***In-situ* HDO of guaiacol over nitrogen-doped activated carbon supported nickel nanoparticles**

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Abstract

In-situ hydrodeoxygenation of guaiacol over Ni-based nitrogen-doped activated carbon supported catalysts is presented in this paper as an economically viable route for bio-resources upgrading. The overriding concept of this paper is to use water as hydrogen donor for the HDO reaction suppressing the input of external high-pressure hydrogen. The effect of nitrogen sources, including polypyrrole (PPy), polyaniline (PANI) and melamine (Mel) on the structural, electronic and ultimately of catalytic features of the design materials have been addressed. Nitrogen-doped samples, are more active than the undoped counterparts in the “H₂-free” HDO process. For instance, the conversion of guaiacol increased by 8% for Ni/PANI-AC compared to that of Ni/AC catalysts. The superior performance of Ni/NC can be attributed to the acid-base properties and modified electronic properties which favours the C-O cleavage and water activation as well as enhances dispersion of Ni particles on the catalysts’ surface.

Keywords: Biomass upgrading, hydrodeoxygenation, nitrogen doped carbon, Ni-based catalysts.

Introduction

The increasing energy demand and climate change call on the utilization of sustainable and low-carbon energy to ease the over-dependency on limited fossil fuels. Over the recent decades, biomass has become the centre of attention among renewable sources considering its distinctive features, such as low price, low-carbon emission, abundant storage and wide distribution [1]. The statistics show that proportion of bioenergy is approximately 11% (44.3 EJ) of the world’s total primary energy supply [2]. Lignocellulose feedstocks can be transformed into bio-oil through pyrolysis technology. However, bio-oil directly produced from fast pyrolysis contains high content of oxygen (up to 60 wt.%) [3]. Undoubtedly, an upgrading process is indispensable to reduce the oxygen content, which can improve the thermal and chemical properties such as stability, heating value, *etc.* Catalytic hydrodeoxygenation (HDO) is a fundamental process for upgrading bio-oil before producing high valued chemicals or transportation fuels. In traditional HDO process, oxygen can be removed in the form of water with the participation of high pressure H₂.

As cornerstones in the chemical industry [4], catalysts maintain the centre status in both research and industrial field. Typically, although noble metal catalysts such as Au, Pd, Ru, Rh [5] and Pt [6], show high activity in HDO process, their industrial application are limited by the high cost and scarcity. The development of efficient non-noble catalysts is undoubted the direction of long-term effect for catalysis community. Among non-noble metal catalysts, Ni-based catalysts are promising candidates in HDO process considering their intrinsic high hydrogenation ability [7]. Carbon materials own the advantages of a lower affinity for coke deposition compared to acidic supports in HDO reactions [8]. The recently developed N-doped carbon (NC) materials have been recognized as promising materials which can be

used as support in heterogeneous catalysis. The enhanced catalytic performance results from (1) the improvement in hydrophilicity and basicity of supports [9], which could enhance the interaction between substrate and support in aqueous reaction system; (2) the lower dissociation energy for H₂ activation results from the modified electronic structure of the carbon matrix and the tuned activity of the sp² carbon and metal particles [10, 11]; (3) N-dopants in the carbon structure can be regarded as favourable anchoring sites or defects for the enhancement of the particle nucleation and reducing the particle size [12]. For instance, as it can be expected that PtCo/NOMC (nitrogen-doped ordered mesoporous carbon) is highly effective for HDO of phenolic compounds, with almost full deoxygenation (HDO degree >99%) and cycloalkanes as the products [13]. The superior performance of N-doped carbon supported catalyst can also be observed in Nie *et al.*'s investigation [14]. It is reported that the Pd/NMC (nitrogen-enriched mesoporous carbon) exhibits 2.9 times higher activity compared to nitrogen-free catalysts, with 100% conversion of vanillin. The outstanding performance of Pd/NMC can be attributed to the percentage change of electron-deficient Pd (Pd^{⊃+}) particles arising from the doping of N together with the co-existence of Pd^{⊃+} and Pd⁰ resulting from the Pd-N interaction [14]. Nowadays, NC support mainly is used in noble metal catalysts. However, to the best of our knowledge, few research investigated the performance of non-noble Ni metal supported on NC in HDO reactions [15].

