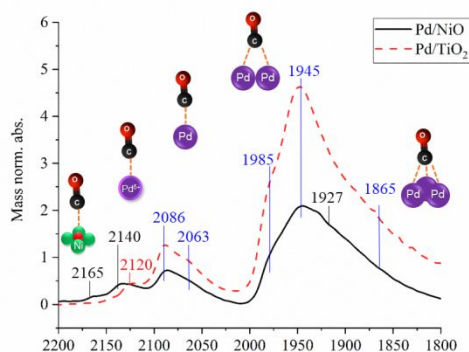


Figure 3. CO adsorption FTIR studies for Pd/NiO (black line) and Pd/TiO₂ (red line). Peaks assigned in blue are present in both catalysts with those is red and black assigned solely to Pd/NiO and Pd/TiO₂ respectively.

To probe the effect of the support in greater detail a density functional theory with dispersion correction (DFT+D₃) study into the adsorption energetics of furfural on Pd(111), NiO(110), TiO₂(111) and Pd₁₆-NiO(110) was undertaken. We first compare the calculated adsorption energies (*E*_{ad}) for the interaction of furfural on Pd(111) and NiO(110) surfaces. All the optimized structures of furfural on Pd(111) and NiO(110) surfaces are shown in Figure S7 and Figure S8. Our calculations show that the furfural molecule with a slanted configuration is more stable on NiO(110) surface (*E*_{ad} = -2.572 eV) as compared to its adsorption on Pd(111) surface (*E*_{ad} = -1.649 eV) with a parallel configuration. Previous studies have also shown that the parallel configuration of furfural on Pd(111) surface is more stable than its other possible orientations and our calculated adsorption energy value for the adsorption of furfural on the Pd(111) surface is comparable with the previously reported values.^{18,46–48} In the former case, the furanic ring is adsorbed *via* the O and C atoms of the -CHO group and O-atom of the furanic ring (See Table S2) but in the latter the interaction is *via* the C-atoms of the furanic ring and O-atom of the -CHO group. Similar calculations are also performed on TiO₂(111) and on a single atomic layer of Pd adsorbed on NiO (110) surface i.e., Pd₁₆-NiO(110) (Figure S9 and S10, Table S3). On the TiO₂(111) surface it is seen that the furfural molecule has a unique mode of interaction; it is adsorbed through two C-atoms of the furanic ring with two O-atoms on the surface leaving the -CHO group non-interactive with the TiO₂(111) surface. On the other hand the adsorption of furfural on Pd₁₆-NiO(110) is *via* the furanic C and aldehydic C and O-atoms. The calculated adsorption energy of the furfural molecule on TiO₂(111) and Pd₁₆-NiO(110) are -4.113 eV and -1.946 eV, respectively. Figure 4 shows the most stable structures of furfural on Pd(111), NiO(110), TiO₂(111) and Pd₁₆-NiO(110) surfaces.

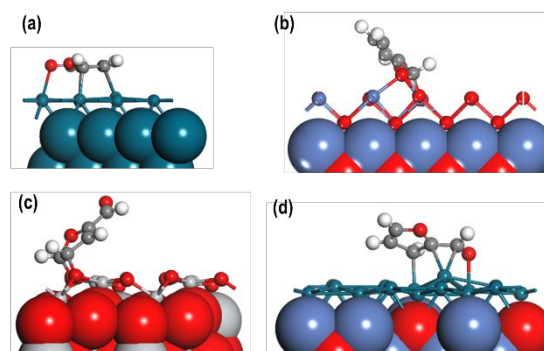


Figure 4. The optimized structures of furfural adsorbed on (a) Pd(111), (b) NiO(110), (c) TiO₂(111) and (d) Pd₁₆/NiO(110) surfaces. For clarity, the furfural molecule and the first two layers of the surfaces are shown as ball and stick and lower layers are shown in the CPK format.

