

# Carbon based catalysts for the hydrodeoxygenation of lignin and related molecules: A powerful tool for the generation of non-petroleum chemical products including hydrocarbons

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## Abstract

Lignin has a complex aromatic framework capable to generate aromatic compounds, which have the capability to replace many chemicals including hydrocarbon fuels derived from unrefined oil. However, the selective cleavage of polymeric lignin to simpler molecules is a demanding task due to excessive oxygen content in it. Hence, reducing the whole oxygen content from lignin by-products is necessary. Hydrodeoxygenation is a process which is capable to reduce the overall oxygen content present in lignin with the support of molecular H<sub>2</sub>. Carbon materials deliver a good opportunity to design catalysts for hydrodeoxygenation by providing chemically inert surface and tunable functional groups to support the metal nanoparticles. **The main objective and novelty of this work is to give an account on the use of carbon material supported heterogeneous catalysts for the HDO of lignin and related molecules for the synthesis of non-petroleum chemical products including hydrocarbons.** Thus, this review represents a variety of carbon catalysts for performing the HDO reaction of lignin or its derivatives. The surface **properties** of the catalysts and mechanistic insights **into the conversion with key active sites** are provided, **which will help the designing of new and effective catalysts for this biomass conversion. Also, the work will help to formulate the policies for the use of lignin based biomass materials for catalytic conversions and sustainable development.**

Keywords: Lignin, hydrodeoxygenation, metal, catalysts and carbon materials.

## 1. Introduction

**Biomass energy is the conversion of biomass into useful forms of energy such as liquid fuels, heat and electricity. It is considered to be an alternative energy source in reducing emissions of air pollutants and greenhouse gases (GHGs); and in energy-intensive sectors for safeguarding energy security [1]. Due to its environmental merits, various regions have**

formulated the policy plans to develop biomass energy. The United States Renewable Fuels Standard sets mandatory target for producing 16 billion gallons of biofuels from lignocellulosic biomass by 2022 [2]. In addition, the United States Department of Energy has identified top twelve building block chemicals produced from lignocellulose for fulfilling the current demand of chemicals and energy [3]. The European Union as a whole has set a target to increase the number of biorefineries [4]. European Union council (EUC) has also adopted a policy to replace at least 20% of the total energy consumption by renewable energy. Moreover, similar policies have been adopted by many developed and developing countries to save the environment [5]. Scientists and environmentalists also make the argument to reduce carbon emissions by maintaining the carbon cycle [6]. These policies would inevitably result in a sustained supply of enormous amounts of lignin.

Plant biomass is made up of renewable organic materials and constitute an ideal source for deriving different chemical products and fuels [7]. The most important elements of plant biomass resources are lignin, cellulose or hemicelluloses [8]. Lignin, along with the cellulose, is an extremely abundant three-dimensional amorphous biopolymeric molecule present in the structural cell wall of the massive vascular plants [9]. It is one of the essentially natural occurring polymers with vigorous material properties [10] and considered as the major source for generating renewable aromatic compounds and polymers [11]. Lignin is predominantly made up of three major monomeric units that are *p*-coumaryl, coniferyl along with sinapyl alcohol [12] (**Fig. 1**). These monolignol subunits contain dissimilar categories of functional moieties such as hydroxy and methoxy, which are the key sites for the adsorption of substantial metal ions occur in plants [13]. Chemical modification of lignin can provide various chemicals like alcohols, phenols, catechol, benzene, cresol, toluene, xylene, syringaldehyde, vanillin, keto acids, vanilic acid, aromatic diacid, quinines, syngas, dimethoxyethane (DME), cyclohexane and fuel additives, [14]. Currently, chemical or biochemical routes are the only two major pathways used for deriving chemicals from lignin [15].

Soil microorganisms like fungi along with bacteria are mainly used for the depolymerisation of lignin or its model molecules [16]. Both the brown as well as white rot fungi used as a depolymerising agent for lignin. The white-rot fungi are well-known to break the lignin matrix by producing numerous types of extracellular oxidative enzymes (oxidoreductases) present in a plant cell wall [17], although the white-rot basidiomycetes de spoiled the methoxyl groups rapidly. The brown-rot fungi can also destroy the wood polysaccharides with minimal modification of lignin in addition to form a brown substance containing

oxidized lignin, which is primarily a resource of perfumed compounds in soil [18]. Bacteria are also reported to affect the breakdown of lignin particularly by rapidly degrading the side group [19]. The biochemical pathways for lignin conversion have disadvantages [20] such as their high sensitivity and slow rate of degradation. These soil microorganisms principally depends upon the nature and growth of the enzymes [21]. Hence, the chemical routes for lignin conversion should be focussed to provide speedy supply for the renewable chemicals and products [22]. Carbon based heterogeneous catalysts are reported to provide an excellent opportunity for the speedy conversion and high product selectivity of lignin into precious chemicals as well as prospect to recycle the catalyst without negotiating the damage of useful metals [23], [24]. Due to these and other explanations, these materials have attracted the attention of researcher and scientists worldwide.

Carbon materials mostly act as a support and catalyst for the chemical transformation of lignin [25]. Their exceptional properties like chemical inertness, outstanding electron conductivity, enhanced porosity and precise surface area promote their use in catalysis for different liquid and gas phase reactions including the lignin conversion into essential molecules [26]. Carbon atoms are able to form different allotropes with distinctive physicochemical properties such as superior electronic conductivity, high specific surface area, excellent stability, tunable surface functional groups and variable porosity [27] depending upon their crystal structures, and exist as activated carbon, carbon black, carbon aerogel, fullerene, diamond, carbon nano-fibers, carbon nano-tube, graphite and graphene [28]. Major features, advantages, and disadvantages of carbon materials are shown in Table 1. These features help us to design supported carbon metal catalysts based upon the reaction requirement [30].

<b>Table 1.</b> Key features, advantages, and disadvantages of carbon material				
<b>S. No.</b>	<b>Carbon materials</b>	<b>Advantages</b>	<b>Disadvantages</b>	<b>References</b>
1.	Activated carbon	<ul style="list-style-type: none"> <li>• Cost-effective</li> <li>• Good porosity</li> <li>• Large surface area</li> <li>• Presence of various functional groups</li> </ul>	<ul style="list-style-type: none"> <li>• Non selective combustible</li> <li>• Difficult to remove after dosing</li> <li>• Difficult to reactivate after use</li> </ul>	AC-1, AC-2

2.	Carbon nanotube	<ul style="list-style-type: none"> <li>• Small and compact</li> <li>• Light weight</li> <li>• Resistant to temperature</li> <li>• Conductive mechanical properties</li> </ul>	<ul style="list-style-type: none"> <li>• Lack of solubility in aqueous media</li> <li>• Expensive to produce</li> <li>• Tedious reactors required for production</li> </ul>	CNT-1
3.	Carbon nanofibers	<ul style="list-style-type: none"> <li>• Inexpensive setup</li> <li>• Flexibility to control fiber composition</li> <li>• High surface area</li> </ul>	<ul style="list-style-type: none"> <li>• Control of pore structure</li> <li>• Difficulty in attaining the situ deposition</li> </ul>	CNF-1
4.	Graphene	<ul style="list-style-type: none"> <li>• Pliable and transparent</li> <li>• Good conductor of both heat and electricity</li> <li>• High porosity</li> <li>• Transparent and lighter material</li> </ul>	<ul style="list-style-type: none"> <li>• It exhibits some toxic qualities</li> <li>• doesn't have a band gap</li> <li>• Susceptibility towards oxidative environments</li> </ul>	Graphene-1
5.	Graphite	<ul style="list-style-type: none"> <li>• Corrosion resistance</li> <li>• Low bulk resistivity</li> </ul>	<ul style="list-style-type: none"> <li>• Poor porosity</li> <li>• High weight and volume</li> </ul>	Graphite-1
6.	Diamond	<ul style="list-style-type: none"> <li>• highest thermal conductivity</li> <li>• Transparent and hardest</li> </ul>	<ul style="list-style-type: none"> <li>• Expensive</li> <li>• Requires high pressures and temperatures</li> </ul>	D-1

The structure, physical and chemical properties of lignin are significantly changed during the thermochemical processes. Lignin is mainly made up of phenolic aromatic compounds and its type mainly depends upon the concentration of these compounds along with the nature of plant species. Most of the lignin is produced from the edible crops globally hence it provides us an easy access to a renewable source. Different conversion modes can be used to obtain various types of aromatic compound from the lignin. Therefore, both chemical and biological methods are being developed for the conversion and depolymerisation of lignin to make this material suitable for bio-refineries [31]. The physical properties of biomass have different effects on its chemical conversion to non-petroleum chemical products. The important physical properties that need to be addressed during biomass conversion are moisture content and particle size. Beside these physical properties, chemical

characteristics such as extractives/volatiles, ash content, and ration of cellulose to lignin also play intricate roles during biomass conversion [32].

Plant biomass acquires much superior oxygen contents in comparison to gas, coals and crude oils obtained from petroleum resources [28]. Hence, it is extremely desirable to reduce its O<sub>2</sub> content in order to make it equivalent to petroleum resources [33]. Hence, efficient technologies to eliminate the extra oxygen content exist in the biomass resources are required. Hydrodeoxygenation (HDO) is one of the efficient tools capable to reduce the excess oxygen content in organic compounds by using molecular hydrogen in combination with a suitable metal catalyst [34], [35]. Carbon material supported catalysts were employed as an efficient catalysts applied for HDO process [36], [37] and have great potential towards the selectivity of the product with the support of surface functional units and their exceptional electronic properties [38]. Other materials such as alumina, silica and zeolites are also reported in literature as the supporting materials for the HDO of lignin and its related molecules. But these materials suffer from several disadvantages such as difficulty in controlling the hydrolysis rate, low compatibility, formation of aggregates/agglomerates and control of shape selectivity. Here in this review, carbon supported metal catalysts with excellent surface properties have been discussed for the HDO of lignin and related molecules. The work will be beneficial for understanding the behavior of carbon based heterogeneous catalysts for this particular reaction and serve a pivotal role in catalyst design for the lignin based bio-refineries. Also, the policy makers can use this document for drafting policies for chemicals or catalysts designs.