Doping nitrogen in carbon matrix can be achieved via different routes, including chemical vapour deposition, thermal treatment with NH₃ or nitrogen plasma treatment [16]. Generally, bulk properties of the material are not modified to a large extent via these routes [17]. In contrast, the use of carbon precursor with already containing nitrogen atoms is more advisable since the doping of nitrogen can be homogeneously distributed both throughout the bulk and the surface of material. Conducting polymers, such as polypyrrole and polyaniline have been extensively used as nitrogen source for preparing N-doped carbons. They own the advantages such as cheap and easy to prepare, also the textual properties of N-C can be tailored by activation treatment. Another important source of nitrogen, melamine, is a common and inexpensive material which can produce N-C via co-pyrolysis process [18]. In the nitrogen doping process, melamine decomposes and sublimes, favouring the incorporation of the N atoms to the carbonaceous material, when it is treated at temperatures above 350 °C [19]. In this work, a mesoporous N-doped carbon material is required since it is suitable to be used in liquid phase reactions with relatively large molecules as reactants. In this sense, N-C were prepared by polymerization of pyrrole and aniline on the surface of a commercial mesoporous carbon. Besides, melamine was also used as nitrogen source in which melamine was co-pyrolysis with AC to dope nitrogen on the surface of AC.

Obtaining a suitable catalyst is indeed of paramount importance to achieve high HDO performances. Along with the catalysts, the reaction conditions and engineering approaches plays a crucial role. In this sense, novel strategies including catalytic transfer hydrogenation, reforming and HDO, metal hydrolysis and HDO, non-thermal plasma, self-supported hydrogenolysis and water assisted *in-situ* HDO, [20, 21] have been proposed for bio-oil upgrading. All these strategies share a common spirit: suppression of external H₂ supply to minimize potential risk in terms of transportation and storage as well as improving the process economic feasibility. Among these "*H₂-free*" HDO strategies, water assisted *in-situ* HDO is perhaps the most promising from an economic perspective and the most challenging from the catalysis side. Water owns multiple excellent features such as cheap, non-toxicity, operationally safe to use, naturally abundant and readily available. Water is typically used as solvent in conventional liquid phase HDO reactions [22-24]. However, few studies investigated the *in-situ* HDO of bio-oil or model compounds by using water as hydrogen source [25, 26].

Under these premises, this study is a proof of concept of an innovative approach for HDO strategy in hydrothermal conditions suppressing the supply of external H₂. For this purpose, a series of Ni-based catalysts supported on AC or NC have been prepared, characterized and studied using guaiacol as model compound within the HDO process which is conducted in a batch reactor under mild reaction conditions. The effect of N-doping on the catalysts' properties and ultimately in the HDO performance

was also a subject of this study which was conceived to inspire the catalysis and biomass community to look into innovative alternatives for bio-resources valorisation

Materials and methods

Materials

Chemicals used for NC synthesis, including pyrrole, aniline, ammonium persulfate, melamine and nickel nitrite hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) were all supplied by Sigma Aldrich. Commercial activated carbon (RGC 30) was provided by Westvaco. Guaiacol, solvent (ethyl acetate and acetone) and chemicals used for calibration (including phenol, o-cresol and catechol) were all supplied by Sigma-Aldrich Co., Ltd.

Methods

Catalyst preparation

Polypyrrole and polyaniline supported on a commercial activated carbon RGC-30 (AC) (PANI-AC and PPy-AC) were prepared via oxidative polymerization. The AC (0.6 g) was dispersed in 150 ml of acetone and was sonicated 30 min. 3 mmol of the monomers (aniline and pyrrole) were dissolved in 100 ml of water and the solution was added to the dispersion of the AC. The mixture was stirred 30 min and the 6 mmol of the oxidant (Ammonium persulfate) previously dissolved in 100 ml of water was added drop by drop in continuous stirring. After 4 hours, the reaction mixture was filtered, washed and dried at 80 °C for 24 hours. The dried sample was pyrolyzed for 4 hours at 900 °C under flowing N_2 (50 ml/min), with a heating rate of 5 °C/min, in order to obtain the N-doped carbon. For the preparation of the Mel-AC support, the AC and melamine were mixed intimately, and the mixture was treated in a tubular furnace for 1 hour at 800 °C under flowing N_2 (50 ml/min), with a heating rate of 3 °C/min.