The DFT study confirmed distinct differences on the nature of furfural adsorption on Pd, TiO₂, NiO, and Pd₁₆-NiO systems. These observations, combined with the selectivity profile of bare NiO, suggested that the difference in activity is associated with how NiO is able to activate furfural. In this scenario, it was hypothesized that the sole role of Pd on the Pd/NiO catalyst is to dissociate hydrogen. This hypothesis is consistent with recent hydrogenation studies on Ru/NiO/Ni(OH)₂/C catalysts, where an analogous mechanism was proposed.⁴⁹ Considering the facile nature of hydrogen dissociation (*E*_{barrier} = 0.030 eV and 0.854 eV for the reverse reaction), which agrees well with our previous studies⁵⁰ (See Figure S11) over Pd surfaces. Therefore, this process would not be expected to be rate limiting. By extension, the catalytic activity would not have a linear correlation with the Pd metal loading (surface area), i.e. fast hydrogen dissociation on Pd surfaces, with slower hydrogenation of furfural on NiO surfaces. To test this hypothesis two further catalysts were prepared – 0.1 wt% Pd/TiO₂ and 0.1 wt% Pd/NiO. The Pd loading was confirmed using AAS and the particle size assessed by HRTEM. The 0.1 wt% Pd/TiO₂ and 0.1 wt% NiO catalysts were found to have particle sizes of 2.2 and 3.8 nm, respectively) (Figure S12).

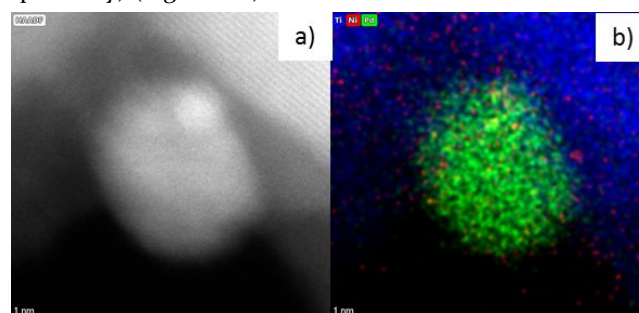


Figure 5. a) HAADF Signal, b) HAADF signal f physical mixture of 1 wt% Pd/TiO₂ and NiO after reaction.

The lower loading supported Pd catalysts were assessed using the same testing procedure reported earlier with the data presented in Table 1. The 0.1 wt% Pd/TiO₂ catalyst

had an activity of $31 \text{ mol (metal mol)}^{-1} \text{ h}^{-1}$, an approximate 10 fold reduction in performance compared to the 1 wt\% Pd/TiO_2 ($321 \text{ mol (metal mol)}^{-1} \text{ h}^{-1}$) (Table 2). For the Pd/TiO_2 catalysts, both the hydrogen dissociation and furfural adsorption happen on the Pd surface. As the Pd loading decreases there is concomitant, and in this case, equal reduction in Pd surface area and as a consequence the rate of turnover. Conversely, the 0.1 wt\% Pd/NiO catalyst shows only a minor loss of activity compared to the 1 wt\% Pd/NiO catalyst – $421 \text{ mol (metal mol)}^{-1} \text{ h}^{-1}$ vs. $471 \text{ mol (metal mol)}^{-1} \text{ h}^{-1}$. The inference is that the hydrogenation mechanism of furfural is indeed different on Pd/NiO compared to Pd/TiO_2 . This supports the proposed hypothesis that the role of Pd is to dissociate hydrogen and that the role of NiO is to bind and activate the substrate. It is worth stating that a minor amount of hydrogenation of furfural on the Pd surface is also possible, as is suggested by the subtle change in selectivity profile compared to NiO. However, seeing as the activity is maintained at such low Pd loadings it would infer that the vast majority of furfural hydrogenation occurs on the NiO.

