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Noble metal supported on activated carbon for “hydrogen free” HDO reactions: exploring economically advantageous routes for biomass valorisation

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Abstract: An innovative route for bio-compounds upgrading via “hydrogen-free” hydrodeoxygenation (HDO) is proposed and evaluated using guaiacol as a model compound in a high-pressure batch reactor. Experimental results showed that noble metal supported on activated carbon catalysts are able to conduct tandem multiple steps including water splitting and subsequent HDO. The activity of Ru/C catalyst is superior to other studied catalysts (*i.e.* Au/C, Pd/C and Rh/C) in our water-only HDO reaction system. The greater dispersion and smaller metal particle size confirmed by the TEM micrographs accounts for the better performance of Ru/C. This material also presents excellent levels of stability as demonstrated in multiple recyclability runs. Overall, the proposed novel approach confirmed the viability of oxygenated bio-compounds upgrading in a water-only reaction system suppressing the need of external H_2 supply and can be rendered as a fundamental finding for the economical biomass valorisation to produce added value bio-fuels.

Introduction

Hydrodeoxygenation (HDO) is a fundamental technology to upgrade bio-oils through catalytic processes to produce deoxygenated fuels or high-value chemicals.[1] Lignin, as one of the three main components of lignocellulose, possesses a great potential for producing aromatics and transportation fuels [2] since it is composed with a variety of phenylpropane-units (C9 units). Hydrodeoxygenation of bio-oil from pyrolysis of lignin [3], and lignin model compounds [4] in particular is currently gaining intensive research attention. Typically, liquid-phase hydrodeoxygenation involves treatment with high pressure (50-100 bar) at high temperature (250-500 ºC) in a solvent (mainly polar protic and non-polar solvent) with H_2 supply.[5] The “Achilles Heel” of this approach is the supply of H_2—an expensive resource which imposes a tremendous economic limitation to the implementation of HDO in large scale production units. Moreover, H_2 exhibits potential safety hazard in transportation and operation processes due to its flammability. More importantly, the production of aromatic hydrocarbon was limited by successive hydrogenation of the aromatic rings or direct hydrogenolysis of C-C bonds in the condition of high pressure H_2.[6] All these drawbacks have encouraged the bio-oil upgrading research towards seeking alternative approaches, which could realize the oxygen removal without the supply of high-pressure H_2. In this sense, hydrodeoxygenation using H donors (*e.g.* alcohols, formic acid) has been considered as a promising method to suppress the supply of external H_2, in which the production of high valued aromatic hydrocarbons, *i.e.* BXT[7] can be enhanced.

Guaiacol, with two different oxygen-containing function groups (including -OH and $-OCH_3$) is the representative of phenolic derivatives and widely employed as lignin model compounds to discern mechanistic information during the bio-oil upgrading process. Numerous studies have report excellent activities of noble metal such as palladium (Pd), rhodium (Rh), platinum (Pt), ruthenium (Ru), *etc.* on various supports in HDO reaction of guaiacol.[8] For example, for the guaiacol HDO over Ru/TiO_2-ZrO_2[8a], Pd/TiO_2[8b], Pt/H-MFI-90[8c] and Rh/ZrO_2[8e] catalysts, conversion of guaiacol all reach 100 % at optimized reaction condition, with total deoxygenated compound, cyclohexane, as the main product. High conversion (>95%) of guaiacol was also obtained over Pt/C [9] and Ru/C [10] catalysts using H donor solvent (2-propanol and decalin) without the supply of external H_2, with partial deoxygenated compound, cyclohexanol, as the main product. All these results indicate the high activity of noble metal catalysts in the HDO reaction. Nevertheless, the systematical comparison of metal effect on the catalytic performance in *in-situ* HDO has not been explored yet. Obviously, a promising but challenging approach for *in-situ* HDO is using cheap and available water as the hydrogen source. If successful this approach would have a tremendous impact the process sustainability and economic efficiency. Indeed, bio-oil has a high water content (15 wt.%-30 wt.% [11]). Water splitting on the surface of the metal catalyst is speculated to provide hydrogen in hydrodeoxygenation process. However, to the best of our knowledge, few studies investigated the *in-situ* HDO by using water as the hydrogen source in bio-oil or model compounds upgrading process [12].