The Ni/NC and Ni/AC were prepared via wet impregnation to obtain 15 wt.% of Ni. Firstly, ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was dissolved in acetone. Secondly, the dried activated carbon (AC) or nitrogen-doped carbon (NC) were added into the solution with stirring. The solvent was slowly removed under vacuum at 60 °C. Finally, the metal catalysts were dry at 80 °C for 24 hours and calcined 1 hour at 800 °C under flowing N_2 . The samples obtained were labelled as Ni/AC, Ni/PANI-AC, Ni/PPy-AC and Ni/Mel-AC.

Catalyst characterization

XRD. X-Ray powder diffraction patterns were recorded on a Bruker D8-Advance with a Göebel mirror and a Kristalloflex K 760–80 F X-Ray generation system, fitted with a Cu cathode and a Ni filter. Spectra were registered between 20 and 80° (2 θ) with a step of 0.05° and a time per step of 3 s.

TPR. Temperature programmed experiments were conducted in a conventional U-shaped quartz reactor. For Temperature programmed reduction with H_2 (H_2 -TPR) a gaseous mixture of 5% H_2/He and flow rate of 50 mL/min, with a heating rate of 10 °C/min was used. Prior the TPR runs, the catalyst was pre-treated with He (50 mL/min) at 150 °C for 1 h. For the temperature programmed desorption a flow rate of 50 mL/min of He, with a heating rate of 10 °C/min was used. The gasses of interest were followed by on-line mass spectrometry (Pfeiffer, OmniStar GSD 301).

N_2 Adsorption Isotherms. The textural properties of the supports were characterised by nitrogen adsorption-desorption measurements at –196 °C in an AUTOS-ORB-6 fully automated manometric equipment. The samples were out-gassed under vacuum at 250 °C for 2 h before each measurement. The BET equation was applied to estimate the specific surface area.

XPS. XPS measurements were performed with a K-ALPHA spectrometer (ThermoFisher Scientific) operated in the constant energy mode with survey scan pass energies of 200 eV and narrow scan energies of 50 eV, to measure the whole energy band as well as selectively measure particular elements. All XPS spectra were acquired using Al-K α radiation (1486.6 eV), with a twin crystal monochromator,

yielding a focused X-ray spot (elliptical in shape with a major axis length of 400 μm) at 3 mA $\times$ 12 kV. Charge compensation was attained with the system flood gun, which provides low energy electrons and low energy argon ions from a single source. For the reference binding energy, the C1s core level was used, located at 284.6 eV. All samples were reduced ex-situ at 800 $^{\circ}\text{C}$, and before recording the spectrum, the samples were maintained in the analysis chamber until a residual pressure of ca. 5×10^{-7} N/m² was reached.

TEM. Conventional TEM analysis was carried out with a JOEL model JEM-210 electron microscope working at 200 kV and equipped with a INCA Energy TEM 100 analytical system and a SIS MegaView II camera. Samples for analysis were suspended in methanol and placed on copper grids with a holey-carbon film support.

Catalytic reactions

The HDO reactions were conducted in a high-pressure batch reactor (Parr Series 5500 HPCL Reactor with a 4848 Reactor Controller) using PTFE gaskets. Catalysts were pre-treated at 400 $^{\circ}\text{C}$ for 1h in a 100 ml/min gas flow ($\text{H}_2:\text{N}_2=1:4$) before being used in the HDO reaction. 1 wt.% of guaiacol in water (0.5g guaiacol) and 0.2g of catalyst were loaded in a glass-lined steel vessel. To avoid any air contamination, N_2 was bubbled through the solution for 5 min under a stirring speed of 300 rpm before closing the reaction vessel. Then, the reactor was heated to the desired temperature (250 $^{\circ}\text{C}$) and hold at this temperature of 4h under a stirring speed of 300 rpm. The pressure of the vessel which mainly generated by high temperature liquid in the vessel was approximate 50 bar during the reaction. After the reaction, the spent catalyst was recovered from the liquid by filtration, washing and drying treatment. The organic products were dissolved and recovered by ethyl acetate extraction.