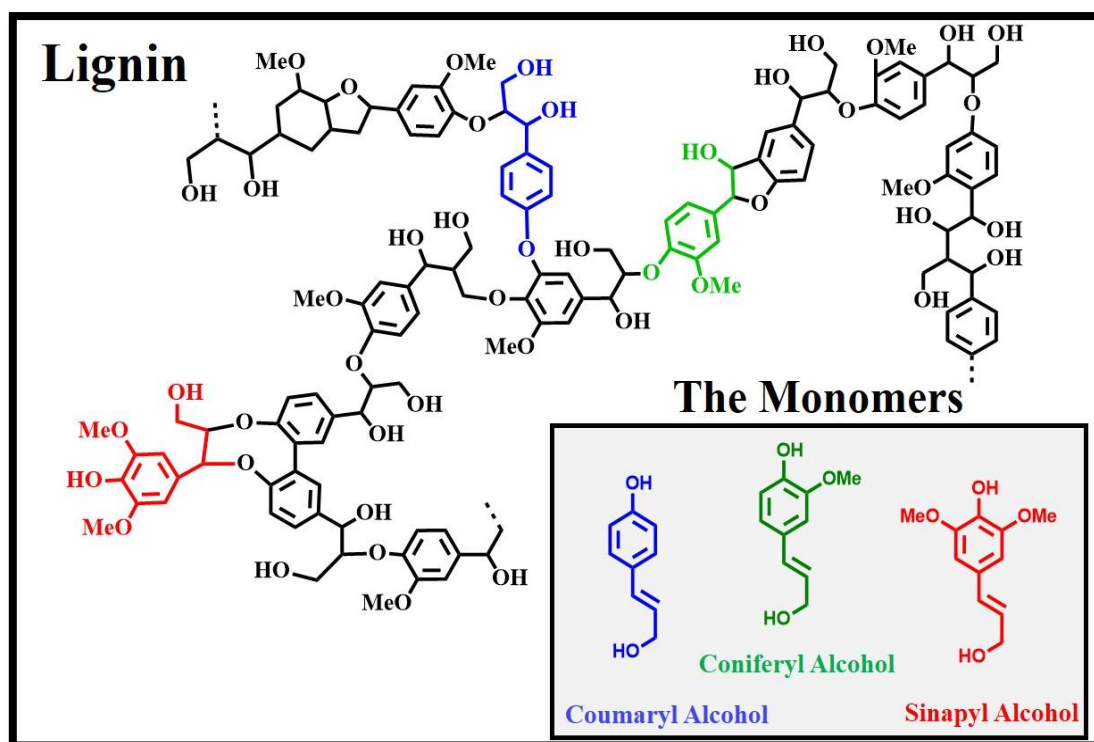
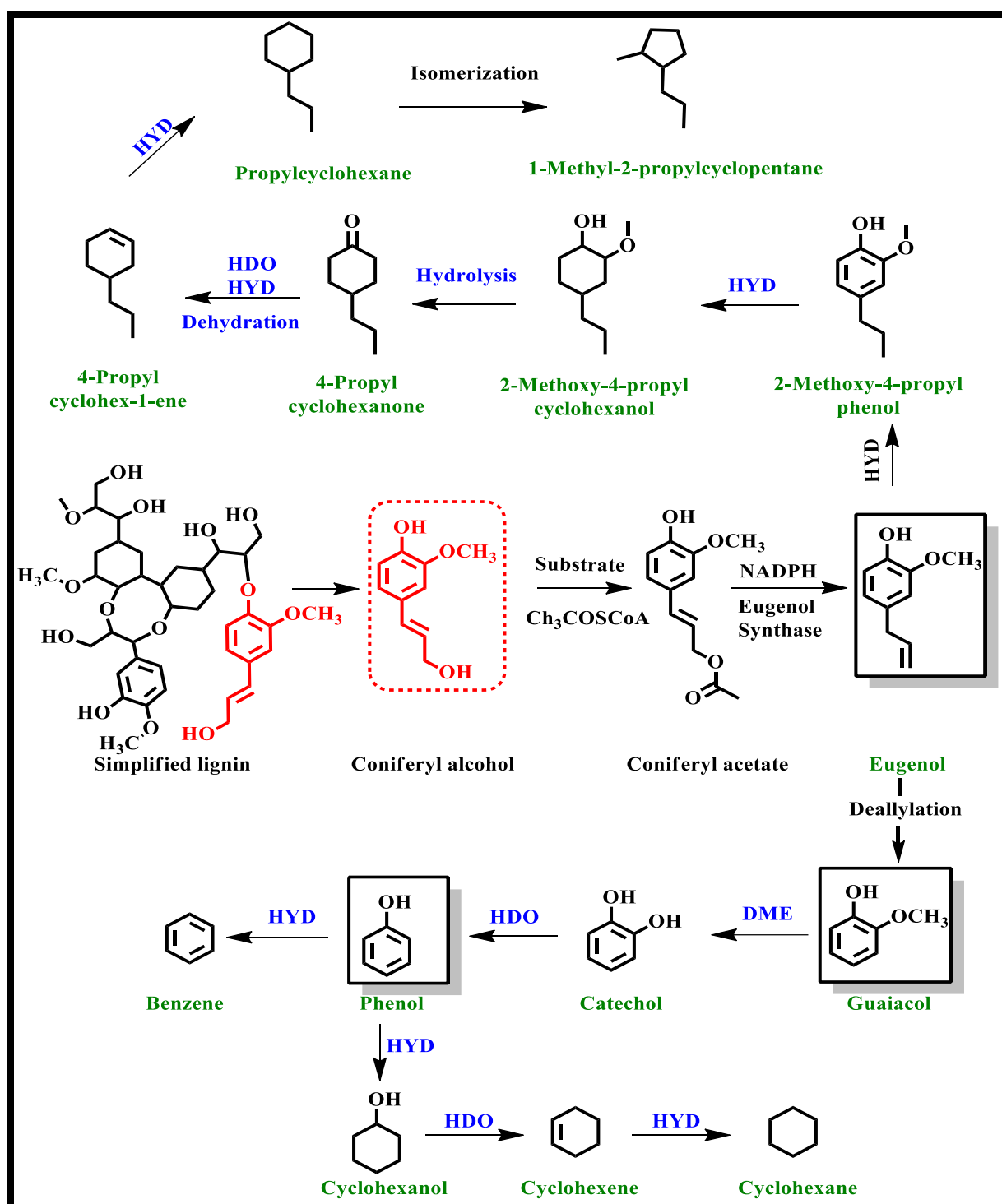


Fig. 1. Polymeric composition of lignin and its monomers.

## 2. Hydrodeoxygenation of Lignin and related molecules

Catalytic hydrotreatment, particularly HDO is a capable way for lignin valorisation that allows upgradation of platform molecules (building blocks) to target chemicals by removing the surface oxygenated groups and hydrogenation of aromatic products or alkenes [39]. It is used to cleave C–O–C linkages in lignin and its products to improve their industrial application [40]. Few commercially available products also have been used as model compounds to study the HDO process of lignin. They include molecules such as guaiacol and catechol that represent the ether linked monomers of lignin; and phenol representing the phenolic products derived from lignin. Different reaction pathways [41] to derive chemicals from simplified lignin by using HDO reaction are presented in **Scheme 1**. These pathways can be combined with other processes such as deallylation [42], hydrolysis (HDL) [43], hydrogenation (HYD) [44] and demethylation (DME) [45] to improve the overall efficiency. The phenolic derivatives produced by hydrolysis can be enriched by hydrogenation and HDO. The complete hydrogenation of phenolic compounds into a cyclic compounds were performed by a metal containing carbon catalyst in the company of Brønsted acidic co-catalyst [46]. Hydrogenation and HDO both make use of molecular H<sub>2</sub>, but only HDO is capable to diminish the oxygen content [47], [48], [49], [50]. Literature reports different

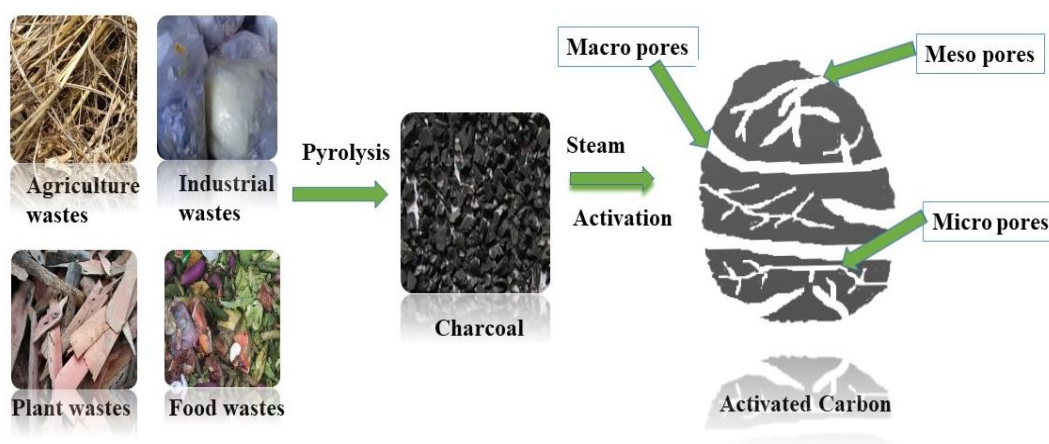
carbon-based catalyst for performing the HDO of lignin, or its model compounds, and are summarised below.



**Scheme 1.** Reaction pathways to derive chemicals from lignin through HDO; which is combined with deallylation, hydrolysis, hydrogenation and demethylation.

## 2.1. Activated carbon (AC) supported catalysts

AC is a highly porous material that has been used for the partition of gases, revitalization of solvents along with the ejection of organic ingredients from drinking H<sub>2</sub>O [51]. Mainly, the AC is prepared from plants [52], [53], agriculture [54], [55] and industrial waste [56], [57] as demonstrated in **Fig.2**. It shows low ash substance, greater surface area as well as high adsorptive capacity due to the porous structure of AC [58]. Moreover, AC contains carbon in both sp<sup>3</sup> or sp<sup>2</sup> hybridised forms and their ratio may vary depending upon the source and reaction temperature during preparation [59]. Generally, the surface region of AC varies between 950 to 2000 m<sup>2</sup>/g with micropore volume of about 0.50 to 1.0 cm<sup>3</sup>/g [60], [61]. It must be observed that AC obtained from natural resources has many heavy metal impurities that are hard to remove [62].



**Fig. 2.** Preparation of AC from various waste items.

A synergistic Pd/C and Zn<sup>II</sup> catalyst [63] depolymerized a wide variety of wood lignin producing a combined yield of up to 54% of 4-propylguaiacol and 4-propylsyringol from lignin in intact biomass. With Pd/C and Zn<sup>II</sup> both the benzylic OH at C<sub>α</sub>, and the primary OH at C<sub>γ</sub> got cleaved yielding majorly propylguaiacol, and propylsyringol as final products. Pd/C alone only cleaves the β-O-4 ether linkage selectively in both lignocellulosic biomass and lignin model compounds to yield (4-(3hydroxypropyl)-2-methoxyphenol) as the end product.

