

Hydrodeoxygenation of model compounds and catalytic systems for pyrolysis bio-oils upgrading

Abstract

Hydrodeoxygenation (HDO) process is the most promising route to upgrade pyrolysis bio-oils for producing liquid transportation fuels. The catalysts used and the quality of bio-oils have played important roles for how successful such process is. This review has addressed recent advances in HDO of pyrolysis bio-oils over many different types of catalysts, concentrating on the investigations of reasons why current catalysts have showed poor stability and have hindered pyrolysis oil HDO process in industrial scale: (i) The chemistry of model compounds from pyrolysis bio-oils is discussed in detail including aldehydes, carboxylic acids, carbohydrates, guaiacols, furfurals, alcohols, and ketones. The reactions occur via different routes over different catalysts with different products. (ii) The reaction mechanisms of different types of catalysts are elaborated, including classical sulfided hydrotreating catalysts, noble metals, sulfides, phosphides, carbides, nitrides, non-precious metals, metal oxides, bimetallic amorphous boron-based catalysts, and reduced metal oxide bronzes. Oxygen from oxy-compounds is absorbed on coordinatively unsaturated metal sites (oxygen vacancies) on metal oxide supports through Lewis acid/base interaction, or on H in -OH that is attached to non-metal oxides such as SiO₂, or even on metal sites such as noble metals. -H donation is available directly from phosphides, carbides, nitrides, Brønsted acid -OH groups or -SH groups and from metals by H spillover. The activated H species then react with oxy-organics and give hydrodeoxygenated products. (iii) The importance of supports and contribution of different supports to HDO are also covered in this review. (iv) Catalyst deactivation mechanisms were elucidated. Coking formation is proven to be the main reason for catalyst deactivation because of polymerization and polycondensation reactions. The extent of coking formation depends on the type of oxy-compounds, nature of catalysts such as acidity, and operation conditions. A robust catalyst that withstands coking, high concentration of water and poisoning, and can be regenerated easily without losing too much activity is highly desired for pyrolysis oil HDO process and finally applied in industrial scale for raw pyrolysis oil upgrading.

Keywords

Hydrodeoxygenation • Pyrolysis bio-oil upgrading • Model compounds • Mechanisms • Deactivation

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1. Introduction

The world demand for energy is increasing continuously and it is expected to double before 2050 [1] due to population growth and the development of society. More than 85% current energy production is mainly from fossil fuels, resulting in net emissions of CO₂, leading to the problems related to climate change, such as global warming. The global energy crisis [2] and environmental concerns are posing big challenges nowadays and the near future.

To address these challenges, the world is stimulated by the use of renewable energies such as wind, solar, biomass and hydroelectricity. Biofuels are emerging as a promising

solution to fossil fuels due to their sustainability (not all) and CO₂ neutral resources. Bio-fuels are derived from biological carbon fixation and are mainly produced from biomass feedstocks. Bio-ethanol and biodiesel, as the main first-generation biofuels, are derived from biomass and some of them are suitable for food. The drawbacks of first-generation biofuels involve low energy efficiency [3] and the competition with agricultural land use for food production. Hence, the second-generation biofuels allow for the use of inedible biomass. The primary obstacle for second-generation biofuels is to degrade biomass, especially lignocellulosic biomass. Accordingly, ideal resources of biomass are explored. The so-called third-generation biofuels, which are derived from microalgae and cyanobacteria (blue-green algae),

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are being investigated [4]. The merits of using microalgae and cyanobacteria include short growth cycles, higher efficiency than conventional crops, better biofuel grade (higher H/C and lower O/C ratios by increasing the heating value, see eq 5).

As the only renewable source for producing liquid transportation fuels, biomass is gaining the most attention. Biomass can be treated in a number of different ways to obtain liquid and gaseous fuels as illustrated in Figure 1. As reported in the literature [5], energy consumption in the transportation sector is about 1/5 of the total energy consumption of the world. Liquid fuels can be obtained by converting biomass via three primary paths, including aqueous sugar production by hydrolysis, bio-oil production by liquefaction and pyrolysis, syngas formation by gasification followed by Fischer-Tropsch (F-T) process. Using supercritical water for bio-oil production [6] or microwave to assist pyrolysis process [7] were found in recently work. Based on the estimated production prices of liquid fuels from biomass reported by the work from Mortensen et. al. [8], HDO is very competitive due to the use of bio-oils as a platform chemical. Moreover, H_2 , used for HDO, can be easily derived from biomass by sugar aqueous reforming, alcohol steam reforming, syngas steam reforming using solar, wind, or nuclear power. Pyrolysis has been reported to be more economic than high pressure liquefaction in bio-oil production [9]. Thus, more studies have been focused on bio-oil production by pyrolysis.