The organic products were identified by gas chromatograph-mass spectrometry (GC-MS). Quantitative analysis was performed with a gas chromatograph-flame ionisation detector (GC, Shimadzu; FID: Agilent cellular model). The injector temperature was kept at 280 $^{\circ}\text{C}$. The GC separation was performed using a Carboxen Packed Analytical Column (30m $\times$ 320 μm $\times$ 0.25 μm). A split ratio of 20:1 was held. The column was firstly held at 50 $^{\circ}\text{C}$ for 1 min, then increased to 240 $^{\circ}\text{C}$ at a heating rate of 5 $^{\circ}\text{C}/\text{min}$ and held at 240 $^{\circ}\text{C}$ for 10 min. Reactant and typical products were quantified based on the external standard method.

The conversion of guaiacol, the selectivities towards typical products (based on C mol) and HDO conversion ratio were calculated using Eq 1, Eq 2 and Eq 3 [27]:

$$\text{Conversion of guaiacol} = \frac{n_{\text{GUA},in} - n_{\text{GUA},out}}{n_{\text{GUA},in}} \times 100\% \quad \text{Eq. 1}$$

$$\text{Selectivity of product } x = \frac{n_x \times N_x}{(n_{\text{G},in} - n_{\text{G},out}) \times N_{\text{GUA}}} \times 100\% \quad \text{Eq. 2}$$

$$\text{HDO conversion: } X_{\text{HDO}}\% = 100 \times \left(1 - \frac{(n_{\text{PHE}} + n_{\text{CRE}} + 2(n_{\text{GUA},out} + n_{\text{CAT}}))}{2(n_{\text{GUA},in})}\right) \quad \text{Eq. 3}$$

$n_{\text{GUA},in}$: Initial mole of guaiacol; $n_{\text{GUA},out}$: Detected mole of guaiacol in the organic phase; n_x : Mole of product x .

N_{GUA} : Number of carbon in guaiacol; N_x : Number of carbon in product x .

GUA : guaiacol; PHE : phenol; CRE : *o*-cresol; CAT : catechol

Results and discussion

Characterization of supports and calcined catalysts

H₂-TPR

Figure 1 shows the H₂-temperature-programmed reduction (TPR) analysis of all calcined catalysts. It is observed that the reduction profiles of all samples show a broad band which can be split in two typical

consumption peaks. The sharp peak at a low temperature range (250-300 °C) corresponds to the reduction of finely dispersed NiO on the support. It should be emphasised that Ni/PANI-AC owns the reduction peak with highest intensity at low temperature, indicating the higher amount of small Ni particles for Ni/PANI-AC. The main peak observed in the TPR profiles (350-450 °C) can be attributed to the reduction of medium-sized Ni particles. Notably, the addition of N in the C structure lowers the reduction temperature of NiO species, as shown by the main peak shifted to a low temperature range. We can then infer a promotional effect of N on the redox properties of the catalysts being the N-doped materials easier to reduce than that on non-doped carbon materials, in fair agreement with previous studies [28]. The enhanced reducibility of Ni/NC could be attributed to the electronic interactions aroused by doping electron-rich nitrogen, resulting in better dispersion of Ni particles on the surface of carbon material.

Figure 1. H₂-TPR profile of the Ni-based catalysts

Textural properties

Table 1 summarised the textural features of the prepared materials including the surface area, pore volume and average pore diameter of calcined catalysts. The doping nitrogen procedure on the carbon structure noticeably decreased the specific surface area and pore volume of samples. Ni/Mel exhibited the highest surface area among N-doped samples, with a value of 551 m²/g, followed by Ni/PANI-AC and Ni/PPy-AC (441 m²/g and 344 m²/g, respectively). Results indicate that the mesopores of carbon support could be partially blocked by nitrogen-containing compounds during the nitrogen doping process. The difference in the loss of the textural parameters relates to the preparation routes of N-doped carbon. The physical mixture route for the preparation of Mel-AC favours the doping of melamine on the outer surface of carbon, resulting in relatively low pore blocking effect. In contrast, polymerization process for the preparation of PPy-AC and PANI-AC takes place inside the pore, thus resulting in a more marked blocking effect.