A further series of control experiments were then performed to assess the hydrogen spillover in greater detail. Initially, the catalytic activity of a physical mixture of 1 wt\% Pd/TiO_2 and NiO was assessed; the intention was

to confirm that the enhancement afforded by the NiO support was linked to the Pd NiO interaction. The catalytic activity of the physical mixture proved different to that of the Pd/TiO_2 alone. The activity increased from 321 to $436 \text{ (metal mol)}^{-1} \text{ h}^{-1}$, a value greater than the addition of the activity of both separate components (1 wt\% Pd/TiO_2 and NiO). Furthermore, there was also a change in the selectivity to THFA, increasing from 23 to 33% . The enhancement observed for the physical mixture of 1 wt\% Pd/TiO_2 and NiO can be explained by the detachment of Ni during the hydrogenation reaction, which decorate Pd nanoparticles as found with HAADF STEM EDX studies (Figure 5). To assess further, whether this increase in performance could be a result of long-range hydrogen spillover, a control experiment of the $0.1 \text{ wt\% Pd/TiO}_2$ with NiO was also performed. Here, the physical mixture showed broadly consistent catalytic performance to the $0.1 \text{ wt\% Pd/TiO}_2$, with no discernible increase in rate; the dissolution and re-adsorption of Pd is negligible at these low loadings so no promotional effect is observed. These two control experiments confirmed that the dual-site hydrogenation mechanism found for Pd/NiO requires the intimate contact of both Pd/NiO .

Table 2 Catalytic activity testing for the hydrogenation of furfural at 50°C and TEM particle size data for lower loading Pd/TiO_2 catalysts and control experiments.

Catalyst ^a	Activity ^b	Selectivity (%) ^c							Pd particle size ^e	
		FA	THFA	2-MF	2-MTHF	Furan	Ethers		Median (nm)	Deviation (nm)
							1	2		
0.1 \% Pd/TiO_2	31	65 ^d	20 ^d	2 ^d	-	2 ^d	3 ^d	-	2.2	0.4
$0.1 \text{ \% Pd/TiO}_2 + \text{NiO}$	45	50	38	2	-	5	2	-	-	-
$1 \text{ \% Pd/TiO}_2 + \text{NiO}$	436	56	33	-	2	-	3	1	-	-
0.1 \% Pd/NiO	421	10	81	-	7	-	-	1	3.8	1.2

FA = furfuryl alcohol, THFA = tetrahydrofurfuryl alcohol, 2-MF = 2-methylfuran, 2-MTHF = 2-methyltetrahydrofuran. ^a Reaction conditions: Furfural = 0.3 M ; F/metal ratio = 500 mol/mol , 50°C , 5 bar H_2 , solvent 2-propanol. ^b Mol of furfural converted per hour per mol of metal, calculated after 15 min reaction $\text{mol (metal mol)}^{-1} \text{ h}^{-1}$. ^c Selectivity at 60% conversion. ^d Selectivity at 10% conversion. ^e Calculated using 100 particles. Histogram shown in Figures S7.

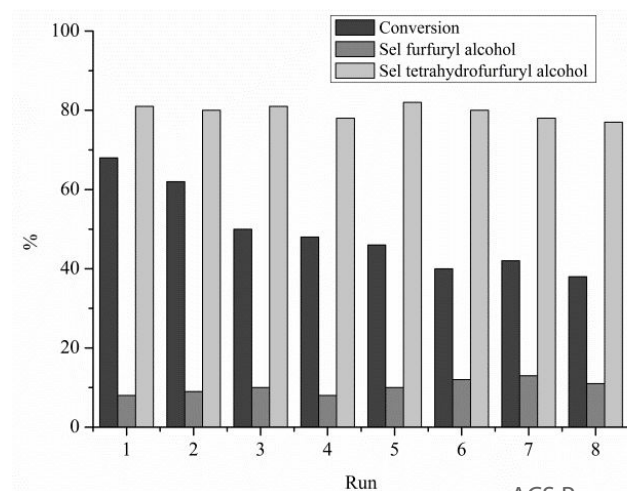
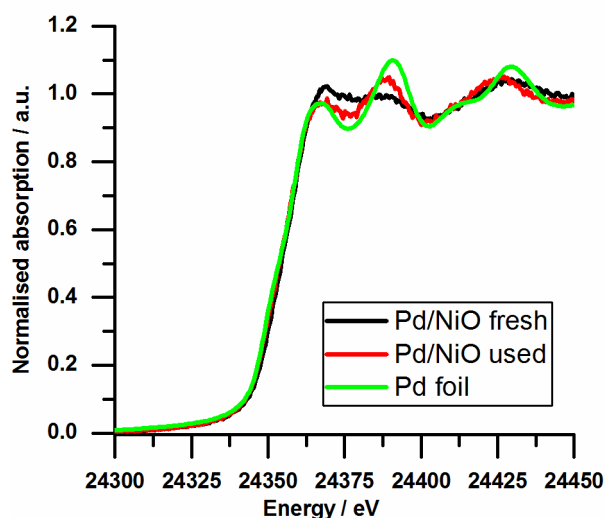