Pyrolysis bio-oils have many advantages, including easier handling and transport, flexibility of use over raw biomass, low nitrogen and sulphur content as compared with petroleum products. Hence, bio-oils have been successfully tested in turbines, boilers and engines [11]. One marked difference between bio-oils and crude oil is the high oxygen content (up to

47%) in bio-oils [12], leading to some unwanted characteristics, including high acidity, low heating value (HV), high viscosity and immiscibility with hydrocarbon fuels. Therefore, bio-oils must be upgraded before being used as transportation fuels.

As shown in Figure 1, bio-oils can be converted to liquid fuels by two typical processes [8,10]: (i) zeolite upgrading without reducing gases (oxygen is released as CO_2 and H_2O) at atmospheric pressure and high temperatures (300-600°C) [13]; (ii) HDO in the presence of catalysts similar to those used in petroleum hydrotreating processes under high pressure. The work by Huber [10] and Jensen [8] suggested that zeolite upgrading is unfeasible due to the low grade of fuels produced (up to 0.6 of both H/C and O/C molar ratios) and high carbon formation (20-40 wt%). In this review, we focus on the HDO of many model compounds and catalytic systems for pyrolysis bio-oils upgrading.

Other reviews within the same field have been reported. The mechanism and kinetics of HDO were summarized by Furimsky [12]. Upgrading wood-based pyrolysis bio-oils by hydrotreating were discussed by Krause [14]. A comparison of HDO and zeolite cracking was published by Jensen [8], they also discussed the general aspects of HDO, HDO reactors and catalyst deactivation. Hydroprocessing of liquefaction bio-oils were reported by Elliott [15]. Recently, catalytic cracking of edible and non-edible oils for the production of biofuels was summarized by Bhatia [16]. This paper is focused on upgrading of pyrolysis bio-oils by HDO process. With this review, we address recent advances in HDO of many model compounds in pyrolysis bio-oils over the different types of catalysts, concentrating on the investigations of reasons why current catalysts have showed poor stability and have hindered pyrolysis oil HDO process in industrial scale.

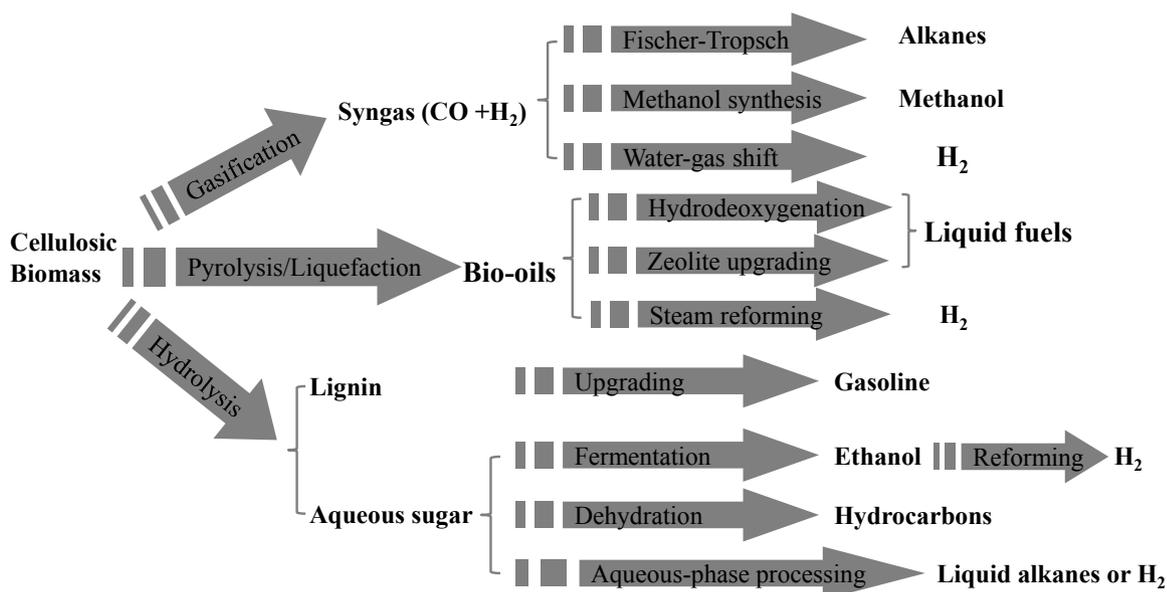


Figure 1. Strategies for fuel production from biomass, cellulosic biomass includes: clean biomass (e.g. forest, shrubs, switch grass and hybrid poplar), urban biomass (e.g. construction/demolition wood) and residual biomass (e.g. corn stover, tops and branches, sawdust and hulls) adapted from Ref [10] with permission from Wiley-VCH.