Table 1 Textural properties of the studied catalysts

Catalyst	S _{BET} (m ² /g)	Pore Volume ^a (cm ³ /g)	Pore size ^b (nm)
Ni/AC	1240	0.76	4.19
Ni/Mel-AC	551	0.36	4.07
Ni/PPy-AC	344	0.24	3.99

Ni/PANI-AC	441	0.26	4.32
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^a D-H desorption cumulative volume of pores

^b BJH desorption average pore diameter

XRD

The XRD patterns of reduced Ni-based catalysts are depicted in Figure 2. The broad characteristic peak centred at around 24.5° is associated to (002) plane reflection of carbon. The intensive diffraction peaks at around 44.5° , 51.8° , and 76.4° are attributed to the (111), (200) and (220) planes of the face-centered-cubic (fcc) structure of metallic Ni (JCPDS 87-0712) [29, 30]. The diffraction peaks at around 37.2° , 43.3° , and 62.9° correspond to the (111), (200), and (220) planes, respectively, of NiO face-centered-cubic phase (JCPDS 04-0835) [30]. Slightly more notorious diffraction peaks of NiO can be observed for reduced Ni/AC, while NiO peaks are weak for reduced Ni/NC, especially for Ni/PPy-AC and Ni/PANI-AC. This result indicated that doping nitrogen in carbon structure could enhance the reduction of NiO to metallic Ni, which is consistence with the H_2 -TPR results. The promotion of NiO reduction is not obvious for Ni/Mel-AC sample since a clear NiO X-ray reflection peak can be found the diffraction pattern. Interestingly, sharper Ni^0 peaks are observed in the XRD of Ni/PPy-AC compared to that of Ni/PANI-AC, indicating smaller particle size and greater dispersion of the Ni^0 cluster within the Ni/PANI-AC catalyst.

Figure 2. XRD patterns of reduced Ni-based catalysts

XPS

The surface chemistry of supports and Ni-based catalysts after reduction is examined by XPS analysis. XPS spectra of N 1s and Ni $2p_{3/2}$ are presented in Figure 3, Figure 4 and Figure 5, respectively. The XPS spectra and relative atomic percentage of different types of N existing in the supports are presented in Figure S1. The binding energies of the main peaks and relative atomic percentage (at%) of N for Ni/NC catalysts are summarized in Table 2. The XPS spectra of N 1s demonstrated that nitrogen is

presented in different forms, including pyridinic (N6, centred at 398.2 eV), pyrrolic (N5, centred at 399.2 eV), quaternary (NQ, centred at 400.5 eV) and N-oxides of pyridine nitrogen (NX, centred at 402.3 eV). The pyridinic-type nitrogen (N6) refers to the N contributing one p-electrons to the π -system. In contrast, pyrrolic-type nitrogen (N5) refers to the N with one more p-electrons to the π -system, which is composed of the contribution of pyridone, lactam and pyrrollic nitrogen groups. The quaternary-type nitrogen (NQ) is incorporated into the activated carbon structure and replaces a carbon atom, which normally includes protonated pyridine, or the namely “graphitic nitrogen”. The oxidized nitrogen, pyridine oxide (NX) normally appears with the highest binding energy in the XPS spectra of N 1s [31, 32].

As shown in Figure 3, four types of N all exist for NC supports. Mel-AC owns the highest surface concentration of nitrogen (7.0 at.%) comparing to PANI-AC (3.7 at.%) and PPy-AC (3.0 at.%). The difference in the surface concentration of nitrogen relates to preparation routes of NC supports. Physical mixture routes for Mel-AC favours the doping of N on the surface of support, resulting in higher surface concentration of nitrogen compared to supports prepared by polymerization process, including PANI-AC and PPy-AC. N6 is dominated for Mel-AC while N5 and NQ are predominant ones for PANI-AC and PPy-AC (Figure 3). In terms of Ni/NC catalysts, four types of N are all observed for Ni/PPy-AC sample while part of type of nitrogen disappear for Ni/PANI-AC and Ni/Mel-AC (Figure 4). Specifically, N5 was not shown in Ni/PANI-AC. N5 and NX were not shown in Ni/Mel-AC (Figure 4). It is speculated that the disappeared N5 acts as coordinative sites for Ni ions, which means all of them were covered evidencing a close N-Ni interaction. NQ is predominant for all N-C supported catalysts. It can be observed that a higher surface concentration of nitrogen for Ni/ Mel-AC surface (4.0 at%) exists compared to Ni/PANI-AC and Ni/PPy-AC, with 2.2 at% and 3.3 at%, respectively. It is interesting to find that higher degree for the losing of N occurred for Ni/PPy-AC catalyst after doping Ni on the support. N6 occupies a larger percentage for Ni/Mel-AC than Ni/PANI-AC and Ni/PPy-AC catalysts. It is reported that N6 sites could enhance both the coordination of metal ions and the anchoring of metal nanoparticles due to their electron-withdrawing capacity [33]. Indeed, Melke *et. al* found that the present of pyridinic-type nitrogen (N6) could result in smaller metal particle size while pyrrolic-type nitrogen (N5) and graphitic nitrogen (NQ) causes larger metal particle size [34].