In our research, different noble metal (Ru, Rh, Pd and Au)-based catalysts have been prepared, characterized and studied in guaiacol *in-situ* HDO reaction using water as hydrogen source. Activated carbon (AC) was selected as the support considering the low affinity for carbon deposition, high selectivity for direct oxygen removal and hydrophobic nature [13]. The catalysts were comprehensively characterized by transmission electron microscopy (TEM), high-angle annular dark field (HAADF) with high resolution transmission electron microscope (HR-TEM),

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inductively coupled plasma mass spectroscopy (ICP-MS), diffuse reflectance infrared fourier transform spectroscopy (DRIFTS), energy dispersive X-ray spectroscopy (EDX) mapping and temperature programmed decomposition in helium (He-TPD). The effect of metal species were investigated. The recycling test over the most active catalysts (Ru/C) was also conducted. This seminal work on “H_2-free” HDO process opens a novel route with potential impact on bio-oil and biomass upgrading technologies.

Experimental

Catalyst preparation

A commercial charcoal powder DARCO® with 100 mesh particle size purchased from Sigma-Aldrich, was employed as the carbon support. Noble metal catalysts, including Pd/C, Rh/C and Ru/C (loading 2 wt.% of reduced metal) were synthesized by using wetness impregnation method. Acetone was used as the solvent for preparing Ru/C and Pd/C while distilled water for that Rh/C catalyst. Prior to the HDO reaction, all these catalysts were reduced under a 300 ml/min gas flow (N_2: H_2=1: 1) at 300 ºC for 2h. It is difficult to obtain well-dispersed gold nanoparticles through wetness impregnation method.[14] Accordingly, the synthesis of the Au/C (2 wt.% Au) catalyst with nano-sized metal particles was realized by colloidal method assisted by polyvinyl alcohol (PVA) where $NaBH_4$ was used as reducing agent .[15] Colloidal route is an appropriate method to obtain homogeneous and reproducible gold nanoparticle size distribution, which allows a more direct gold size/activity correlation investigation.[16] Further details about the catalysts preparation can be found in our previous work.[17]

Catalyst characterization

TEM. The size and size distributions of the metal nanoparticles were measured by transmission electron microscopy. TEM micrographs were acquired with a FEI Talos electron microscope operated at an acceleration voltage of 200 kV, equipped with a Field Emission filament. Digital images were taken with a side mounted Ceta 16M camera. For TEM preparation, a few milligrams of each sample were deposited directly on a 300 mesh holey carbon coated copper TEM-grid. The mean particles sizes were estimated from TEM micrographs by single particle measurements of at least 200 particles.

The mean metal particle diameter was considered on the basis of its homogeneity, dispersion and number of particles. The average particle size was estimated according to *Eq. 1,*

$$D_p = \frac{\sum n_i d_i^3}{\sum n_i d_i^2} \qquad \text{Eq. 1}$$

where d_i is the geometric diameter of the i^{th} particle, and n_i is the number of particles with this diameter.

ICP-MS. Metal content in the catalysts was measured by inductively coupled plasma mass spectroscopy (ICP-MS) using a Spectro ICP spectrometer (Model: ULTIMA 2). The samples were burned in air at 1073 K and and the residue was disolved in aqua regia for the ICP analysis.

HAADF-STEM and HR-TEM. HAADF-STEM observations were performed with a FEI Talos F200X CTEM/STEM, operated at 200 kV. High-resolution images were formed by scanning a probe across to the sample and by recording scattering electrons synchronously with an annular detector set from 50 to 110 mrad.

HR-TEM micrographs were operated at an acceleration voltage of 200 kV, a spherical aberration coefficient of 0.6 mm, a beam convergence of 0.2 mrad and spread of defocus of 4.9 nm. Digital images were taken with a side mounted Ceta 16M camera.

DRIFTS. The diffuse reflectance infrared Fourier Transform Spectra (DRIFTS) were obtained on a JASCO FTIR 6200 spectrometer with a DRIFTS accessory Pike model EASI-DIFF, at room temperature and accumulating 100 scans with a resolution of 4 cm^{-1}.

He-TPD. Ru/C sample (50 mg) was decomposed in a quartz U reactor under a 50 ml/min flow of an inert gas (helium) from room temperature up to 500°C at a heating rate of 10°C/min and the gaseous products emitted followed by mass spectrometry (Pfeiffer vacuum). m/z signals from 2 to 100 were continuously monitored.