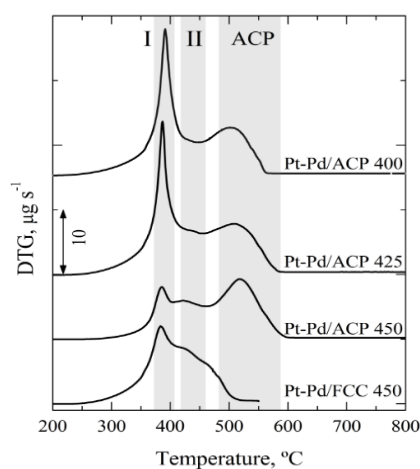
Lignin biomass materials such as softwood and wheat straw were depolymerised [64] with the help of AC supported phosphide metal catalysts NiMoP/AC and CoMo/Al<sub>2</sub>O<sub>3</sub> to produce bio based pungent substances (predominantly alkyl phenols) through a dual stage thermochemical HDO reaction. The NiMoP/AC catalyst was principally prepared through sequential or co-impregnation process by using appropriate metal salt and ammonium dihydrogen phosphate. The resulting material was calcined and reduced to give the catalysts which were further used in reaction. The HDO reaction was mainly performed in stainless steel autoclave by using 100 bar H<sub>2</sub> pressure under room temperature. HDO mainly gave a



solution of many aromatic compounds including guaiacol, cresol, methoxybenzene, catechol and syringol throughout in addition to alkyl phenols. The oil taken from pyrolysis process of lignin resources was first hydrodeoxygenated into guaiacol and catechol by using a commercially available alumina supported bimetallic catalyst CoMo/Al<sub>2</sub>O<sub>3</sub>, because its resistance towards sulphur. The two compounds were generally converted into alkylphenols by HDO reaction at 400°C. Bimetallic catalyst NiMoP/AC gave alkyl phenols such as guaiacols, catechols and aromatic compounds by direct HDO of lignin at 350 and 400°C. Ni containing bimetallic phosphide catalyst NiMoP/AC maintained greater activities as compared to that of sulfided Al<sub>2</sub>O<sub>3</sub> catalyst. The selectivity of the products in phosphide as well as sulfide metal catalysts were comparable, except that of metal sulfided catalyst gave more hydrogenated compounds. The phosphide metal catalyst mainly gave in completely hydrogenated hydrocarbon such as cyclohexylbenzene. The phosphide Ni catalyst preferred the isomerization compounds hexylcyclohexane and (2-methylcyclopentyl) cyclohexane, formed with ring contraction and ring opening of one six-member rings of bicyclohexane respectively. These products might have been formed due to metal and Brönsted acid positions on the surface of catalyst [65].

The HDO of bio-oil (detected from poplar sawdust) into benzene and toluene [66] was performed by using Pt-Pd bimetallic catalyst along with activated carbon containing phosphorus (ACP) and fluid catalytical cracking (FCC) hydro-processing unit. The catalyst support was prepared through olive stone throughout chemical activation technique by using H<sub>3</sub>PO<sub>4</sub>. The bimetallic Pt-Pd/ACP catalyst was mostly prepared via wet impregnation approach by using an aqueous mixture of HPtCl<sub>6</sub>·6HCl as well as PdCl<sub>2</sub> after that slightly acidified through HCl after that heated in a furnace under of N<sub>2</sub> at 400°C. The Pt-Pd/FCC bimetallic catalyst was mainly prepared through wet impregnation process by using Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> and Pd(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> metal precursor and calcined for 3 h at 500°C in air. The activity or selectivity of the prepared bimetallic catalyst Pt-Pd/ACP has been **increased** the main reaction of bio-oil, after that compared along with other commercially equilibrated bimetallic catalyst (Pt-Pd/FCC). The bio-oil reaction was operated in a bed reactor on different temperature conditions ranging from 400–450°C at 65bar H<sub>2</sub> pressure. The prepared bimetallic catalysts were principally characterized by thermogravimetric analysis of temperature program oxidation (TPO). The significance of the reaction temperature on the formation of prepared catalysts were observed by TPO peaks (200–800°C) of Pt-Pd/ACP as

demonstrated in **Fig. 3**. The TPO chart showed dual peaks between 350–550°C, which were shown the occurrence of **coke I** and a **less visible shoulder** as compared to that of **coke II**.

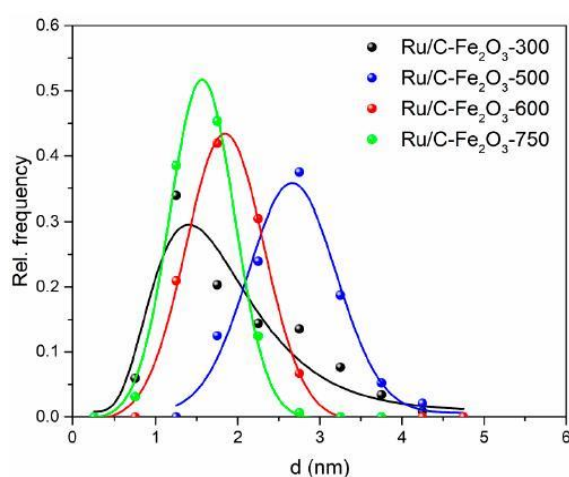


**Fig. 3.** TPO peaks profile for Pt-Pd/ACP metal catalyst at three distinct temperatures along with Pt-Pd/FCC at 450°C. **Reproduced with copyright from reference**[66]. Copyright (2017) Elsevier.

The reduced peak of **coke I** resembles the elevated reaction temperature (450 °C) and higher activity of the catalyst. Two portions of coke were identified in the TPO peak profile of the catalysts, and the amount of both portions displayed a correlation with the catalytic activity and reaction temperature. **However, they promote the production of hydrocarbon, which was the precursors of the coke II** observed in the TPO profile of the used catalyst at the maximum reaction temperature. Pt-Pd/ACP450 catalyst decreased the activity and hydrocarbon selectivity in the HDO reaction of bio oil. These out comes occur because of the instantaneous formation of the coke placed on the surface of catalyst, which is reliable for active sites blockage.

Catalytic HDO and HYD of eugenol [67] were investigated with Fe<sub>2</sub>O<sub>3</sub> based catalytic system, which gave deoxygenated products 4-propylphenol, benzene, toluene and cyclohexane. The catalyst was prepared in four steps. At first, Fe<sup>2+</sup> and Fe<sup>3+</sup> ions were adsorbed onto citrate ion, followed by addition of glucose. Then, the whole reaction mixture was put in an autoclave and then heated for 12 h at 180°C. The dried powder of C-Fe<sub>2</sub>O<sub>3</sub> was heated in a furnace under different temperatures conditions and finally treated with the pink solutions of Ru (III) 2,4-pentadioante and isopropanol in batch autoclave at 150°C under Ar. The results indicate remarkable movement of the synthesised catalysts in the deallylation of eugenol towards guaiacol followed by its HDO that further forms the deoxygenated products. The reaction was mainly completed in an autoclave. The selectivity could be easily tuned by

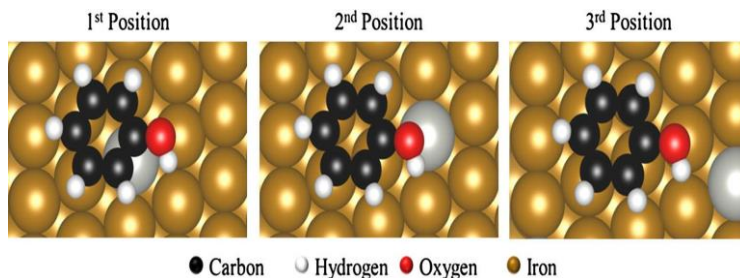
carbonising the catalysts at different temperatures, volume of Ru nanoparticles and its phase dispersity. The involvement from the Fe-phase was not significant during the overall catalytic HDO reaction. The movement HDO reaction was increased with the elevation in annealing temperature at 600 °C and afterwards a gradual reduction in the catalytic activity was observed. The particle mass of catalyst Ru/C-Fe<sub>2</sub>O<sub>3</sub> at 300°C appeared more efficient and the surface was covered with Ru nanoparticles that are principally clustered and showed comparatively substantial size distribution. Whereas, at 500°C the particles of Ru/C-Fe<sub>2</sub>O<sub>3</sub> catalyst were entirely covered with Ru nanoparticles having greatest average mass distribution. Particles of Ru appear similar in shape on the surface, but they were less densely covered with smaller, spherical and larger plate-like size distribution at 600°C. **Fig. 4** mainly shows the mass distribution of catalyst was irregular at 750°C.



**Fig. 4.** Empirical size distribution of functions of Ru nanoparticles on the surface of AC prepared at various temperatures. **Reproduced with copyright from reference**[67].

Eugenol was used to obtain 4-propylguaiacol **with 44.3% selectivity** by HDO reaction [68] with the help of Ni metal on two different supports, alumina silicate Zeolite HZSM-5 and AC. Eugenol is a sweet-smelling molecule that can be obtained from volatile fraction of lignocellulosic bio-oils. Both Ni/AC and Ni/HZSM-5 metal catalysts were mainly prepared through wet impregnation technique under vacuum and ultrasonic conditions and reduced by H<sub>2</sub> at 773 K for 5 h to obtain the catalyst. The reaction of eugenol was completed in a batch reactor by using two different solvents, H<sub>2</sub>O and n-hexane independently. The movement of Ni/AC catalyst in H<sub>2</sub>O was superior to that of n-hexane, in the reaction whereas Ni/HZSM-5 showed the reverse results. It was detected that the percentage of formation of hydrocarbons was increased in the company of HZSM-5, where the large rock crystal range of Ni/AC showed a less hydrocarbon formation.

Vapour stage HDO reaction of guaiacol with 38% selectivity was performed with different transition metal based catalysts such as Pd, Pt, Cu, Fe, Ru, and PdFe on activated carbon support [69]. These catalysts were considered for their capability to produce benzene with other related molecules. The metal catalysts were mainly prepared through wet impregnation technique by using metal precursors as well as calcined at 350°C under the flow of Ar. The major reaction was mainly carried out in a tube-shaped reactor below ambient pressure. Throughout the reaction, the phenol was detected as the key intermediate in all the tested catalysts. Metal catalysts, specifically Fe/AC, exhibited smaller activity but displayed higher HDO selectivity towards cresol, benzene, phenol, and toluene without showing any tendency for ring opening and ring saturation products. The movement of individual metals on AC support can be enhanced by making their bimetallic analogues. One such catalyst prepared was PdFe/AC, which was found to show a significant HDO activity with elevated yield to benzene/toluene at 450 °C. The effective phase catalytic HDO for phenolic compounds was measured on the surface of PdFe by the adsorption of phenolic molecules on Fe(110) shell through Pd atom using DFT study. Three different arrangements of phenol through rising space from the adsorbate to the surface region of Pd atom were mainly considered, as presented in Fig. 5.



**Fig. 5.** Adsorption configurations of phenol on Fe(110) surface with Pd atom. **Reproduced with copyright from reference**[69]. Copyright (2013) Elsevier.

When the distance within the Pd molecule and phenol adsorbate increased, both adsorption energy as well as carbon–oxygen bond length experienced an increase in their values. This superior increase within the adsorption intensity of phenolic molecules with ever-increasing distance from the Pd atom indicated that adsorption of the phenol is more favourable upon the Fe surface of catalyst.