2. HDO of pyrolysis bio-oils

HDO process, by saturating bonds of C=C, C=O and aromatic rings while removing oxygen in presence of H₂ and catalysts, is targeted for the production of renewable liquid fuels including gasoline and diesel [17]. This process is very attractive due to high carbon efficiency (theoretical carbon efficiency of 100% as all carbons are converted to hydrocarbons with no CO₂ emissions) and technology compatibility with existing petroleum hydrotreating technology (Due to the immiscible nature of bio-oil to petroleum products, pretreatment is required [15]). The process is very similar to hydrodenitrogenation (HDN) and hydrodesulfurization (HDS), and proceeds simultaneously with HDN and HDS during hydroprocessing of various feeds for fuel production. Generally, the relative removal of heteroatoms during hydrotreating takes place following the order of HDS>HDO>HDN if analogous O-, N-, and S-containing compounds predominate [12]. A special case was reported by Oyama [18] that HDO was about 10 times greater than HDS over vanadium nitride catalysts.

Pyrolysis bio-oil is a complex mixture of oxygenates with more than 300 different compounds identified [11]. According to the work by Bridgwater [19], bio-oils produced from many pyrolysis included mostly water (20-30 wt%), lignin fragments (15-30 wt%), aldehydes (10-20 wt%), carboxylic acids (10-15 wt%), carbohydrates (5-10 wt%), phenols (2-5 wt%), furfurals (1-4 wt%), alcohols (2-5 wt%) and ketones (1-5 wt%). Due to the reactivity differences in multifunctional groups of bio-oils, a wide range of operation temperature between 300°C and 450°C is usually chosen for HDO of bio-oils. Grange [20] summarized the influence of the temperature and H₂ consumption to investigate the reactivity of some model compounds over a commercial CoMoS/Al₂O₃ hydrotreating catalyst as shown in Table 1. The different molecules and groups are able to be hydrodeoxygenated at different temperatures as indicated from the iso-reactive temperatures (the temperature at which the conversion rates reach an identical value [20]). Olefins, aliphatic ethers and alcohols are estimated to be even more reactive than the ketone group. Furimsky [12] has summarized the HDO reactivity of oxy-groups in the tentative order as shown in (1).

alcohols > ketones > alkylethers > carboxylic acids
 ≈ m- and p-phenols ≈ naphthol > phenol > diarylethers
 ≈ o-phenols ≈ alkylfurans > benzofurans > dibenzofurans (1)

The upgrading of bio-oils by HDO requires relatively high pressure (7-20 Mpa) [14] to convert some of the compounds in bio-oils that have a low HDO reactivity to O-free products [12]. Meanwhile, high hydrogen pressure leads to complete hydrogenation of unsaturated hydrocarbon products.

To achieve desired HDO conversions of feedstocks with different content and types of oxygen atoms, HDO of bio-oils typically consists of two stages [12,21,22]. First stage is called stabilization stage or mild hydrotreating which occurred below 300°C to avoid coking formation and polymerization of the oxy-compounds during the following deoxygenation step, *i.e.*, biphenols, ethers and methoxyphenols are converted to phenols. Large amount of hydrogen was consumed for efficient oxygen removal under more severe reaction conditions (about 350°C) at second stage, *i.e.*, carboxylic acid, esters, phenols, furans, and etc. are converted. The first stage is suitable for producing partial deoxygenated fuels to be used for generation of heat and electricity [23] at lower cost or for some useful chemicals [22]. The second stage can be applied to generate fully deoxygenated fuels that can be used in transportations.

3. Chemistry of model compounds

As discussed earlier, the compositions and oxygen content of bio-oils from different sources resulted in different reactivity in the HDO process. Even for the same model compound, the reactions proceeded via different routes over different catalysts, producing different products. Therefore, the main strategy to study upgrading of pyrolysis bio-oils is to study the different model compounds, which is of great importance in order to understand the behaviours of different bio-oil components. By understanding of chemistry and reaction mechanisms, one can control the selectivity of specified products and explore the insights for upgrading real pyrolysis bio-oils and even more complex feedstocks to desired fuels and chemicals.