Catalytic experiment

The HDO reactions were conducted in a high-pressure batch reactor (Parr Series 5500 HPCL Reactor with a 4848 Reactor Controller). Approximately 0.5 g of guaiacol, 49.5 g of distilled water and 0.2 g of catalyst were loaded in a glass-lined stainless steel vessel of 300mL. To avoid any air presence, N_2 was bubbled through the loaded reactor for 10 mins under a stirring speed of 300 rpm before closing the reaction system. Then, the reactor was heated to the reaction temperature 250 ºC and hold at this temperature of 4h under a stirring speed of 300 rpm. Typically, the pressure of vessel reaches 50 bar at the reaction condition. After the reaction and the system cooling down to room temperature, the spent catalyst was separated from the liquid by filtration and followed by drying. The organic products were dissolved and recovered with ethyl acetate. Identification of organic products was conducted by a gas chromatograph-mass spectrometry system (GC/MS). Quantitative analysis was performed with a gas chromatograph-flame ionisation detector (GC/FID). The GC injector temperature was 280 ºC. The GC separation was performed using a Carboxen Packed Analytical Column (30m×320μm×0.25μm). A split ratio of 20:1 was held. The column was firstly held at 50 ºC for 1 min, then increased to 240 ºC at a heating rate of 5 ºC/min and held at 240 ºC for 10 min.

The conversion of guaiacol and selectivity (based on C mol) of typical products can be calculated using *Eq. 2* and *Eq. 3*:

$$\text{Conversion of guaiacol} = \frac{(m_{G,in}-m_{G,out})/M_G \times N_G}{m_{G,in}/M_G \times N_G} \times 100\% \qquad \text{Eq.2}$$

$$\text{Selectivity of product } x = \frac{m_x/M_x \times N_x}{(m_{G,in}-m_{G,out})/M_G \times N_G} \times 100\% \qquad \text{Eq.3}$$

$m_{G,in}$: Initial mass of guaiacol; $m_{G,out}$: Detected mass of guaiacol in the organic phase; m_x: Mass of product x.

M_G: Molar mass of guaiacol; M_x: Molar mass of product x.

N_G: Number of Carbon in guaiacol; N_x: Number of Carbon in product x.

Results and Discussion

Catalysis characterization

The samples were thoughtfully characterised in our previous work.[17] Briefly, the samples are composed by noble metals nanoparticles supported on commercial activated char. The commercial charcoal powder (C_{darco}) used in this study contained 75.7 wt.% C, 0.2 wt.% H, 0.4 wt.% N and 23.7 wt. % O on a dry ash free basis.[17] The XRD diffraction patterns show an excellent metallic particles dispersion and also indicate that the C_{darco} bare support does not suffer any remarkable structural modification upon metals deposition.[17] In terms of textural properties, the samples are mesoporous materials with a type IV isotherm.[17] Overall there are not significant discrepancies in terms of texture and structure (XRD) among the studied series.

TEM. Particle size is key in the HDO process since the activation of the reactive molecules typically takes place on the metal-support interface.[18] Figure 1 shows representative TEM images of the prepared catalysts (Au/C, Pd/C, Rh/C and Ru/C), no large agglomerations being observed. The distribution of metal particle size has been calculated based on the TEM micrographs (Table 1). Results showed that all catalysts, apart from Rh, presented a monomodal distribution with the mean values of metal particle lower than 7 nm. In particular, Ru/C exhibited extremely homogeneous dispersion on the C support, with the smallest particle size, 2.6 nm (Table 1).

As previously reported, greater deoxygenation ability in guaiacol HDO reaction was observed for Ru/C compared to other noble metals such as Pd/C and Rh/C.[8d] The superior catalytic performance of Ru/C can be also found in Jelle and co-workers' study. Ru/C is superior to catalysts with different support, such as Ru/TiO_2 and Ru/Al_2O_3 and other noble metal-based catalysts, such as Pt/C and Pd/C, achieving high deoxygenation ratio (up to 90wt.%) in bio-oil upgrading process.[19]

Table 1 also shows the dispersion of the active phase, which was calculated from TEM data, assuming cuboctahedra particles and the active phase loading measured by ICP analysis. Metallic dispersion are somehow comparable with values *ca.* 20-30% except for the Ru based catalysts that outstands with a calculated metallic dispersion of 48%.

ICP-MS. The ICP-MS results are also summarized in Table 1. For all the synthesized catalysts, the deposited amount of noble metal is close to a nominal loading of 2 wt.% indicating successful immobilization of the metal on the carbon surface.

DRIFTS. Surface groups may influence the catalytic activity in the HDO reaction and hence a DRIFTS study is relevant to ascertain the chemical functionalities present in the prepared solids. Figure 2 shows representative DRIFTS spectra of the studied catalysts. The spectra are dominated by an adsorption band at 1590 cm^{-1}, that is due to the ν(C=C) vibrations belonging to the sp^2 rings, those around 1430 assigned to aliphatic C-C bonds and/or carboxylate groups.[20] and a wide set of bands in the 1000-1300 cm^{-1} region that includes mainly bands associated with C-O stretching in ethers, lactones, phenols and carboxylic anhydrides.[21] Additionally, the spectral features that appear in the region 700-900 cm^{-1} can be attributed to the ν(C-H) vibrations out of the plane of aromatic compounds and C-H stretching bands of aliphatic species are observed in the 2800-3000 cm^{-1} range.[22]