The catalytic HDO of phenolic monomer (guaiacol) and raw bio-oil [70] were performed by Ru catalysts generally supported on three carbon materials such as AC, multi walled nanotubes (MWCNT), and carbon aerogels (CARF). All the three transition metal catalysts were generally prepared through wet impregnation process along with an aqueous

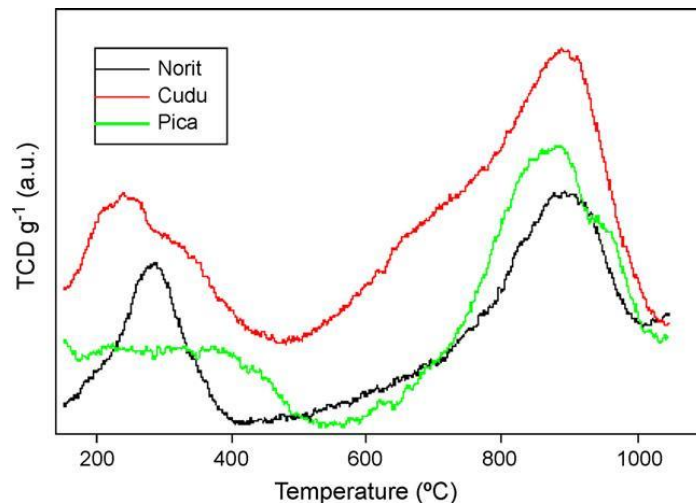
mixture of  $\text{RuCl}_3$  at  $800^\circ\text{C}$ . The impregnated raw material was calcined with air flow at  $400^\circ\text{C}$ , and then further reduced by  $\text{H}_2$ . The hydrodeoxygenation reaction of natural bio-oil or guaiacol was principally done in a fixed batch autoclave. Ru/AC as well as Ru/CARF showed poorer oxygen removals as related to that of Ru/MWCNT, even though they displayed elevated Ru dispersion with additional oxygen functional moieties present on the carbon supports. The conversion of guaiacol and removal of oxygen were 96.1% and 65.6% for Ru/AC, 81.7% as well as 48.0% for Ru/CARF, whereas 98.1% and 81.6% for Ru/MWCNT, catalyst, respectively. The unpleasant properties of carbon surfaces were observed to be almost similar; therefore, the pore structures of these catalysts were indicated to control the catalytic activity. Brunauer Emmett Teller (BET) study was done to check the pore configuration of the carbon material supports and 82% of the surface region was attributed to micropores in AC, but merely 8% of the surface in MWCNT was attached to micropores. This alteration in the pore area may have affected the unprotected effective sites and hence difference in the activity of catalysts.

Phenolic compound obtained from lignin such as guaiacol were hydrodeoxygenated [71] with bimetallic RuRe catalyst supported by AC. Bimetallic metal catalyst (RuRe/AC) was mainly prepared by sequential impregnation method of dried Ru/AC with aqueous mixture of  $\text{NH}_4\text{ReO}_4$  as precursor and then, dried and exposed to molecular hydrogen for 3h in a flowing mixture of  $\text{H}_2$  and  $\text{N}_2$ . The reaction of guaiacol was completed in an autoclave with 20 bar of  $\text{H}_2$  pressure at  $200\text{--}240^\circ\text{C}$  with a ramping ratio of  $10^\circ\text{C}/\text{min}$ . The Ru and Re metal catalysts supported by AC displayed lower activity towards HDO in comparison to the expensive metal analogues. Benzene was formed with the minimum volume of cresol, toluene and trimethyl benzene with RuRe/AC catalyst throughout the reaction without forming any ring saturated compounds. Therefore, the method is useful to produce sweet-smelling compounds with low or no oxygen content. The results obtained from RuRe catalyst showed that carbon support affected the movement for HDO reaction. The micropores in AC materials were offering small sites for the large phenolic reactants leading to low activity of RuRe/AC metal catalyst. Moreover, the surface can also influence the growth of bimetallic nanoparticles, which are essential for the resourceful hydrogenolysis of the C-OH bond of guaiacol.

Aqueous phase HDO of lignin was investigated through model compounds (guaiacol, phenol and catechol) [72] by four metals supported by AC. The reactions were catalyzed by Ru, Pd, Pt along with Rh metal supported by AC to obtain cyclohexanol and 4-methyl-

cyclohexanol as major compounds. The conversions of these model compounds through commercially accessible catalysts can follow three major reaction pathways that include direct HYD of aromatic ring, demethoxylation including demethylation reaction. All the three catalysts containing Pd, Pt and Rh were deactivated during the HDO reaction, but Ru/AC got the maximum conversion among all. The TEM analysis of the catalysts has indicated that coke formation occurred on Pt, Pd as well as Rh catalysts, whereas Ru catalyst totally hydrogenates guaiacol because of the unique reaction pathway in which phenol was formed as the crucial intermediate that further gave cyclohexanol as well as 2-methoxy-cyclohexanol as major products.

The HDO reaction of 2-methoxyphenol [73] (oxygenated phenol derivative and a model bio oil compound) was carried out in presence of three different ACs (Pica, Norit, Cudu) metal supported catalysts with different chemical and textural applications. **It was concluded that molybdenum nitride (MoN) was an active site for Mo<sub>2</sub>N in the HDO of this reaction.** The all three catalysts were mostly prepared through wet impregnation method using (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O as precursor salt and calcined at 500°C. XPS and TPD profile were used to demonstrate that catalysts surface was rich in acidic sites. TPD profiles of the three different supports as demonstrated in **Fig. 6**.



**Fig. 6.** TPD profile of Norit, Cudu and Pica activated carbons. **Reproduced with copyright from reference**[73]. Copyright (2011) Elsevier.

Activated carbon Norit as well as Cudu bear peaks between 250–400°C and all the supports showed peaks between 800–1000°C, while the Cudu activated carbon also exhibited a shoulder at 600–800°C. The AC shown peaks at low temperature in the range of 250–400°C and medium temperature range between 600–800°C were allocated to carboxylic, phenolic as well as anhydride groups, respectively. The high temperature peaks between 800–1000°C

were transferred to quinone functional groups. The main reaction of 2-methoxyphenol was mainly conducted in an autoclave under 50 bar of H<sub>2</sub> pressure at 300°C. The Mo<sub>2</sub>N/Norit metal catalyst showed greater HDO activity as compared to both Mo<sub>2</sub>N/Cudu as well as Mo<sub>2</sub>N/Pica catalysts. The conversion of the HDO was enhanced when Mo<sub>2</sub>N/Norit metal catalyst was activated with H<sub>2</sub> at 400°C for 6 h due to increase in the surface nitridation. The Mo<sub>2</sub>N/Norit metal catalyst showed superior phenol/catechol fraction as compared to that of the Mo<sub>2</sub>N/Pica as well as Mo<sub>2</sub>N/Cudu metal catalysts. The phenol/catechol fraction was unaffected via H<sub>2</sub> stimulation time.

Finally, it can be concluded that the activity or selectivity of the AC material supported transition metal catalysts mainly depends on the adsorption power of metal, coke deposition, size arrangement of particles. Therefore, it also influenced through functional moieties present on material surface, and different temperature conditions used during the reaction. The different chemicals obtained from HDO reaction of lignin or its model molecules with the help of AC support are shown in **Table 1**.

<b>Table 2.</b> Activated carbon supported metal catalysts used to derive chemicals from lignin					
<b>S. No.</b>	<b>Source (model lignin compound)</b>	<b>Active Metal(s)</b>	<b>Catalyst</b>	<b>Products with yield (%)</b>	<b>Reference</b>
1.	Lignin (softwood / wheat straw)	Mo, Ni	NiMoP/AC	Guaiacol (90%), Phenol (75%) and Catechol (89%)	[64]
2.	Bio-oil (poplar sawdust)	Pt, Pd,	Pt-Pd/ACP	Benzene (70%) and Toluene (75%)	[66]
3.	Eugenol	Ru	Ru/AC	4-Propylphenol (58%)	[67]
4.	Eugenol	Ni	Ni/AC & HZSM-5	Propylcyclohexane (83.4%)	[68]
5.	Guaiacol	Cu, Fe, Pt, Pd, Ru, PdFe	Cu/AC, Fe/AC, Pt/AC,	Benzene (85%), Phenol (78.8%) and Toluene (83.2%)	[69]

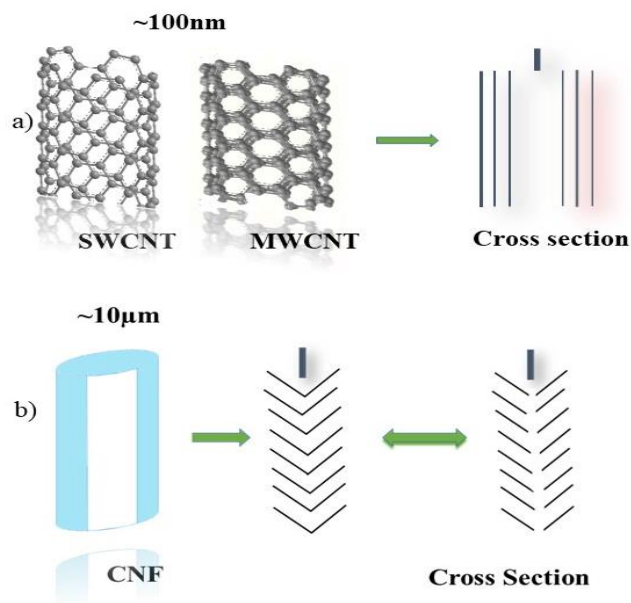


				Pd/AC, Ru/AC, PdFe/AC		
6.	Guaiacol		Ru	Ru/AC	Cyclohexane (24.7%)	[70]
7.	Guaiacol		Ru, Re	RuRe/AC	Cyclohexane (24.9) and Cyclohexanol (86.2%)	[71]
8.	Guaiacol, and Catechol	Phenol	Pt, Pd, Rh, Ru	Pt/AC, Pd/AC, Rh/AC, Ru/AC	Cyclohexanol (65%) and 2-methyl-cyclohexanol (25%)	[72]
9.	2-Methoxyphenol		MoN	Mo <sub>2</sub> N/Norit , Mo <sub>2</sub> N/Pica Mo <sub>2</sub> N/Cud u	Phenol (80%) and Catechol (30%)	[73]

## 2.2. Carbon nanotube (CNT) and carbon nanofiber (CNF) supported catalysts

Carbon nanotubes are the cylinders made up of graphite sheets that may or may not be blocked at the ends [74]. Both the single walled CNTs having diameter smaller than 1nm as well as multi-walled CNTs along with the diameter higher than 100nm are known [75]. Mainly carbon nanotubes operated as a composite catalyst [76], [77] to decrease the amount of metal without compromising its effectiveness [78]. Plant biomass itself mainly used to make nanotubes from the cell barrier of plant with large polymeric lignin content [79]. The CNF is also having a tube-like structure solid from inside. It can be manufactured by decomposition as well as graphitization of affluent organic carbon covering polymer [80]. CNT mostly a single or multi-layered material, whereas CNF is not categorised into such types [81]. CNFs can reach up to few microns in diameter and hence due to their bigger size, they have more disordered bamboo like structure (not a perfect cylinder like CNT), less oriented with multiple defects. **Fig.7.** demonstrates the morphology and cross-section of both the materials. However, the surface of both CNT and CNF [82] is rich in sp<sup>2</sup> hybridised carbon that impart lot of common properties to both the materials [83].