Different nickel species exist on the surface of catalyst as shown in Ni 2p_{3/2} spectra (Figure 3). The first band with low B.E at around 852-853 eV can be assigned to metallic nickel species. The following second and third peaks correspond to Ni²⁺ ions species as reported elsewhere [35, 36]. The binding energy of Ni⁰ slightly shift to a lower energy region for Ni/NC compared to that of Ni/AC. Similar phenomenon can also be observed for Ni/NHPC (nitrogen-doped hierarchical porous carbon) [28]. Previous study reported that Ni atoms could bond to N atoms in the carbon skeleton [15]. The shift is probably due to N atoms and reflects a preferential electron donation to Ni nanoparticles. In comparison, the binding energy of Ni⁰ follow the order: Ni/PPy<Ni/PANI<Ni/Mel≈Ni/AC. Also the Ni/C ratio reported in Table 2 provides an idea of Ni dispersion of the samples' surface. Higher dispersion of Ni⁰ was achieved for Ni/PANI-AC (0.57) compared to that of Ni/Mel-AC (0.18) and Ni/PPy-AC (0.40). These results are indeed consistent with the TPR and XRD observations as high proportion of small Ni cluster with enhanced reducibility are present in the Ni/PANI-AC (Figure 1 and Figure 2).

In summary, Ni/PANI-AC is deemed as promising system since it owns more active sites (Ni⁰) (XRD and XPS) and highest proportion smaller Ni clusters (TPR) thus better dispersion of Ni is achieved on the support. Interestingly, Ni/Mel-AC owns the advantage of highest surface nitrogen content and concentration of N6 sites (XPS) and largest BET value while Ni/PPy presents strongest interaction among Ni-N-C (TPR and XPS).

Figure 3 Core level XPS of N 1s region for nitrogen doped carbon supports after reduction treatment.

Figure 4. Core level XPS of N 1s region for Ni-based catalysts after reduction treatment.

Figure 5. Core level XPS of Ni 2p_{3/2} spectra for Ni-based catalysts after reduction treatment

Table 2 Binding energies of and Ni2p_{3/2} and N 1s levels of reduced catalysts and relative atomic percentage of different species

Catalysts	Ni 2p _{3/2}			N 1s				
	Ni ⁰	Ni ²⁺	Ni ⁰ /C* 10 ²	N	Pyridinic N (N6)	Pyrrolic N (N5)	Quaternary N (NQ)	Pyridine oxide N
	B.E. (eV)	B.E. (eV)		at.%	B.E. (eV)	B.E. (eV)	B.E. (eV)	B.E. (eV)
Ni/AC	852.7 (32.0%)	853.6; 856.2 (68.0%)	0.22		-	-	-	
Ni/Mel- AC	852.8 (25.4%)	854.8; 856.4 (74.6%)	0.18	4.02	398.4 (45.5%)	-	400.1 (54.5%)	
Ni/PANI -AC	852.5 (28.0%)	853.7; 855.8 (72.0%)	0.57	2.22	398.3 (23.9%)	-	400.1 (56.3%)	401.5 (19.8%)
Ni/PPy- AC	852.4 (36.2%)	853.4; 855.2 (63.8%)	0.40	3.27	398.1 (27.5%)	399.3 (14.4%)	400.6 (52.0%)	402.2 (6.1%)