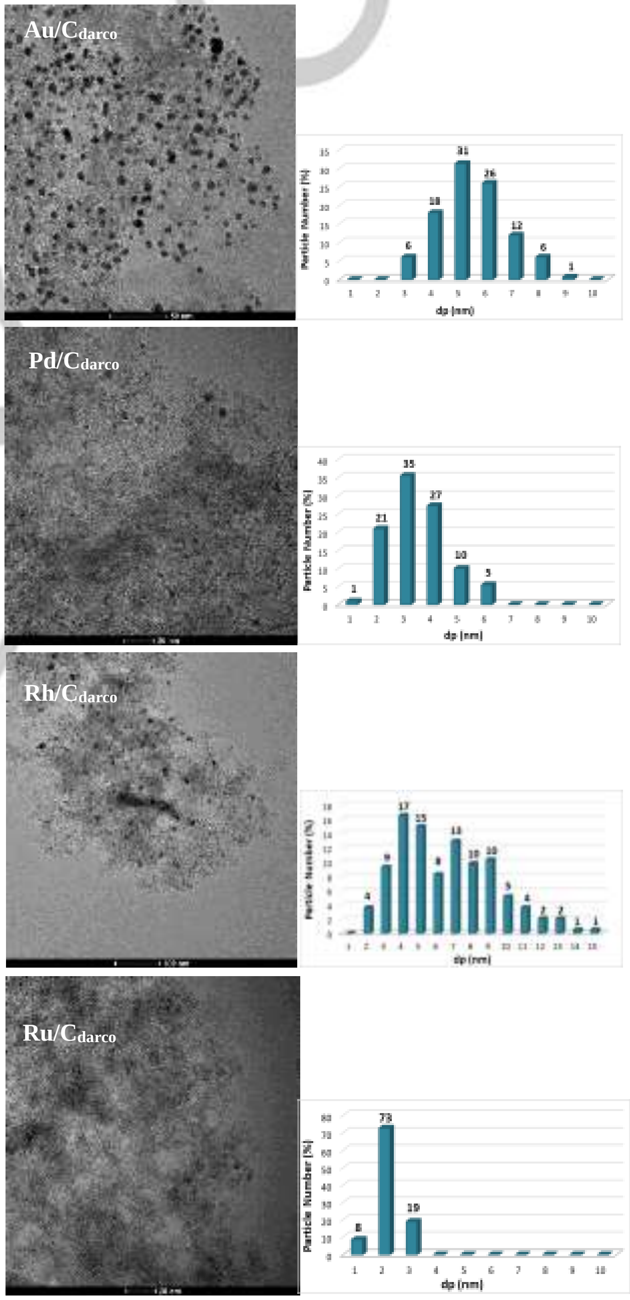

Figure 1. TEM micrographs of catalysts and metal particle size distribution.

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Table 1. Mean metal content, particle size and dispersion

Sample	wt.% Metal (ICP)]	Average metal particle size (TEM, nm)	Dispersion (%) ±0.5
Ru/AC	2.0	2.6	48
Rh/AC	1.4	6.7	20
Pd/AC	2.0	3.9	33
Au/AC	2.0	6.0	22
Ru/AC PR [a]	-	2.9	44
Rh/AC PR [a]	-	4.9	27
Pd/AC PR [a]	-	13.6	11

[a] PR:Post reaction

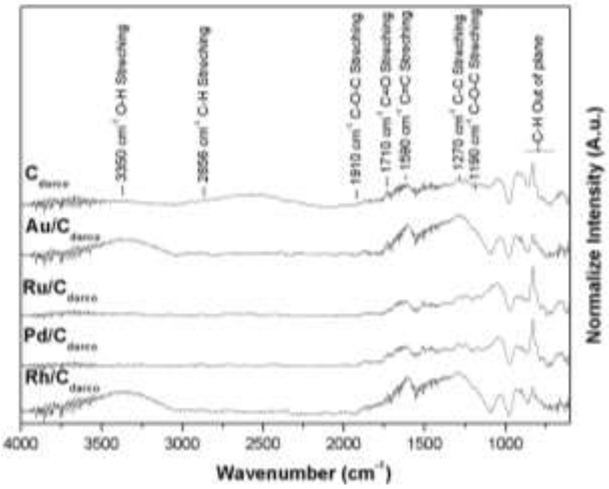

Figure 2. DRIFTS spectra of C $_{darco}$ support and prepared catalysts

On the other hand, the bands observed in the 1950-1600 cm^{-1} range can be attributed to the C=O stretching vibration of carbonyl groups in aldehydes, ketones, carboxylic acids, esters, and acid anhydride.[20a] The wide band observed in the 3200-3700 cm^{-1} range indicates the presence of hydroxyl groups that are interacting with the physisorbed water by hydrogen bonds, although the univocal assignment in this region is complex since it includes contributions from various groups.