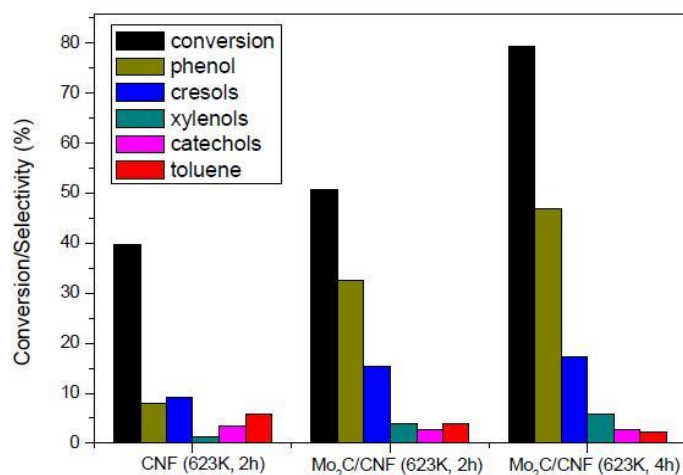
**Fig.7.** Different cross-sections of (a) carbon nanotubes and (b) carbon nanofibers.

The HDO reaction of eugenol [84] was performed with a CNT based catalyst for the development of alkane fuels ranging from C<sub>6</sub> to C<sub>9</sub> carbons in a monophasic and biphasic system. For this reaction, the CNT supported Ru metal catalyst (Ru/CNT) was manufactured by the wet impregnation technique using RuCl<sub>3</sub>·3H<sub>2</sub>O as a precursor and reduced at 250°C in a mixture of H<sub>2</sub> and N<sub>2</sub>. The reaction was completed in a Parr reactor outfitted with magnetic stirrer at 5.0 MPa H<sub>2</sub> pressure. The monophasic reaction was carried out in H<sub>2</sub>O that gave a minimum yield of 56.5% and biphasic reaction was mainly carried out in H<sub>2</sub>O/n-dodecane system that provided a maximum yield of 82% propylcyclohexane. The reaction showed 94% yield and 98% selectivity of alkanes (C<sub>6</sub>-C<sub>9</sub>) in the biphasic system containing water and n-dodecane (1:1) mixture. Decrease in the yield of propylcyclohexane was detected with the increase in organic solvent ratios. For example, only 4% yield of propylcyclopentane was observed, when the HDO reaction was completed in a pure organic solvent. The study thus clearly indicated that H<sub>2</sub>O was essential solvent for HDO reaction to obtain alkanes. The H<sup>+</sup> ions were generated from H<sub>2</sub>O under the hydrothermal conditions, which were helpful in the deoxygenation of the intermediates. Biphasic systems showed superior advantages over monophasic systems in the HDO reactions and CNT was helpful in improving the selectivity towards the desirable products.

Monometallic and bimetallic catalysts for example, Ni, Fe and Fe-Ni supported on CNT were mainly used for the HDO reaction of guaiacol [85] to obtain cyclohexane along with phenol as major products. These bimetallic (Fe-Ni/CNT) and monometallic (Ni/CNT, Fe/CNT) catalysts were mainly prepared by co-impregnation process with the help of

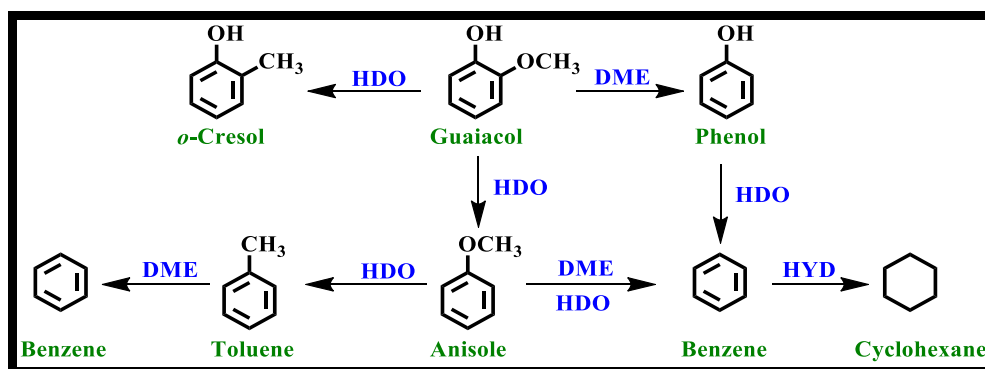
aqueous solutions of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  along with  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ . After impregnation, the mixture was dried, calcined and reduced in  $\text{H}_2$  gas atmosphere. The key reaction of guaiacol to produce cyclohexane and phenol was performed in an autoclave in the presence of  $\text{H}_2$  gas. The bimetallic Fe-Ni/CNT catalyst demonstrated superior reducibility as compared to that of Ni/CNT catalyst. Result distribution was modified by modifying the Ni/Fe atomic percentages, which mostly shown 99.8% selectivity of cyclohexane with 83.7% of phenol under 583K at Fe/Ni ratio of 1:5 and 5:1 respectively. The mean nanoparticle size of Ni, Fe and Ni-Fe on CNT surface was 8.7nm, 5.1nm and 5.3-7.3nm. Nanoparticle size was found to increase with increase in temperature over the CNT supported transition metal catalysts. The selectivity of cyclohexanol increased from 31% to 69%, and that of cyclohexane decreased from 53% to 4.6% with increasing nanoparticle size.

The HDO of lignin model molecule such as guaiacol into cresol as well as phenol was performed [86] with  $\text{Mo}_2\text{C}/\text{CNF}$  metal catalyst. The catalyst was prepared via wet impregnation method, followed by carbothermal reduction. The overall reaction was completed in an autoclave under 2 MPa of  $\text{H}_2$  pressure with 50% selectivity. The  $\text{Mo}_2\text{C}/\text{CNF}$  metal catalyst exhibited higher catalytic activity towards removal of methoxy ( $-\text{OCH}_3$ ) groups, whereas lower activity towards HYD and removal of hydroxyl ( $-\text{OH}$ ) groups was observed with the rise in the overall reaction temperature. The selectivities of phenol and cresols were very high, whereas the selectivity of toluene was much higher than that of cyclohexane and benzene. The reactions show diversification in the reaction routes, and variation in the selectivity for products as presented in **Fig.8**. The demethoxylation reaction was almost missing at 573K. The selectivity for xylenols as well as for phenol was significantly superior as compared to that of bare support (CNF), whereas for  $\text{Mo}_2\text{C}/\text{CNF}$ , the selectivity for cresols was very much smaller. Comparison of CNF support with  $\text{Mo}_2\text{C}/\text{CNF}$  revealed that the guaiacol transfer increased from 39.7% to 50.6% with higher selectivities for cresols, phenol and xylenols.



**Fig.8.** Conversions and product selectivities during the HDO of guaiacol at 573K over the bare CNF support and Mo<sub>2</sub>C/CNF catalyst. Reproduced with copyright from reference[86]. Copyright (2018) Elsevier.

The CNF-supported metal carbide catalysts such as W<sub>2</sub>C as well as Mo<sub>2</sub>C were used for the selective HDO of guaiacol [87] (**Scheme 2**) with low hydrogenation activity. The W<sub>2</sub>C/CNF metal catalyst was mainly prepared by impregnation with ammonium metatungstate solution at 1000°C and Mo<sub>2</sub>C/CNF by pore volume impregnation by using an ammonium molybdate at 900°C under N<sub>2</sub> atmosphere. After impregnation, the samples were kept for 24 h at 80°C under vacuum. The reaction of model molecule was mainly completed in a high-level pressure autoclave. High conversions and elevated selectivity were observed towards phenol with 66% selectivity by using W<sub>2</sub>C/CNF or Mo<sub>2</sub>C/CNF metal catalysts at 350°C under 55 bar H<sub>2</sub> pressure in dodecane. Transformation and selectivity enhanced with reaction temperature for W<sub>2</sub>C/CNF and complete conversion was observed at 370°C with 66% selectivity towards phenol and 21% for cresols. The Mo<sub>2</sub>C/CNF catalyst demonstrates a superior selectivity with almost total conversion (95%) obtained at 325°C. The Mo<sub>2</sub>C/CNF metal catalyst showed higher activity or selectivity towards phenol and anisole. Whereas the W<sub>2</sub>C/CNF metal catalyst was very responsive to oxygen and little quantity of WO<sub>x</sub> phase was detected after the catalytic HDO reaction. Furthermore, carbon nanofibers were preferably suited as support for molybdenum or tungsten carbides, because of its high surface region and mesoporosity.