Catalytic activity

The catalytic activity of different Ni-based catalysts in guaiacol HDO process tested at 250 °C is shown in Figure 6. Remarkably, all catalysts with nitrogen doping in the carbon skeleton are more active than the undoped catalyst in terms of the guaiacol conversion. Specifically, the guaiacol conversion over the more active catalysts, Ni/PPy-AC and Ni/PANI-AC, increased by 4 mol% and 8 mol.% respectively, compared to the results exhibited by the Ni/AC undoped catalyst. The addition of nitrogen provides Lewis basic sites which helps anchor and activate guaiacol. Besides, the nitrogen incorporation plays a vital role by inducing the formation of chemical bonding between the organic compound and the carbon material. The superior performance of Ni/PANI-AC can be attributed to its greater concentration of

active sites which also benefit of larger dispersion of Ni particles as intended from the characterisation study

Three predominate monoaromatic compounds, including phenol, o-cresol and catechol is evident in the HDO process. Compounds with more complex structure, such as cyclopentane, 1,1,3-trimethyl; [1,1-biphenyl]-4,4-diol, 3-3-dimethoxy-, were also observed as main products but not quantified. Catechol is the leading product among monoaromatic products for both catalytic and non-catalytic HDO process. It is typically produced through the demethylation (DME) of guaiacol along with the release of CH₄. Unfortunately, the selectivity towards fully or almost fully deoxygenated products is modest and similar for all studied catalysts.

Figure 6. HDO of guaiacol over different Ni-based catalysts

Table 3 Catalytic hydrodeoxygenation of guaiacol over Ni-based catalysts

N o.	Catalyst	Reaction condition	Hydrogen donor	Conversion	Main products	selectivity	Reactor	Ref.
1	15%Ni/Al ₂ O ₃ -SiO ₂	T=300 °C; P=50 bar; t=1 h	H ₂	≈68%	Methyl-guaiacol; Phenol; Cyclohexane; Anisol; Cresol; benzene	≈25%; ≈14%; ≈3%; ≈2%; ≈2%;	Batch	[37]

						≈1%		
2	16.7%Ni/TiO ₂ -A	T=300 °C;P=pre 40 bar T=4 h	H ₂	≈85%	Phenol; Cresol;	≈81% ≈15%	Batch	[38]
3	10%NiZr/CMK-3	T=300 °C P= pre 50 bar T=4 h	H ₂	≈88%	Cyclohexane; Cyclohexanol; methoxycyclohexanol	≈7.2% ≈ 35.5%; ≈ 51.0%	Batch	[39]
4	Ni/SiO ₂ + Hβ zeolite	T=140 °C P=pre 30 bar T=3 h	H ₂	>99%	cyclohexane	Y≈ 91.7%	Batch	[40]
5	15%Ni2%Mo/CeO ₂ -C	T=250 °C P=50 bar t=4 h	H ₂ O	≈18%	Phenol; o-cresol; Catechol	≈0.5% ≈1.5% ≈15.7%	Batch	[26]
6	15%Ni/AC	T=250 °C P=50 bar t=4 h	H ₂ O	≈11%	Phenol; o-cresol; Catechol	1.58%; 2.70%; 21.36%	Batch	This study
7	15%Ni/PANI-AC	T=250 °C P=50 bar t=4 h	H ₂ O	≈18%	Phenol; o-cresol; Catechol	0.34%; 1.39%; 12.37%	Batch	This study

In order to establish an accurate comparison with the current state of the art systems, Table 3 summarised some recent reported results of liquid-phase guaiacol HDO over Ni-based catalysts. Apparently, higher conversion of guaiacol and higher HDO degree was achieved in conventional HDO in which H₂ is used as hydrogen source. The catalytic performance presented in this work and our previous study (ref. [26]) needs further improvement comparing with results of conventional HDO. However, we must emphasise that our HDO happens in H₂-free reaction system, which is a very challenging and ambitious approach. Hence, although we achieve lower activity/selectivity results, our strategy deserves further consideration.

As a matter of fundamental understanding of the H₂-free reaction and in order to rule out the possible contribution of hydrogen released from the functional groups of supports, a He-TPD analysis was conducted (Figure S2). It can be observed that H₂ only be released from support at high temperature (>400 °C for Mel; >800 °C for AC, PANI-AC and PPy-AC) which are certainly beyond the selected temperatures for our catalytic runs (250 °C). This is indeed an excellent indication that the support will not be the source of hydrogen for HDO at mild reaction condition and our approach relies on an autogenous source of hydrogen during the hydrothermal process.