The metal deposition does not affect substantially the shape of the spectra, although a notorious loss of the surface groups is produced. Also, it is interesting to note that those catalysts prepared by impregnation in acetone (Pd and Ru) lead to carbonaceous materials where the amount of surface hydroxyl groups is lower than in the case of the catalysts prepared in water media (Au and Rh).

Catalytic behaviour

Carbon support and four noble metal based catalysts, including Pd/C, Rh/C, Au/C and Ru/C were tested in the HDO of guaiacol without the supply of external H_2, at 250 ºC for 4h. A non-catalytic experiment was performed at the same reaction condition for sake of comparison. As shown in Figure 3, the conversion of guaiacol without catalyst was incomplete, with only 9.87 wt.% of conversion. The conversion of guaiacol remains at low level over C support. In comparison, the present of noble catalyst improved the conversion of guaiacol during *in-situ* HDO process. For example, the conversion of guaiacol obtained over Au/C (23.46 wt.%) and Ru/C (25.07 wt.%) catalysts was more than twice compared to that of blank result. The superior catalytic performance of Ru/C could be ascribed to the higher dispersion and small particle size of Ru particles on the carbon supported by TEM analysis and also the higher intrinsic activity of Ru, since no apparent different textural properties (S_{BET}) exist among these catalysts.[17] Very importantly, Ru/C preserve stable physicochemical features after the HDO reaction (as supported by the characterization of the spent catalysts).

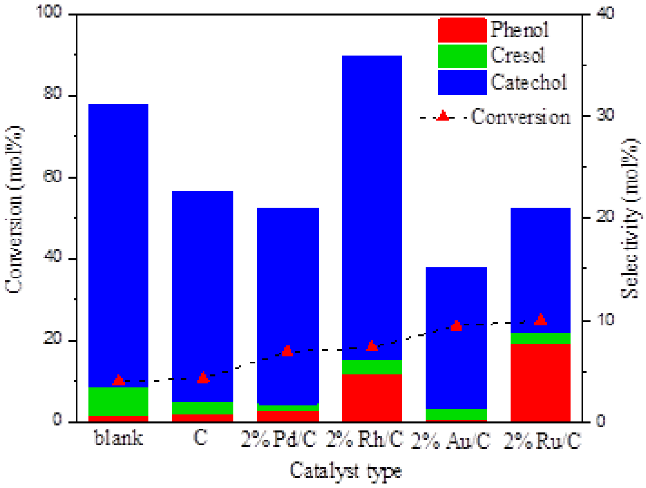

Figure 3. Activity of noble catalysts in in-situ HDO Process

A simplified representation of the HDO pathways of guaiacol based on the observed product distribution is proposed in Figure 4. Three typical mono-aromatic compounds, namely phenol, cresol and catechol, were detected in the organic phase. Unfortunatally, bezene was not produced during the experiment. It is quite challenging to realize the entire deoxygenation since the HDO reaction was conducted suppresing external hydrogen supply. Guaiacol can undergo a transalkylation process in which the methyl group on the methoxy group is transferred to the aromatic ring at the ortho position to produce methyl-catechol. Then, the two phenolic hydroxyls can be hydrogenolyzed to produce *m*-cresol and *o*-cresol. The high selectivity of catechol in all the product distribution indicates the presence of other HDO pathways. The formation of catechol is the most preferred process, because the C(sp^3)-O bond is most likely to be broken since it presents the lowest bond energy.[23] Guaiacol could undergo demethylation (DME) process to produce catechol as well as CH_4. Catechol can further produce partially deoxygenated product, phenol, through dehydroxylation (DHO) reaction during HDO process with H_2 supply.[23] In contrast, the dehydroxylation (DHO) reaction hardly happen in the water-only reaction system, which is the determinant for the low deoxygenation ratio in HDO process. In this case, the further enhancement towards the production of deoxygenated products lies in the dihydroxylation reaction for the HDO using water as hydrogen donor. Another possible pathway