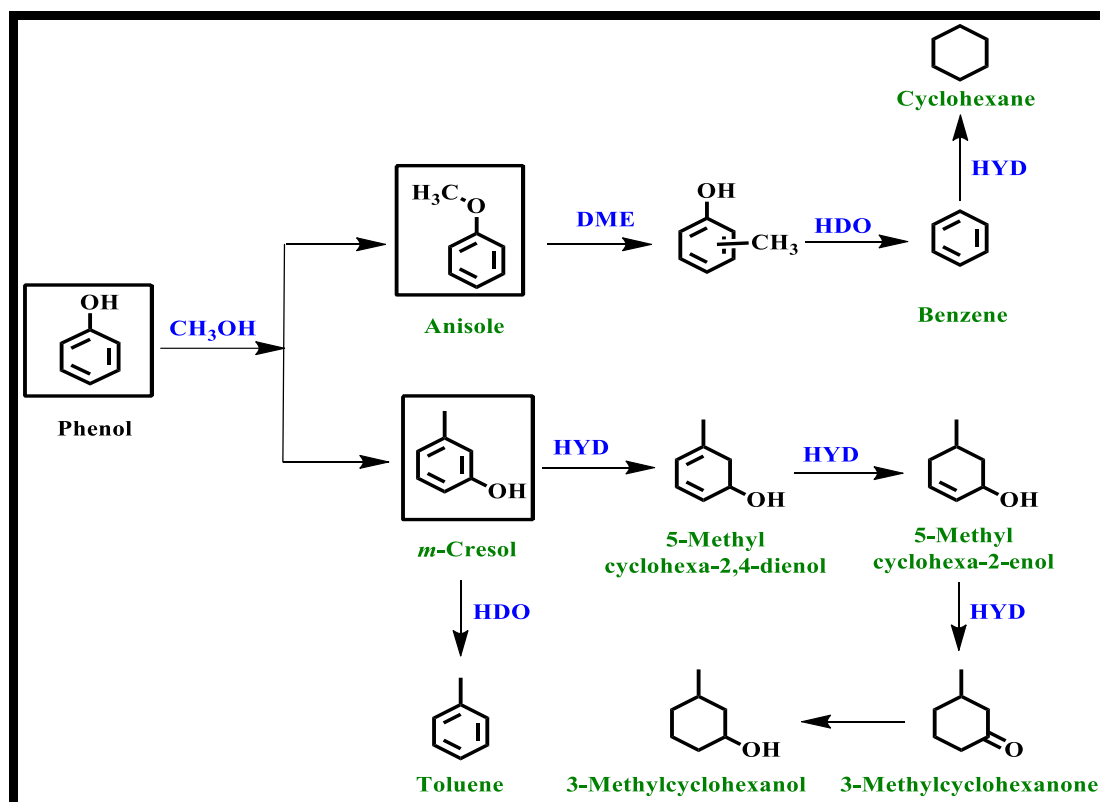


**Scheme 2.** Conversion of guaiacol by HDO, DME and HYD into various products.

Monometallic as well as bimetallic monolith (Inconel) transition metal catalysts for example, Pt, Sn, Pt-Sn and Pt-Sn/CNF supported on Inconel were mainly used for the HDO reaction of guaiacol as well as anisole [88] to produce phenol along with benzene. The Inconel monoliths were dispersed with HNO<sub>3</sub> solution, impregnated with metal under room temperature after that, calcined in existence of air flow. The monolith catalysts were principally reduced *in situ* for 2 h under flow of H<sub>2</sub> at 330°C, 600°C and 450°C for the Pt, Sn and Pt-Sn catalysts respectively, and through copper-impregnation, CNFs were mostly full-grown on the shell of monolith. The reaction for both molecules were completed in quartz cylinder at 400°C under atmospheric pressure. When monolith was coated with CNFs, the securing positions for functional species (Pt, Sn) and surface region were increased, therefore the productivity of benzene and phenol were increased. The bimetallic catalyst (Pt-Sn) shown greater activity as well as stability as compared with monometallic catalysts (Pt, Sn). The monolith without CNF support shows low conversion in HDO reaction. When CNF was formed on the surface of Inconel monolith, the execution of the Pt-Sn bimetallic catalyst was excellent. The CNF increased surface region and then improved the uptake of metal for the HDO reaction.

Carbon nanofiber backed rhenium oxide metal catalyst ReO<sub>x</sub>/CNF<sub>ox</sub> was used [89] for the HDO reaction of phenol (**Scheme 3**) into benzene with 59% selectivity. The CNF supported Re oxide metal catalyst was principally prepared through wet impregnation technique using aqueous mixture of ammonium perrhenate and calcined at 573 K in static air. The catalytic HDO reaction was completed in a stirred batch autoclave at 573K under 3MPa H<sub>2</sub> pressure. The result distribution and activity of HDO reaction showed strong affinity towards H<sub>2</sub> pressure. A superior pressure improved the movement and the HYD capabilities but reduce the selectivity of product. The best ReO<sub>x</sub>/CNF<sub>ox</sub> metal catalyst was also used for HDO reaction of other lignin model molecules such as anisole, guaiacol and *o*-cresol which

shown excellent potential for selectively eliminating the oxygen moiety without C–C chain bond cleavage.

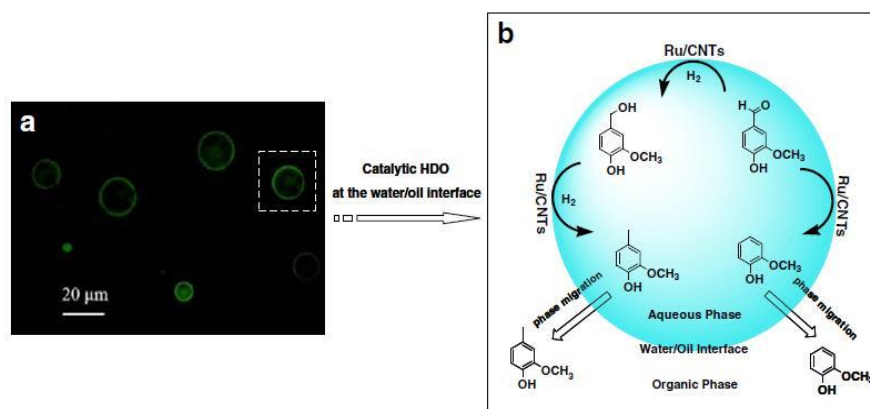


**Scheme 3.** Schematic representation for the synthesis of hydrocarbons and alcohols through HDO, HYD and DME of phenol in methanol.

Carbon nanotube backed molybdenum metal catalyst (Mo/CNT) was mainly used for the HDO reaction of anisole (model compound of lignin) [90] into phenol, 2-methylphenol and benzene **along with 80% selectivity**. The Mo/CNT catalyst was synthesized from functionalized CNT by its impregnation with a molybdenum containing precursor and then metal nanoparticles were deposited on the support in a flow reactor with the help of H<sub>2</sub> gas. Catalytic HDO reaction of gas phase reactants were completed in a fixed bed reactor under 8 bars H<sub>2</sub> pressure at the temperature range of 573–673K. Both hydrogenolysis and HDO reactions were followed by trans-alkylation along with alkylation. Anisole is transformed to benzene by HDO reaction and to phenol by hydrogenolysis, and construction of methyl-substituted phenols occurs by trans-alkylation and alkylation. The activity or selectivity of the **transition** metal catalyst found to be better in comparison to other catalysts with same metal on alumina. The catalytic species upon the surface of nanotubes were resistant to sintering due to solid interaction and displayed extensive shelf life.

The CNT supported Ru metal catalyst, accumulated in the water/oil interface showed tremendous activity as well as selectivity (**96%**) for HDO reaction of vanillin [91] to phenol,

guaiacol as well as syringol under 1MPa H<sub>2</sub> pressure at 150°C. The Ru/CNT metal catalyst was prepared through wet impregnation technique. The flaked CNTs were impregnated in an aqueous combination of RuCl<sub>3</sub> under ultrasonic condition and reduced by H<sub>2</sub> at 400°C. The HYD movement for the mentioned catalyst was analyzed for hydrodeoxygenation reaction of vanillin in an autoclave. Fluorescence microscope image of the catalytic system shows that Ru/CNT nanoparticles were mostly scattered on the surfaces of the emulsion droplets to form a pickering emulsion (**Fig.9**) and provides superior interfacial surface region for the HDO reaction. Vanillin or vanillyl alcohol are extremely soluble in the aqueous medium and the products *p*-creosol and 2-methoxyphenol are solvable in the organic phase. Therefore, pickering emulsion also improved the H<sub>2</sub> concentration at the boundary, because H<sub>2</sub> has elevated solubility in organic phase than in H<sub>2</sub>O. Thus, these emulsions could control the selective product distribution during the reaction.



**Fig.9.** (a) Fluorescence microscope picture of pickering emulsion developed with Ru/CNT nanoparticles (b) HDO of vanillin by using Ru/CNT metal catalyst at water/oil interface. **Reproduced with copyright from reference**[91]. Copyright (2014) Elsevier.

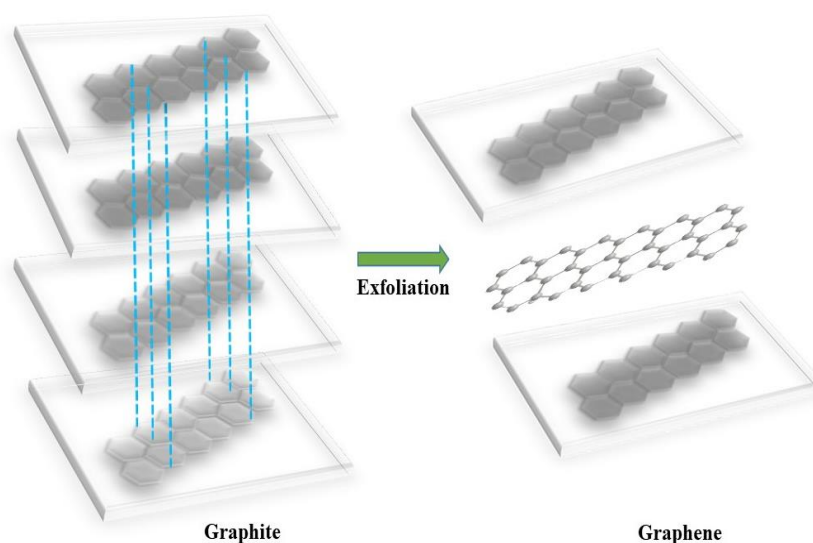
Finally, we can say that high hydro-deoxygenation activity of CNT or CNF supported catalysts mostly tuned by modifying the surface area or surface functional groups of the transition metal catalyst, size of nanoparticles and different temperature conditions. Sometimes, choosing the appropriate solvent system (monophasic or biphasic) can significantly enhance the HDO activity. Different chemicals obtained from HDO reaction of lignin or its model compounds by using CNT and CNF supported catalysts are presented in **Table 3**.

**Table 3.** CNT and CNF support materials used to derive chemicals from lignin or related molecules

S. No.	Source (model lignin compound)	Active Metal(s)	Catalyst	Products with Yield (%)	References
1.	Eugenol	Ru	Ru/CNT	Propylcyclohexane (94%)	[84]
2.	Guaiacol	Ni, Fe	Ni/CNT Fe/CNT Ni-Fe/CNT	Phenol(82.3%), and Cyclohexanol (79%), Cyclohexenol (86%) and Benzene (85.4%)	[85]
3.	Guaiacol	Mo	Mo <sub>2</sub> C/CNF	Cresol (79.1%)and Phenol (69.9%)	[86]
4.	Guaiacol	Mo,W	Mo <sub>2</sub> C/CNF W <sub>2</sub> C/CNF	Phenol (82%)	[87]
5.	Guaiacol and Anisole	Pt-Sn	Pt-Sn/CNF Inconel	Phenol (90%) and Benzene (74%)	[88]
6.	Phenol	Re	ReO <sub>x</sub> /CNF ReO <sub>x</sub> /CNF <sub>ox</sub>	Cyclohexane (35%) and Cyclohexene (70%)	[89]
7.	Anisole	Mo	Mo/CNT	Benzene (67%) and Phenol (60%)	[90]
8.	Vanillin	Ru	Ru/CNT	<b>Vanillyl</b> alcohol (74%)	[91]

### 2.3. Graphene supported catalysts

Graphene generally manufactured by the exfoliation process of graphite [92] as demonstrated in **Fig. 10**. The oxidation of graphene with concentrated acids or some other oxidising agents generates graphene oxide (GO). The reduction of surface functional moieties of oxidised GO generated reduced graphene oxide (rGO). Graphene can also be produced from sodium lingo sulfonate (LS) obtained from lignin by sulfite pulping method [93]. Graphene mainly shows valuable performance because of its superior precise surface area and excellent conductivity. It is mainly used in electronics, sensors, reinforcement of composite materials, energy storage gadgets and catalysis [94].