The bond dissociation energies between carbon and oxygen from model compounds in pyrolysis oil are different (Table 2). The

Table 1. Activation energy and temperatures of iso-reactivity for HDO of different molecules or groups over CoMoS catalyst. Data from Ref [20] with permission from Elsevier.

Molecules/groups	Activation energy (kcal/mol)	Iso-reactive temperatures (°C)
Ketone	12	203
Carboxylic acid	26	283
Methoxy phenol	27	301
4-Methylphenol	33.6	340
2-Ethylphenol	35.8	367
Dibenzofuran	34.1	417

bond strength between O to C in ethers is 46 kJ/mol less than that from alcohols, indicating that O abstraction from aliphatic ethers is easier than that from aliphatic alcohols.

3.1 Carboxylic acids

The acidity of bio-oils is high with the low pH value of 2-3 due to carboxylic acid such as acetic acids and formic acids, rendering bio-oils very corrosive and even worse at elevated temperatures [24].

According to the literature [25-28], HDO of carboxylic acids proceeds by three general routes (Figure 2):

1) Ketonization by C-O bond cleavage to generate ketones, and further by hydrogenation to produce alcohols;

2) Hydrogenolysis by the C-O bond cleavage to produce aldehyde, followed by further hydrogenation to form alcohols, and then dehydration and hydrogenation to yield alkane, or the alcohols reacts with carboxylic acids to form esters;

3) Decomposition (decarboxylation and decarbonylation) of carboxylic acids by breaking C-C bond to produce alkanes with one less carbon, CO, and CO₂. CO can be further hydrogenated to methane.

Aqueous-phase HDO of propanoic acid over the Ru/C, Ru/ZrO₂ and Ru/Al₂O₃ catalysts were investigated at 300°C and 6.4 MPa in a continuous-flow trickle-bed reactor [28]. Propanoic acid is converted by two major routes: hydrogenolysis followed by hydrogenation to propanol or dehydration-hydrogenation to propane; decomposition (C-C bond cleavage) to form methane and ethane. The C-C bond cleavage is improved at high temperature and with high metal loadings. Aqueous-phase HDO of propanoic acid was further studied at 6.4 MPa in the temperature range of 150-230°C on the Ru/ZrO₂ and Ru-Mo/ZrO₂ catalysts. Both C-C bond cleavage and C=O hydrogenation occur over these two catalysts. However, Ru/ZrO₂ favors C-C bond cleavage reaction, which produces more ethane and methane. Ru-Mo/ZrO₂ favors C=O hydrogenation reaction, which produces more propanol and propane. Increasing temperatures lead to improvements in the C-C bond cleavage and decreases in C=O hydrogenation.

HDO of acetic acid over Pt supported on transition metal oxides was researched in a fixed bed reactor at 300°C and 4 MPa [29]. Ethane production by route 2) is the highest over Pt/TiO₂ due to moderate acidity and proper metal-oxygen bond

strength in oxide support. Moreover, traces of CO, ethanol, acetone, and ethyl acetate are observed. However, these products are much more over Pt/CeO₂ and Pt/ZrO₂ catalysts, and much less of acetaldehyde and ethane is produced. Thus, route 2) and decarboxylation are the major reactions over Pt/TiO₂, while routes 1)-3) occur on the other two catalysts.

HDO of oleic acid (C₁₇H₃₃COOH) over Mo₂N, WN and VN supported on Al₂O₃ was studied at 380-410 °C and 7.15 MPa H₂ [30]. n-C₁₈H₃₈ is the major product over Mo₂N by route 2), while n-C₁₇H₃₆ and n-C₁₈H₃₈ are the major products over the WN and VN catalysts, indicating the latter two catalysts favor decarboxylation and decarbonylation reactions.

3.2 Ketones, aldehydes, and alcohols

HDO of aldehydes can theoretically proceed via four major routes [31,32] by transformation of carbonyl group into methyl group or CO as indicated in Figure 3. The conversion of alcohols is shown in step 2 and 3, while ketone conversion involves all the steps but is not shown in Figure 3 due to different molecular formula.

1) Direct hydrogenolysis of C=O bond (Direct hydrogenolysis mechanism) [31];

2) Hydrogenation of C=O bond to form alcohols, and then hydrogenolysis of C-O bond to produce alkanes (hydrogenation-hydrogenolytic mechanism);

3) Hydrogenation of C=O bond to form alcohols, and then dehydration to produce olefins and subsequently C=C bond re-hydrogenation to form corresponding alkanes (hydrogenation-hydrogenolytic mechanism);

4) Decarbonylation of C=O to form CO and alkane with one less carbon.