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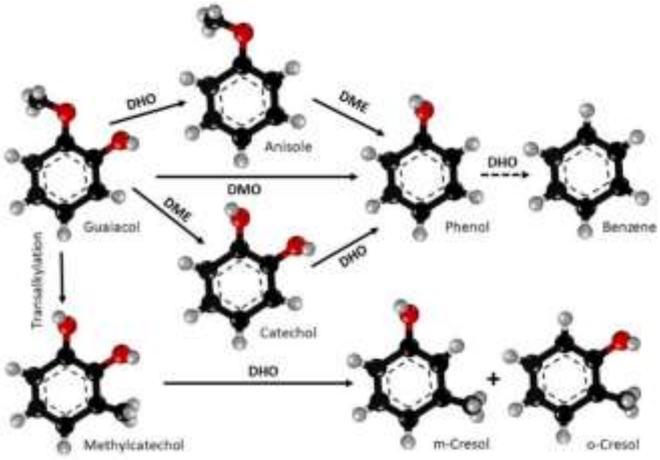

Figure 4. Proposed reaction pathways of guaiacol HDO over noble metal catalysts (DMO: Demethoxylation DME: Demethylation; DHO: Dehydroxylation).

for the production of phenol is the direct demethoxylation (DMO) of guaiacol. The presence of this pathway can be judged by the detection methanol in the product distribution. Anisole can be derived from the hydrogenation of C (sp2)-OH bonds. Anisole can be further hydrodeoxygenated to phenol. The possibility of this pathway can be further speculated from the product distribution and the short HDO reaction time, since no anisole was detected in our HDO products (4h's reaction). The production of partial deoxygenated products, phenol and cresol is greatly improved over Rh/C and Ru/C catalysts, indicating the superior ability of demethoxylation and/or dihydroxylation. The highest conversion of guaiacol and selectivity of deoxygenated products indicate Ru/C is the best performing catalysts compared to other noble metal catalysts for the upgrading of guaiacol suppressing external H_2 supply.

One of the main challenges in a "H_2-fee" HDO process is to incorporate the H_2 from water splitting into the organic molecules. Hence, in order to rule out the possible contribution of hydrogen released from the support's functional groups whose presence is evident in the DRIFTS analysis, a TPD analysis of the studied samples was conducted. The He-TPD results of Ru/C catalyst can been seen in Figure 5. H_2O (m/z=18), CO_2 (m/z=44), CO (m/z=28) and H_2 (m/z=2) released from the catalyst during the temperature programmed process. H_2 can only be found when temperature is higher than 375 °C (the signal of m/z=2 observed at 58°C comes from H_2O desorption). This result confirms that our catalysts do not provide any hydrogen during the *in-situ* HDO at the selected reaction temperature (250 °C) and hence the only source of H_2 is water via water splitting. Also carbon gasification ($C+H_2O \rightarrow CO+ H_2$) is discarded under the studied conditions since it requires much higher temperatures as previously reported [23]

Characterization of spent catalysts

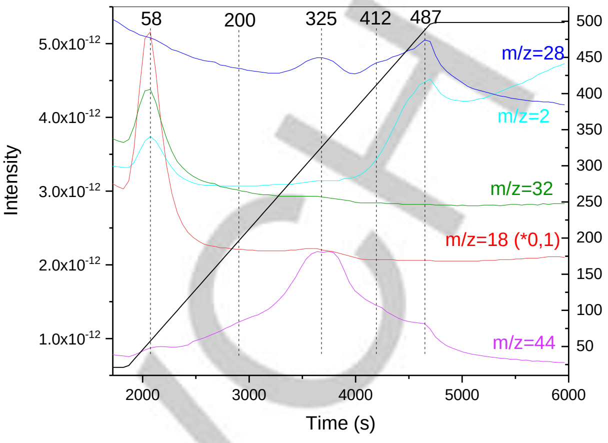

Figure 5. He-TPD profile of Ru/C catalyst

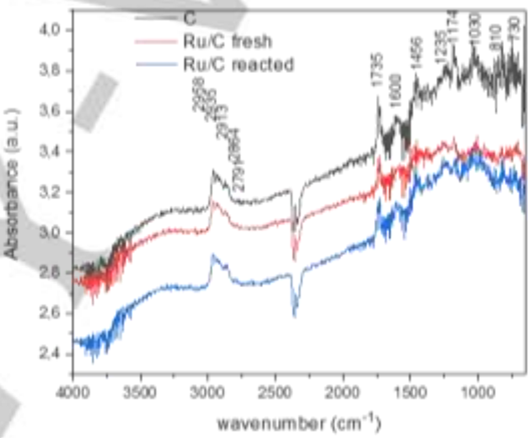

Figure 6. DRIFS spectra of support, fresh and spent Ru/C catalysts

DRIFTS. Representative DRIFTS spectra comparing fresh and reacted Ru/C catalysts are shown in Figure 6. There is no apparent difference between the fresh and spent Ru/C catalysts, indicating the Ru/C is kept stable during the HDO reaction and the functional groups remain unchanged corroborating the TPD results.