Figure 6. Reusability study for 1 wt\% Pd/NiO detailing changes to conversion and selectivity over 8 cycles, reaction time 5h. Recycling experiments were performed by reusing the catalyst in the next run without any additional pretreatment.

The initial catalytic activity screening has found that Pd/NiO offers a unique dual site mechanism for the hydrogenation of furfural. To investigate the catalyst further a catalytic reusability study, over 8 cycles, was performed (Figure 6). The reusability study found that there was an initial reduction in the conversion of furfural, reducing from ~ 65 to 50% between the first and third runs, with a more gradual decline in conversion to $\sim 40\%$ by the

1 eighth cycle. The final three catalytic screening cycles show
 2 a plateau region with no further reduction in catalytic
 3 activity. Throughout all the reusability studies, the
 4 selectivity to THFA remains broadly constant indicating
 5 the same mechanistic pathway dominates for every cycle.
 6 It has been established that the hydrogenation of furfural
 7 on Pd/TiO₂ deactivates through the formation of Pd
 8 carbide, which promotes a less advantageous adsorption of
 9 furfural.¹⁸ To test if the formation of Pd carbide is
 10 responsible for this deactivation ex situ X-ray absorption
 11 fine structure (XAFS) measurements were performed at
 12 the Pd K-edge before and after catalytic testing (Figure 7).



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Figure 7. Pd K edge XANES of 1% Pd/NiO before and after reaction and a reference Pd foil.

The X-ray absorption near edge data (XANES) shown in Figure 7 demonstrate that the height of the main edge of the fresh Pd/NiO catalyst is greater than both the Pd foil and used Pd/NiO. This difference in height can be attributed to a greater degree of oxidized Pd in the fresh Pd/NiO catalyst. Small Pd nanoparticles have a high proportion of surface sites that readily adsorb oxygen on exposure to air. The height of the main edge for the used Pd/NiO catalyst is the same as the Pd foil, confirming the presence of PdO. There are two features in the XANES spectrum of the used Pd/NiO indicative of Pd carbide; there is a broadening of the first peak maximum and a shift to lower energy of the second peak maximum as a result of lattice expansion. The shift in the position of the second peak maximum is observed for both hydridic and carbidic forms of Pd, however, the broadening of the first peak is only observed for Pd carbide.^{51,52} Furthermore, the insertion/removal of hydride into the Pd lattice is such that without an overpressure of hydrogen present any incorporated hydride would quickly diffuse out from the Pd nanoparticle. The lack of oxygen coordination on the Pd surface, inferred from the XANES, is consistent with previous studies where heteroatoms are inserted into the Pd lattice.⁵³

Analysis of the extended X-ray absorption fine structure (EXAFS) was also performed with the results shown in Table S1 and Figure 8. The EXAFS fitting parameters for the fresh Pd/NiO catalyst confirms that Pd is present as metallic Pd nanoparticles with an oxidised surface layer. There are no Pd-Pd scattering paths at longer distances, indicative of PdO, needed to model the data, and we can therefore discount the presence of large PdO crystallites. The EXAFS data for the used Pd/NiO catalyst can be modelled using a single Pd-Pd scattering path. The expansion of the Pd lattice from 2.74 Å to 2.79 Å is consistent with that previously reported for bulk Pd carbide formation.⁵¹ The reduced Pd-Pd coordination number of the used Pd/NiO catalyst from 12 to 9 is indicative of small nanoparticles (<5 nm) of Pd.