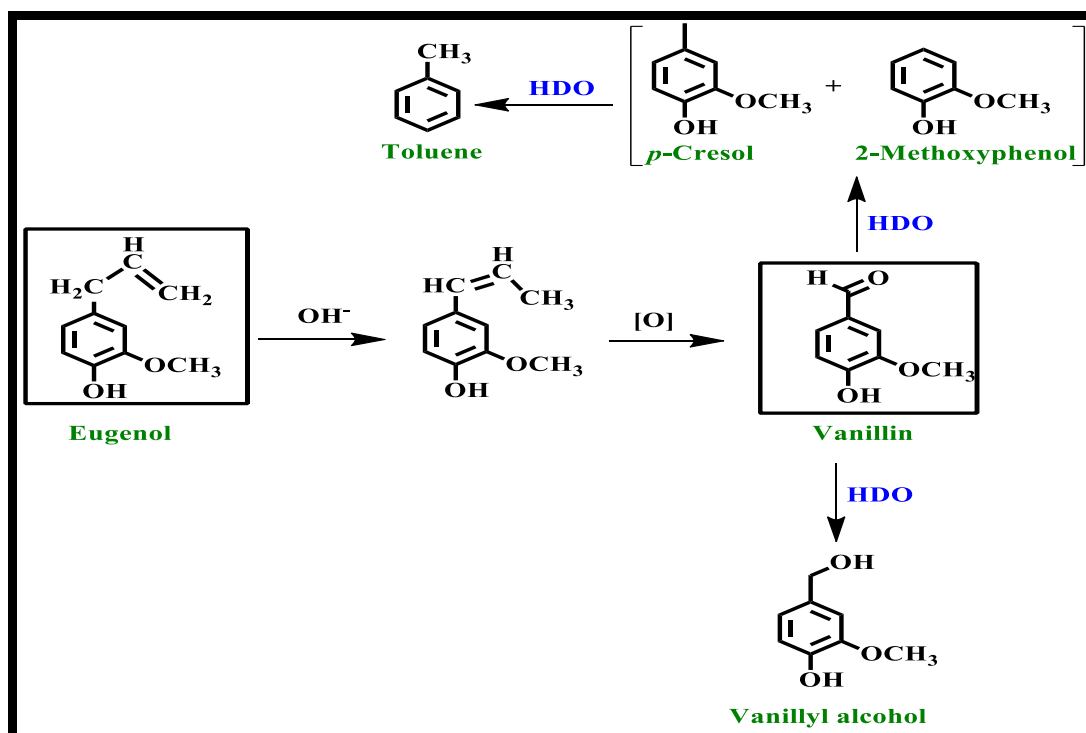
**Fig.10.** Preparation of graphene from graphite by exfoliation.

The HDO reaction for guaiacol was performed [95] with the help of bimetallic Rh/Ni catalyst supported by rGO **having 96% selectivity towards benzene**. The Rh/Ni/rGO metal catalyst was prepared by a wet impregnation after that calcination by using appropriate rhodium and nickel salt. The Rh/Ni/rGO catalyst show larger metal aggregation due to low Rh/Ni interactions with the rGO support, resulting in a lesser surface area for this catalyst. The catalytic HDO reaction was principally done in a vapour phase flatbed reactor at 370°C as well as at 420°C below atmospheric pressure. The HDO reaction of guaiacol into benzene by using Rh/Ni/rGO catalysts was incomplete due to the production of secondary oxygenated products. The higher number of oxygen functionalities in guaiacol was also responsible for coke sedimentation on catalyst surface and thus decreasing its activity.

The HDO of vanillin (**Scheme 4**) [96] with Pd/PRGO/Ce-MOF metal catalyst was very helpful to obtain 4-methylguaiacol. The catalyst was prepared by dispersing GO in DMF and adding Ce-MOF, palladium nitrate and hydrazine hydrate to it under microwave treatment. The HDO reaction was performed in H<sub>2</sub>O as a solvent with H<sub>2</sub> at room



temperature. The catalytic activity of heterogeneous catalysts depends upon the hybrid support containing metal organic framework (MOF) crystals and moderately reduced graphene oxide (PRGO) nano sheets as support. The needle shaped rocks of Ce-MOF were surrounded through PRGO nanosheets, which turned into integral elements of the catalyst support. They provided smooth surface to host the MOF crystals and served as thin protective layers on them. GO surface also helped in dispersion of metal nanoparticles and increased their efficiency.



**Scheme 4.** HDO of eugenol followed through vanillin.

Finally, it can be concluded that the activity or selectivity of the graphene supported metal catalysts mostly depend upon the surface area of the catalyst, dispersion and/or distribution for metal nanoparticles, coke deposition and surface functional moieties of support. Sometimes, the different electronic configuration of graphene or graphite imparts useful properties to the catalyst. Various chemicals obtained from HDO reaction of raw bio-oils obtained from lignin or its model molecules using graphene and graphite supported catalysts are shown in **Table 2**.

**Table 4.** Graphene and graphite support catalysts used to derive chemicals from lignin related molecules

S. No.	Source (model lignin compound)	Active Metal(s)	Catalyst	Products yield (%)	with references
1.	Guaiacol	Rh, Ni	Rh/Ni-rGO	Phenol (65%), Benzene (55%)	[95]
2.	Guaiacol	Ru	Ru/ Graphene	Cyclohexane (24.7%)	[70]
3.	Vanillin	Pd	Pd/PRGO/Ce-MoF	4-methylguaiacol(95%)	[96]

The reaction severity, catalysts, choice of solvent, temperature, selection of carbon support as well as metal and pressure of H<sub>2</sub> gas were the major factors that control the yield, selectivity and composition of the product during HDO reaction of lignin or the related molecules. The use of carbon materials has provided untarnished atomic lattice in the catalyst with exceptional mechanical, electrical, optical and thermal properties. All of these properties with its specific surface area and the probability to interact with organic compound through  $\pi$ -stacking interactions make carbon material excellent support material in the progress of heterogeneous catalysis [97]. The active metal(s) was supported on appropriate carbon support with specific properties for designing a bifunctional catalytic system to get the desirable activity and selectivity.

For example, the HDO reaction of lignin with NiMoP/AC (as depicted in table 2) displayed better product yield when compared with that of Pt-Pd/ACP catalyst. However, for lignin related molecules ReRu/AC showed better yield and selectivity of hydrocarbons as compared to that of Pd, Pt, Cu, Fe, Ru, and PdFe activated carbon supported metal catalyst. In the case of CNT and CNF support materials used to derive chemicals from lignin or related molecules, Ru/CNT Showed better product yield in comparison to Ni, Fe and Mo supported with CNT; and Pt-Sn/CNF Inconel was found to be the most promising catalyst in comparison to Mo, W and ReOx supported with CNF. As shown in table 4, Pd/PRGO/Ce-

MoF showed better product yield when compared with RhNi/rGO and Ru/graphene. On the other hand, the advantages of using carbon support instead of using other types of metal oxide support in the lignin conversion have also been reported. The carbon material supported metal catalysts exhibited high hydrocarbons yields and selectivity at mild temperature under low H<sub>2</sub> pressures when compared to oxygen containing metal supports such as Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, ZrO<sub>2</sub>, TiO<sub>2</sub>, MgO and CeO<sub>2</sub> [99] [100]. By supporting active metal catalyst on other support such as alumina offers less scope to tune the surface and make an excellent combination of active metal center with surface of support [98].

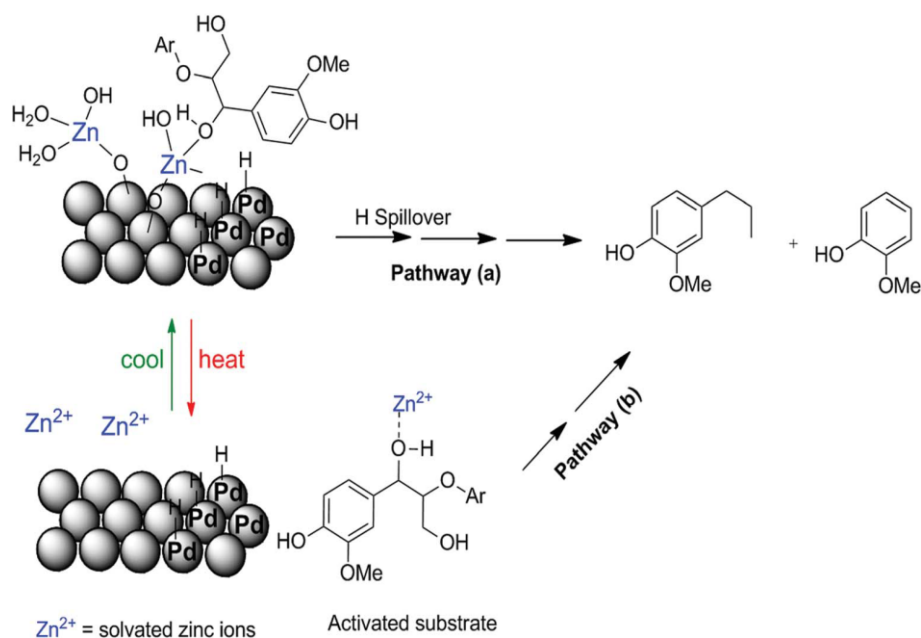
HDO reaction of lignin with the carbon based catalysts have been proven to be efficient, provided the carbon support is impregnated with an appropriate active metal centre. It has been observed that bifunctional carbon based catalysts containing mutually active hydrogenating and acidic sites were used to increase the hydrocarbon content in lignin derivatives. The hydrogenating sites were frequently provided by metals in the HDO catalysts while the acidic sites were mainly provided by the carbon supports. It is usually certified that complex acidic sites of the carbon supports are promising for the conversion of lignin derived phenolics and also facilitate dehydration of intermediate products during the HDO reaction. The exterior acidic sites encourage the degradation of bulky oxygen containing molecules obtained from lignin to smaller compounds while the interior acidic sites are accountable for aromatization of slighter oxygen containing molecules. Thus, the aromatization capability of carbon supports increases with the increasing in the acidity of both exterior and interior acidic sites [101].