Table 2. Bond dissociation energy from different oxy-compounds. Data from Ref [12] with permission from Elsevier.

Groups	Bond dissociation energy (kJ/mol)
RO-R	339
R-OH	385
RO-Ar	422
Ar-OH	468

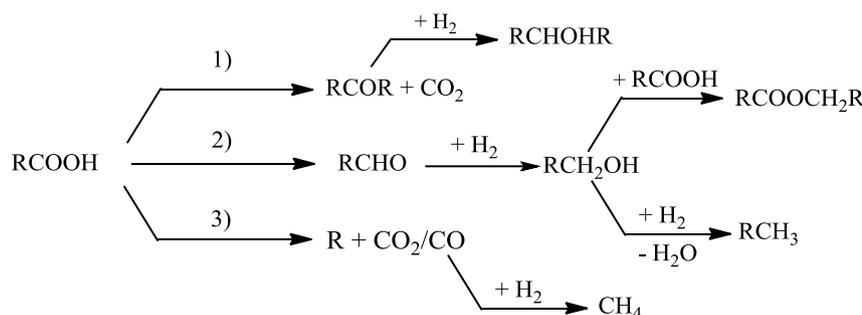


Figure 2. Main reaction pathways of HDO of carboxylic acids, R stands for alkyl groups.

HDO of benzaldehyde in hexane over Pd supported on zeolites and activated carbon was reported at 130 °C and 6 MPa [31] in an autoclave. Toluene is formed by direct hydrogenolysis of C=O bond or hydrogenation-hydrogenolysis route with benzylalcohol as an intermediate. The toluene selectivity is much higher in hexane than in methanol for all the Pd-based catalysts.

HDO of aldehydes by direct decarbonylation over Pd(OAc)₂ in cyclohexane or dichloroethane medium in the presence of molecular sieves in air or N₂ was reported in the temperature range of 100°C-140°C [32]. A wide variety of aldehydes are decarbonylated including non-functional aryl aldehydes, functional aldehydes, heterocyclic aldehydes, lkenyaldehydes. The process does not need any exogenous ligand for palladium as well as CO-scavenger.

DFT calculation was employed for understanding the propanal HDO pathways over MoS₂ and NiMoS active phases [33]. Route 2) in Figure 3 is involved in propanol transformation to propane through C=O hydrogenation and C-O bond breaking. Ni addition to MoS₂ promotes both C=O hydrogenation and C-O cleavage.

HDO of C3 alcohols (1- and 2-propanol, 1,2- and 1,3-propanediol, and glycerol) over Pt/Al₂O₃ was studied at 200°C and 4MPa in a batch reactor [34]. Dehydrogenation of 1-propanol to propanal was the first step, followed by decarbonylation or disproportionation reactions. The former one produces ethane, while the latter one gives propionic acid, which

undergoes decarboxylation to ethane. In case of 2-propanol and 1,2-propanediol, dehydrogenation on Pt produces acetone and acetol, respectively. In case of 1,3-propanediol and glycerol, dehydration on Al₂O₃ followed by hydrogenation on Pt is the main elementary reaction pathways for production of propanol or 1,2-propanediol. The detailed reaction pathways are presented in Figure 4.

3.3 Carbohydrates

HDO of carbohydrates usually proceed through dehydration first to produce 5-hydroxymethylfurfural (HMF), followed by hydrogenation to 5-(hydroxymethyl)tetrahydrofuran-2-carbaldehyde (HMTHFA). These two reactant units undergo aldol condensation reactions to form large molecules with more carbons, and then followed by multi-step hydrogenation/dehydration processes to form C₉-C₁₅ alkanes as shown in Figure 5 [35]. Catalysts with metal sites and acid sites such as Pt/SiO₂-Al₂O₃ and Pt/Al₂O₃ are used for dehydration of C6-sugar and hydrogenation of HMF prior to react with Mg-Al-oxide and NaOH catalysts for aldol condensation reactions [35].