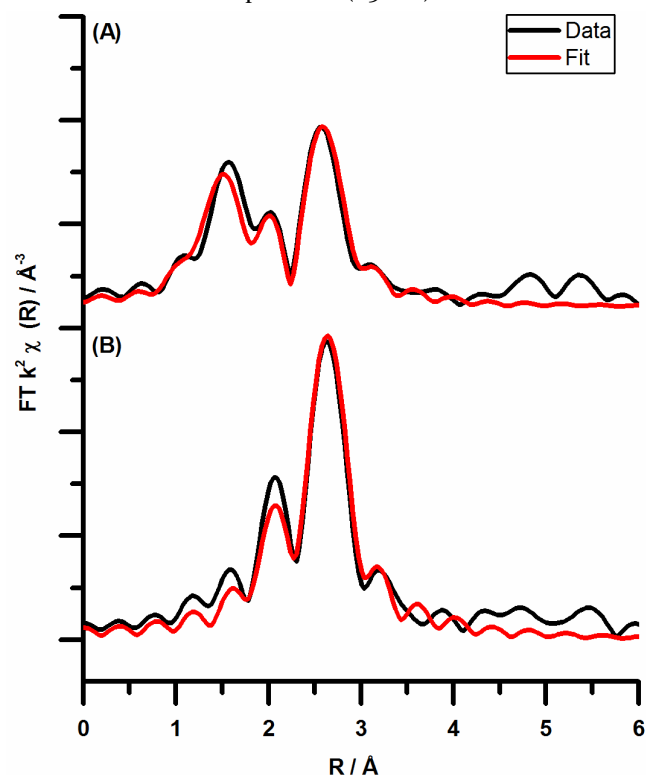


Figure 8. k^2 weighted Fourier transform EXAFS data with simulated fit for (a) the fresh Pd/NiO and (b) the used Pd/NiO.

The XAFS data confirms that there is a structural change during furfural hydrogenation on Pd/NiO that is consistent with the formation of Pd carbide. Previously, it has been shown that there is a less favourable binding of furfural on carbidic Pd, which is responsible for the loss of activity during reusability studies. However, in the case of Pd/NiO, it has been established that the activity arises from furfural adsorbed on the NiO surface. In this instance it is proposed that the loss of activity stems from the reduced ability of Pd carbide to dissociate hydrogen, which has also been found previously.⁵⁴

CONCLUSION

This study reports a synergistic interaction between Pd NPs and NiO that is responsible for directing the selectivity of furfural hydrogenation, alongside being able to maintain catalytic activity at low Pd loading. This study proposes that the hydrogenation of furfural proceeds via a dual-site hydrogenation mechanism with the following steps: i) hydrogen dissociation on Pd surfaces, (ii) spillover of H_{ads} onto the NiO support, (iii) parallel adsorption of furfural through both the furan ring and alcohol group onto the support, and (iv) hydrogenation of furfural on the NiO surface to yield THFA as the major product.

Initially, the nature of CO_{ads} on surfaces of Pd NPs through FTIR spectroscopy was used to assess the available catalytic sites. However, although there were subtle differences the changes were not distinct enough to account for the different selectivity profiles of the 1 wt% Pd/TiO₂ and 1 wt% Pd/NiO samples. This led to the hypothesis that the NiO surface could be responsible for furfural adsorption and hydrogenation for the Pd/NiO catalyst. In this scenario, the role of Pd would be to dissociate hydrogen, which subsequently spills over onto the NiO support. Considering that hydrogen dissociation on Pd is a facile process, and unlikely to be rate limiting, we determined that the dual-site hydrogenation mechanism proposed could sustain similar activities at reduced Pd loading.

This assertion was confirmed by assessing the catalytic activity of 0.1 wt% Pd/NiO and 0.1 wt% Pd/TiO₂. With respect to their 1 wt% loading counterparts, the TiO₂ supported system showed an ~ 10 fold reduction in catalytic activity. However, the activity of both NiO supported catalysts was broadly similar.

The design strategy presented in this work can be extended to further substrate and is an important step in designing catalysts for the selective transformation of bio-derived feedstocks that are less reliant on precious metals.

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Author Contributions

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