### 3. Mechanistic details

The role of metal catalyst is to cleave the ether (-O-) linkage and simultaneously remove the excess O<sub>2</sub> in lignin with the help of molecular hydrogen [102]. The product formed may or may not retain O<sub>2</sub> in the end product [103]. The metal containing carbon material based catalysts through acidic support are the key leaders to achieve the high degree of deoxygenation [104][105]. They are also preferred due to their excellent stability, low cost and high electrical conductivity [106]. Technically, the catalyst plays the following double roles. It activates the molecular H<sub>2</sub> and then utilises it for eliminating the ether linkage in the monomer units. Porous carbon materials also act as hydrogen storage materials helping to enhance the achievability of the HDO reaction. A large number of other porous materials such as zeolites, metal-organic frameworks and porous polymers have also been examined

and assessed as H<sub>2</sub> storage materials but carbon-based materials are most precisely studied candidates due to their high surface area, low density and pore volume, high thermal and chemical stability and easy manufacturing in large scale [107]. Moreover, due to the versatile bonding ability from sp<sup>1</sup> to sp<sup>2</sup> or sp<sup>3</sup> hybridization, carbons exhibit a variety of allotropes which can be used as catalytic supports. Therefore, HDO process involves the initiation of free radicals as well as ionic intermediates that may be formed during the cleavage of hydrogen or interaction of acidic group with the intermediates and metal ions. This fact is supported by various mechanistic studies, where people have reported ionic or free radical mechanism for the HDO process. Though a complete distinction within the two is still missing and is a problem of investigation [108], [109].

### 3.1. Ionic mechanism



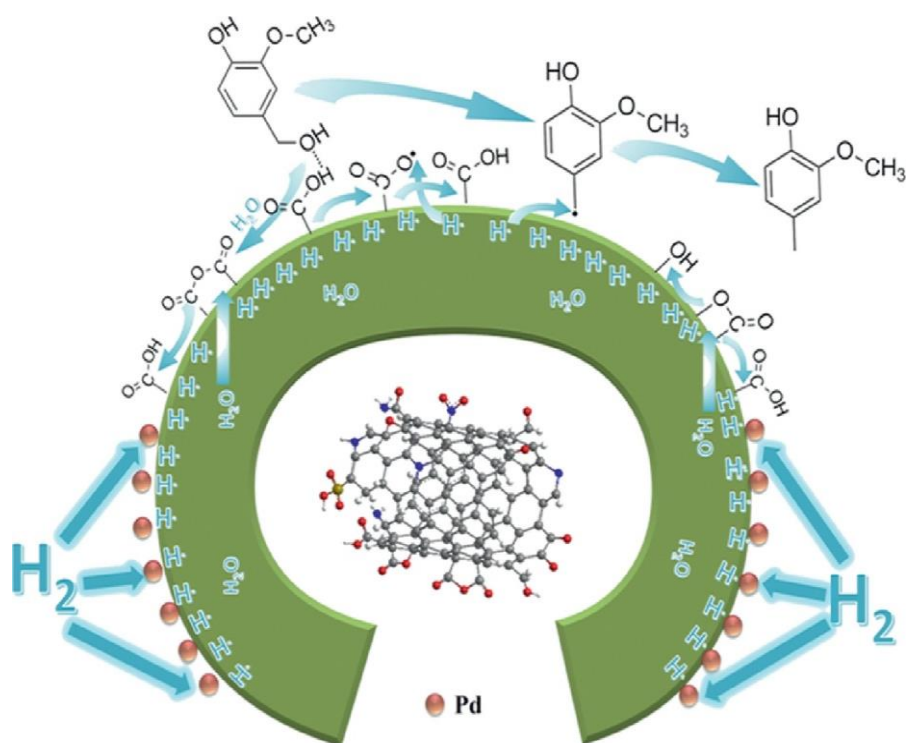
**Scheme 5.** Ionic mechanism for HDO of lignin model molecule. Reproduced with copyright from reference [110]. Copyright (2013) RSC.

The hydrodeoxygenation reaction involves the generation of ionic species that further initiate the C-O bond breaking in lignin molecule. Christopher Marcum and co-workers have suggested that metal hydride is formed during the HDO reaction and hydride ions are transferred from metal hydride to the  $\beta$ -O-4 oxygen initiating the C-O bond breaking [111]. Removal of hydride from M-H to the ether linkage results in the development of M<sup>+</sup> on the surface, and [M(II)-OH]<sup>-</sup> anion. Coordination of M(II) makes OH a better leaving group which causes the HDO. Catalyst regeneration takes place by the reaction of M<sup>+</sup> with H<sub>2</sub> to form M-H and solvated H<sup>+</sup> ions. The solvated H<sup>+</sup> ions protonate the [M(II)-OH]<sup>-</sup> anion to give H<sub>2</sub>O and a M(II) complex that can bind another lignin molecule. This mechanism has been

justified by detection of Zn(II) sites and metallic Pd(0) nanoparticles on catalyst surface under catalyst operating conditions [112]. The Zn<sup>2+</sup> ions play the significant role in the HDO reaction by two possible ways. It can activate the substrate by binding to OH groups [110] and increasing their reactivity with Pd-H on the surface by transferring hydrogen (hydrogen spill over). Alternatively, the zinc ions may desorb into the mixture, bind to the substrate and activates its cleavage upon coming in contact with Pd-H sites on the catalyst surface [113]. Zinc ions are reabsorbed upon the carbon surface with decreasing the reaction temperature. So, it is important to sustain the required temperature (**Scheme 5**). Control experiments using different substituents in model compounds, solvents and deuterated analogues suggested that  $\beta$ -benzylic-H of the substrate facilitates cleavage of the ether bonds [114].

### 3.2. Free radical mechanism

The radical mechanism has been reported for the HDO of model lignin compounds supported through density functional theory results [115], [116]. Recently, it was proved that HDO of lignin involves generation of radicles while studying the process in vanillyl alcohol by Pd/C catalyst [117], [118], [119]. The pathway basically shows that during hydrogenation the free radicals remain generated and simultaneously the acidic groups on the catalytic support activate the OH groups as presented in **Scheme 6**. As the radicals are initially generated, the reaction propagates through a radical mechanism rather than through the ionic intermediates. The findings were supported by the addition of radical blockage 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) in the HDO reaction mass which ceased the reaction. A recent study on TEMPO oxidation has been described which shows that it is a free electron transfer reagent [120].



**Scheme 6.** Free radical mechanism for HDO of lignin model molecule. Reproduced with copyright from reference [119]. Copyright (2017) Elsevier.

#### 4. Practical implications of this study

Most of the lignin (along with other biomass components) is used in industry for getting heat through the process of burning, which displays a small efficiency. Conversion of lignin to possible hydrocarbons through catalytic HDO reaction has the potential to obtain liquid fuels or chemicals starting from non-petroleum resources [121]. In general, the catalyst activity, selectivity, reusability and lifetime are important parameters for practical HDO catalysts in the depolymerization of lignin. However, the selective lignin conversion using such catalysts to well defined products with high yields, minimum hydrogen consumption and mild reaction condition is hampered by several challenges in the current research. The first challenge is derived from the intrinsic heterogeneity of lignin and robust structure [123]. The second challenge is the high reactivity of the intermediates deconstructed from lignin, which are prone to side reactions to generate stable repolymerized products via the formation of new C-C bonds, making it difficult to produce high yields of desired products [124]. The third challenge is mainly caused by the high complexity of the products from lignin [125].

For the first challenge, since most of the linkages among lignin's aromatic units contain C-O-C bonds therefore, selective cleavage of these C-O-C bonds could efficiently depolymerize lignin into various aromatic monomers and dimers. A large segment of earlier

research on lignin valorization, containing novel catalysts and using the pre-activation methodologies (e.g. by selective preoxidation), has been devoted to elimination of C-O-C bonds while avoiding harsh conditions. Several strategies to report the second challenge must be attempted such as the consumption of catching agents, including boric acid, diols, phenol, 2-naphthol, and p-cresol, to stabilize the reactive species and reduce char formation. A feasible approach to address the third challenge is to rapidly convert lignin or lignin deconstruction intermediates to hydrocarbon fuels (e.g. jet fuel) using catalytic hydrodeoxygenation (HDO) processing before additional condensation reactions can occur. Rapid HDO process reactions, which involves hydrocracking, hydrogenation, and deoxygenation is necessary in order to stabilize labile lignin deconstruction intermediates and convert them into fuel-range products before condensation reactions can occur.

In addition, coking is also another biggest challenge for HDO reaction of lignin, because it has close relationships with the structures of the carbon supported metal catalysts. However, some phenols are reported to be important coke precursors, for example hydroxyphenol, methoxy-phenol, phenol or methylanisol and thus the pretreatment of the catalyst is necessary. Besides this, catalyst properties, the severity of conditions is another important factor that affects and decreases the extent of coking with the increase of reaction temperature, pressure of hydrogen and contact time.

The work will be helpful for identifying the active metal components, reaction conditions, and surface properties of carbon based catalysts for the HDO of lignin. Moreover, the mechanistic part will help to understand the process thoroughly, which is really required for designing a good catalyst. Future research should focus on the application and production of cost-effective carbon material supported heterogeneous catalysts and synergizing the cost of catalyst at enormous scale. Moreover, major challenges to improve the catalysts optimal reaction conditions and further understanding the kinetics of complex bio-oils, as well as the accessibility of sustainable and cost-effective hydrogen source are also required.

## **5. Conclusions**

This review summarises a sequence of carbon supported metal catalysts for the HDO reaction of lignin or its model molecules. Almost all carbon materials ranging from conventional activated carbon to advance materials such as graphene have been used for this purpose. The activity of catalyst generally depends upon the selection of active metal component on all the supports. Transition metals such as Ru, Pd, Pt, Ni or a combination of them is a good choice in this regard. It should be observed that no metal free catalyst has

been utilized for this conversion. To the best of our knowledge, only one metal free catalyst (bare CNF) has been shown to be active for the HDO reaction of guaiacol at very high reaction temperature. The appropriate metal incorporation ensures the cleavage of molecular hydrogen and surface functional groups further ensure the removal of oxygen atoms from the lignin monomers. The process seems to be affected by the various other parameters such as reaction temperature, size of the metal nanoparticles, poisoning of the active sites and surface region of the carbon material support. Sometimes, choosing the appropriate solvent can impart significant activity to the catalyst. For instance, the CNT and CNF supported metal catalysts exhibited good activity in biphasic solvent system. **Among all the catalytic supports. Activated carbon seems the first choice of the researchers due to its easy availability and low cost.** However, the metal free catalysts are not reported for the HDO reaction of lignin and related molecules that shows the deficiency of literature in this regard and hence an active research area in the future. The deoxygenation reaction proceeds by two types of routes that may involve ionic or free radical intermediates.

#### **Author Contribution**

VS and TG have equally contributed to the manuscript and were involved in literature search and compilation. MV has compiled the mechanistic part in the review. AV has reviewed the content and involved in discussion. NG is involved in all stages of planning and execution of this review.

#### **Dedication**

The authors dedicate this review to Professor Dangsheng Su, Dalian Institute of Chemical Physics. Professor Su has recently passed away and has enormous contribution in the field of heterogeneous carbon catalysis. He was the mentor of AV and NG during their postdoctoral years.

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