Solid acid catalysts (Zr-P, SiO₂-Al₂O₃, WO_x/ZrO₂, γ-Al₂O₃, and HY zeolite) have also been designed for aqueous-phase HDO of xylose at 160°C in a batch reactor [36]. Furfural production is the triple dehydration reaction of xylose. Furfural selectivity is found to increase with the Brønsted acid/Lewis acid site ratio. Notably, Zr-P exhibits furfural selectivity as much as 30 times higher than

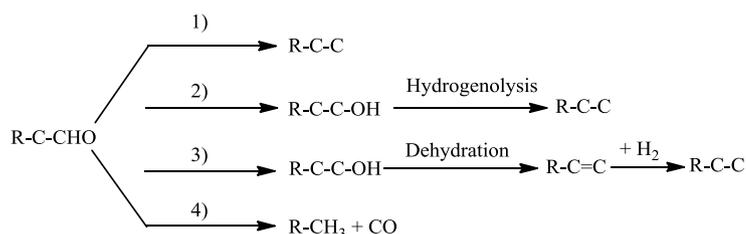


Figure 3. Main reaction pathways of HDO of aldehydes and alcohols, R stands for alkyl groups.

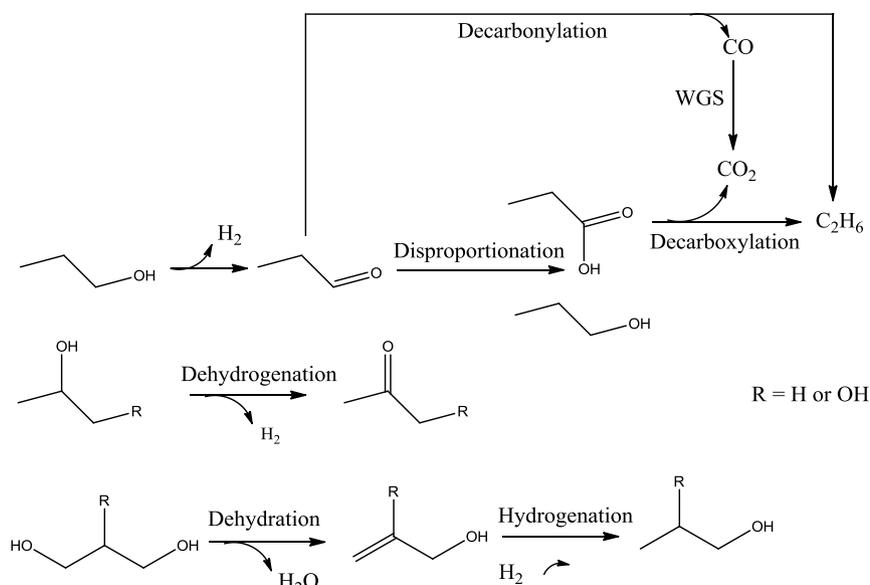


Figure 4. Reaction pathways of HDO of C3 alcohols, R stands for H or OH.

the catalysts with higher Lewis acid site concentrations at 20% xylose conversion. Moreover, ion-exchange polymer resins with high Brønsted acid site concentrations show similar furfural selectivity to Zr-P and HCl. Lewis acid sites are found to catalyse the side reaction between xylose and furfural to form humins. Thus, it is desirable to have a high ratio of Brønsted to Lewis acid sites in developing a more efficient catalyst for aqueous-phase HDO of carbohydrates.

3.4 Guaiacols (GUA)

Guaiacol conversion routes are mainly determined by methoxy group, phenolic group, and the benzene ring [13,37-42]. The main reaction pathways are illustrated in Figure 6.

Methoxy group reaction routes:

- 1) Demethylation to produce catechol, which is subsequently deoxygenated to phenol;

- 2) Demethoxylation to produce phenol directly;

Phenolic group reaction route:

- 3) Cleavage of C-O between hydroxyl group and the aromatic ring to produce methoxybenzene;

Benzene ring reaction route:

- 4) Hydrogenation of aromatic ring followed by the rupture of methyl group or hydroxyl group;

Phenol is one of the major compounds in lignin-derived an important intermediate from GUA HDO. Phenol HDO proceeds via two parallel reaction routes as indicated in Figure 6 [37,40,43-50]:

- 5) Hydrogenolysis-hydrogenation: direct hydrogenolysis of C-O bonds, then followed by hydrogenation of benzene ring to cyclohexane;

- 6) Hydrogenation-hydrogenolysis: hydrogenation of aromatic ring followed by dehydration forming C=C bond and re-hydrogenation of the double bond to cyclohexane.