TEM of spent catalysts. Considering metallic sintering as the main danger for catalyst deactivation in HDO processes (particularly taking into account the high pressures used in the reaction) a detailed post reaction TEM study was conducted. Figure 7 as well as Figures S1 to S6 in the supporting info show the results of this study.

Clearly, the spent samples of Au and Pd based catalysts, suffer for sintering of the active phase since their average particle size increase from 6 nm to 28.5 nm and 3.9 to 13.6 respectively (Table 1). However, this effect is relaxed for the Ru catalyst, where the sintering of the active phase is almost negligible (Table 1) showing very similar particle size

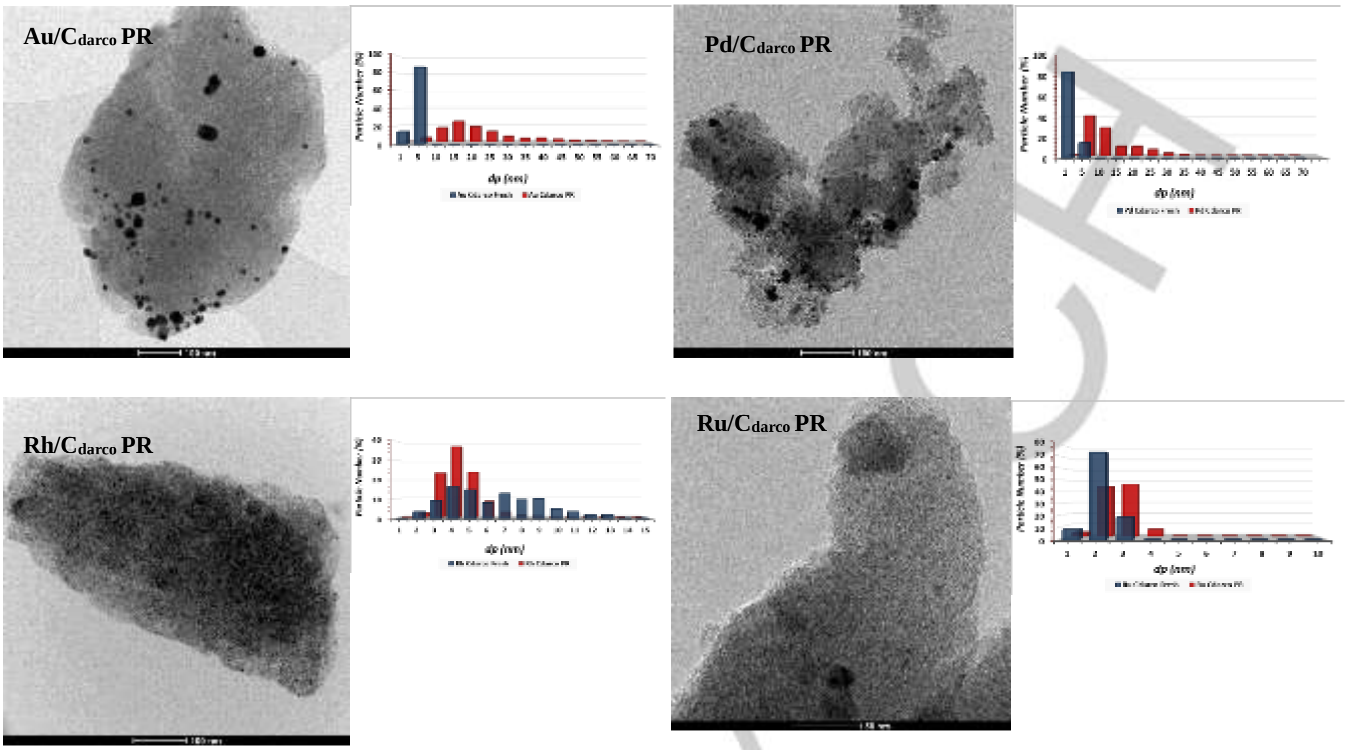

Figure 7. TEM and metal particle size distribution of spent catalysts

distributions. A particular case occurs for the rhodium catalysts where a clear evidence of redispersion/breaking of the metallic nanoparticles under reaction conditions was found, leading to lower particle sizes in the spent catalyst. This behavior has been extensively reported previously for noble metal nanoparticles under reductive atmosphere (H_2, CO, *etc.*) and high temperatures or pressure.[24].