Characterization of spent catalysts

The XRD analysis of spent samples provides some information concerning the stability of catalysts, i.e. carbon decomposition and active phase changes can be identified. Figure 7 shows the XRD patterns of all spent samples. Generally, catalysts are likely to be oxidised by oxygen-containing intermediates under high temperature and pressure in a hydrothermal reaction media (250 °C, 50 bar). The typical diffraction peaks of metallic Ni at $2\theta=44.5^\circ$, 51.8° , and 76.4° disappeared for Ni/AC and Ni/Mel spent catalysts. In contrast, they remain in Ni/PANI and Ni/PPy-AC spent catalysts. These results agree well with the XRD of reduced catalysts since Ni^0 is the main phase for Ni/PANI-AC and Ni/PPy-AC. Besides, our observations pointed out that the addition of nitrogen in the carbon structure could stabilize metallic Ni, especially for Ni/PANI-AC and Ni/PPy-AC catalysts. In other words, the electronic interaction N-Ni prevents Ni oxidation resulting in a more robust catalysts for bio-compounds upgrading in hydrothermal conditions.

Figure 7. XRD of the Ni-based catalysts after the reaction

The XPS spectra of Ni $2p_{3/2}$ and N 1s were shown in Figure S3 and Figure S4 respectively. Peak related to metallic Ni disappeared, indicating that the metallic Ni on the surface of catalysts were all oxidised to Ni^{2+} during the HDO reaction (Figure S3). Hence, contrasting the XPS info with the XRD data it seems that we definitely have surface oxidation of Ni but still in the presence of N there is some remaining metallic Ni species in the bulk of the sample. As for the nitrogen evolution during the reaction, forms of nitrogen in NC supported catalyst significantly changed during HDO (Figure S4). It can be observed that N5 and NX no longer exist in Ni/PPy-AC after the HDO reaction. It is speculated that electronic transfer between N species and metal particles shifts the binding energy of N5 towards lower values, thus overlapping with the diffraction peak of N6. This would also explain the larger intensity of N6 for spent Ni/PPy-AC compared to reduced samples. It is also interesting to observe that new peak of NX were observed for spent Ni/Mel evidencing further evolution of the N species during the reaction for this particular sample.

In order to visualize the structural and morphological changes of catalysts, TEM micrographs of fresh and spent catalysts were compared (Figure 8). Metal particles are well dispersed on carbon support being in principle the PANI sample the one with the greatest metallic dispersion in fair agreement with

the XPS results. No metal sintering can be observed for both fresh and spent catalysts. This is in fact a plausible phenomenon since the HDO reaction happens in an aqueous media under relatively aggressive reaction conditions. In any case the absence of sintering is a highly commendable achievement which also validates the suitability of the developed catalysts for the H₂-free HDO process in hydrothermal conditions.

Figure 8 TEM images of reduced (fresh) and spent catalysts.

Conclusions

This work showcases a novel strategy for biomass valorisation via *in-situ* HDO process using economically appealing catalysts. Ni supported on N-doped carbon catalysts are proven to be effective model compounds HDO under hydrothermal conditions. When compared to the reference nitrogen-free sample the doped catalysts presented a better activity/selectivity balance indicating its superior catalytic behaviour. Such advantageous behaviour is ascribed to the electronic and acid-base properties modification arising from N introduction the carbon structure. Among the different sources of N, Ni/PANI-AC is a more efficient than Ni/PPy-AC and Ni/Mel-AC. Indeed, the PANI system presented the highest concentration of metallic Ni atoms in the surface as well as the best dispersion and smaller Ni particles size among the studies series. Interestingly, surface area did not pose great effect on the catalytic activities. Presumably for real feedstocks (i.e. bigger molecules) the textural properties will play a more relevant role in the process. Importantly, no obvious metal sintering can be observed for spent samples, indicating some degree of robustness of catalysts under the studied conditions.

Despite the relatively modest performance results, this paper provides a new angle on bio-compounds conversion technologies. Certainly, the take home messages are: (i) we should pursue economically appealing routes for biomass conversion bypassing the need of external hydrogen supply (ii) H_2 -free HDO processes are achievable using water as reaction media (iii) advanced catalysts are needed to satisfy the conversion and selectivity requirements of a realistic application (iv) Ni dispersed on N-doped carbons are promising candidates to be further explore in this challenging reaction.

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