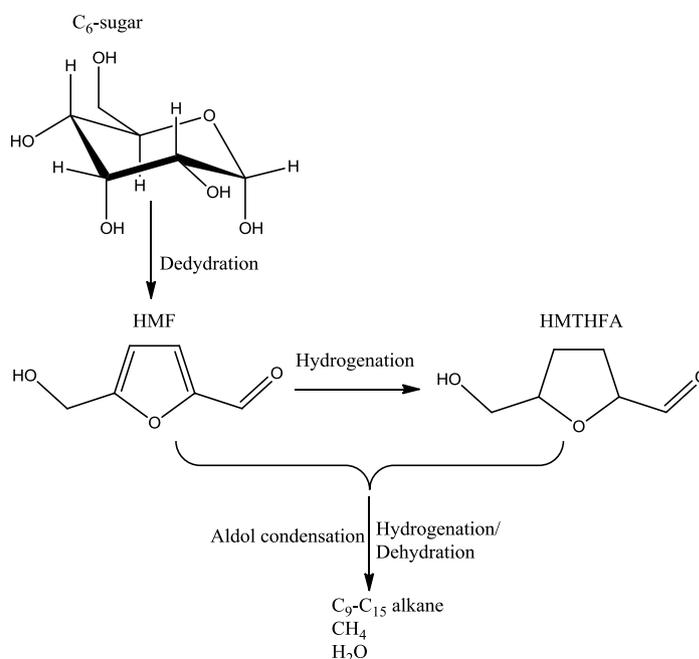


Figure 5. Main reaction pathways of HDO of Carbohydrates based on Ref [35].

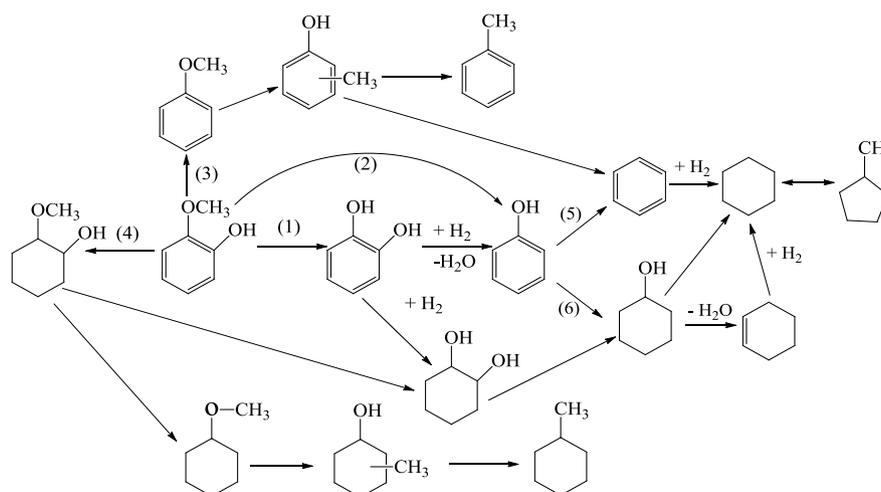


Figure 6. Main reaction pathways of guaiacol HDO.

On sulfided CoMo and NiMo catalysts, GUA HDO starts with demethylation or demethoxylation, and dehydroxylation, followed by the benzene ring hydrogenation [48,51-53]. However, hydrogenation of the GUA's benzene ring has been reported as the first step over Rh-based catalysts [39,53], followed by demethoxylation or dehydroxylation. The same reaction pathways occurred over Pd/C and H_3PO_4 component at 200°C and 5 MPa in an autoclave [49]. These observations agree with our recent work for GUA HDO over Pt/TiO₂ and non sulfided NiMo/Al₂O₃ catalysts at 300°C and 7.1 MPa in a fixed bed reactor [54].

Noble metals (Pt, Rh, Pd, and Ru) supported on nitric-acid-treated carbon black (NAC) selectively produce 2-methoxycyclohexanol by hydrogenation of the benzene ring at 250°C and 4 MPa in a batch reactor due to less acid sites on the catalyst [39]. However, the deoxygenation activity increases, and more cyclohexane is produced when these noble metals are supported on Al₂O₃ and SiO₂-Al₂O₃ since more acid sites are introduced. Notably, Pt, Rh and Pd on SiO₂-Al₂O₃ allow for only cyclohexane production. The acid sites are responsible for deoxygenation of GUA, while metal sites are relative to the benzene ring hydrogenation over those noble metal supported catalysts.