Further structural information regarding the sintering phenomena was gathered by HAADF HRTEM of the fresh and spent samples (Fig. S1 and S3, supporting material) EDX mapping analysis (Fig. S2 and S4) and HRTEM (Fig. S5). In principle the sintering process may induce modifications on the preferential exposition for certain family of planes. In that case we could identify those planes and obtain fundamental information about the metallic sintering process for samples and potentially prevent it. Unfortunately, the HR-TEM images reveal a simultaneous growing of the gold and palladium particles affecting all the exposed family of planes. Hence we cannot spot whether there is a particular family of planes susceptible to sinter. Anyway, in practical terms the HR-TEM back up the TEM experiments indicating the superior stability of the Ru and Rh based materials against Au and Pd which are certainly poorer choice for this process in terms of stability.

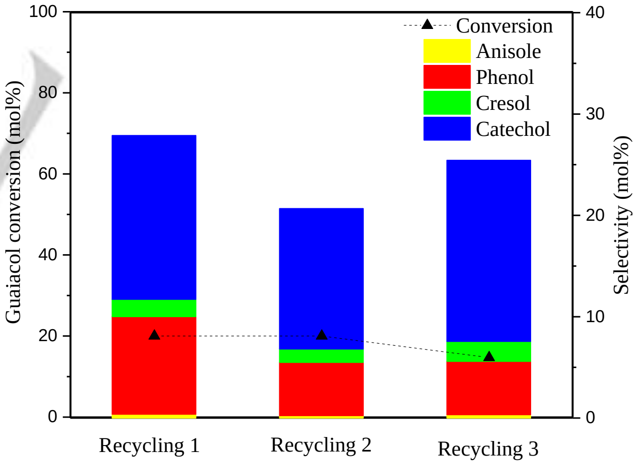

Figure 8. Recycling tests of Ru/C catalyst

Recycling test. The stability of the best performing catalyst, Ru/C, was investigated in a recyclability test, in which the activity of Ru/C catalyst was tested in three consecutive runs. As shown in Figure 8, the activity of Ru/C catalyst remain at high level even though a slightly decrease of guaiacol conversion can be seen after the third activity test. The excellent stability results displayed by the Ru/C catalysts is backed up by the TEM images of spent sample after the multiple cycles (Figure S6 supporting info). As shown in Figures S6 (supporting info) no sintering at all was observed after 3 consecutive runs validating the robustness of this catalyst for the H_2-free HDO process. Leaching of the active phase cannot be fully discarded and perhaps it accounts for the subtle activity drop after 3 cycles. In any case the obtained results with the Ru/C catalyst are very encouraging.

Conclusions

This work showcase an innovative route for biomass valorisation via "H_2-free" hydrodeoxygenation reactions. We propose the production of hydrogen through water splitting and its further implication in a HDO reaction to achieve bio-compounds deoxygenation. To verify the practicability of this route, HDO of guaiacol was conducted over a series of noble metal catalysts in a high-pressure batch reactor. Results showed that the conversion of guaiacol were all improved over noble metal based catalysts, compared with a non-catalytic process. The conversion of guaiacol in the best case is around 25% under the selected conditions in catalytic HDO reactions.

Among the studied noble metal catalysts (*i.e.* Au/C, Pd/C, Rh/C and Ru/C), Ru/C owns the highest activity in our "H_2-free" HDO reaction system. The high activity of Ru/C can be attributed to the greater dispersion and small particle size of metal as corroborated by TEM and HR-TEM. Moreover, the Ru/C catalyst is a robust system with an excellent behaviour during the recyclability test. Catalyst's recyclability is indeed a fundamental aspect when a real application is envisaged and we foresee a great potential for Ru/C type systems.

Overall, this seminal work validates the viability of "H_2-free" bio-compounds upgrading reactions. We sympathise with the not extremely high conversion values reported in this work but still the fact the partial deoxygenation and molecules upgrading can be achieved without external hydrogen supply is a highly commendable result that could represent tremendous advantages from operational cost and process safety perspective. Building upon the results of this paper we hope to inspire the catalysis community to develop highly active materials for this process that may revolutionise our current understanding of biomass upgrading technologies.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Keywords: Hydrodeoxygenation • water splitting • noble metal catalysts •activated carbon • guaiacol

Table of Contents

This work showcases an economically appealing route for oxygenated bio-compounds upgrading via "H2-free" HDO reactions. We have applied noble metal based catalysts in the partial de-oxygenation of guaiacol as a model molecule in a high-pressure batch reactor in which water is used as hydrogen source. The activity of Ru/C catalyst is superior to other studied catalysts (i.e. Au/C, Pd/C and Rh/C) which is probably due to its greater dispersion and smaller metal particle size and also to the intrinsic activity of Ru for this process. Although still on an early stage we believe this route constitutes a promising approach to develop cost-effective processes for biomass valorisation

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