Non-precious metal catalysts such as Ni or/and Cu Supported on CeO₂-ZrO₂ and γ -Al₂O₃ were found to produce 1-methylcyclohexane-1,2-diol and cyclohexanone with high molar ratio (13% to 56%) in liquid products at 320 °C and 17 MPa H₂ in an autoclave by Bykova *et. al.* [40]. 1-methylcyclohexane-1,2-diol is produced by methyl group migration to the aromatic ring followed by hydrogenation of the aromatic ring, while cyclohexanone is generated by route 3). Transalkylation reactions with the methyl group transfer into the aromatic ring occur when using catalysts with acidic nature of the support, especially with γ -Al₂O₃ or SiO₂-Al₂O₃ [37,55,56]. NiCu supported on SiO₂ and SiO₂-ZrO₂-La₂O₃ mainly allows for cyclohexane production, while cyclohexane and benzene are the major products over Ni/SiO₂. For all the NiCu or Ni catalysts, C-O bond hydrogenolysis starts to prevail over the aromatic ring hydrogenation when reaction temperature increases in the range of between 280°C and 360°C, leading to a higher HDO degree. In case of Fe/SiO₂ catalyst [57], benzene and toluene are mainly produced from phenol, which is generated by GUA demethoxylation at 350°C-450°C and atmospheric pressure in a fixed be reactor. Co/Kieselguhr allows for formation of cyclohexane and cyclohexene from benzene and/or toluene under the same reaction conditions.

Mo₂N was found to be active for phenol and catechol production from GUA when supported on commercial activated carbons (Pica, Norit and Cudu) at 300°C and 5MPa H₂ in a batch reactor [38]. Both demethylation and demethoxylation occur simultaneously over the Mo₂N catalysts. Maximum activity is achieved at intermediate relative dispersion, which indicates controlling dispersion by optimizing support textural/chemical properties is an important parameter to in HDO reactions using metal nitrides. Mo₂N supported on activated carbon were further investigated for the effects of nitriding methods

under the same reaction conditions. Catalysts prepared using N₂/H₂, have more highly dispersed Mo oxynitride than those prepared via ammonolysis, leading to a higher HDO activity. The transformation of GUA proceeds mostly through the direct demethoxylation route, bypassing the formation of catechol [42]. Incorporation of Co to prepare bimetallic nitrided catalysts does not improve the HDO activity. Mo nitride supported on Al₂O₃ and SBA-15 silica was studied by Ghampson *et. al.* at 300°C and 5 MPa [58]. Catechol production by demethylation and phenol production by demethoxylation occur on both catalysts. However, Mo₂N/Al₂O₃ favors demethylation, while Mo₂N/SBA-15 silica favors demethoxylation reactions.

MoS₂ supported on two activated carbons with marked differences in porosity and oxygen surface functionality was studied at 300 °C and 5 MPa in a batch reactor [59]. Demethylation and demethoxylation reaction are involved in the reaction pathways, forming catechol and phenol as the major products. A small amount of benzene, cyclohexene, cyclohexane, and hexane are also produced from phenol. The same reaction pathways were reported for ReS₂/SiO₂ and ReS₂/Al₂O₃ at 300 °C and 5 MPa for HDO and HDS co-processing by Sepúlveda *et. al.* [60]. However, ReS₂/SiO₂ favors demethoxylation for phenol production, while ReS₂/Al₂O₃ shows less selectivity of phenol production, and has catechol production. The sulfiding pretreatment has a great effect on the performance of Re/ZrO₂ and Re/ZrO₂-sulfated catalysts under the same reaction conditions [61]. Both catalysts sulfided under N₂/H₂S mixture show higher activity as compared under H₂/H₂S mixture. Moreover, a lower H₂S partial pressure decreases the GAU HDO activity and changes the (phenol/cathecol) ratio, favoring the formation of catechol by demethylation reactions.

Transition-metal phosphides (Ni₂P, Co₂P and WP) supported on SiO₂ at 300°C and at atmospheric pressure were investigated by Zhao *et. al.* [62] with a space velocity of 1.4 h⁻¹. The major products are phenol and benzene, which are produced by demethylation route over the Co₂P/SiO₂ and WP/ SiO₂ catalysts. However, in the case of Ni₂P/SiO₂, dehydroxylation and elimination of oxygen in the methoxy group are the major routes for phenol and benzene production, where the latter route is not observed in the above catalysts discussed. The reaction pathway is confirmed by experiments at a much low contact time (with a space velocity of 59 h⁻¹). Under such reaction conditions, only demethylation route occurs over 5wt% Pd/Al₂O₃, while dehydroxylation route take place over sulfided CoMo/Al₂O₃, producing catechol and methoxybenzene, respectively.

The major products over sulfided CoMo/Al₂O₃ in PHE HDO at 300°C and 2.85 MPa were benzene, cyclohexene, and cyclohexane, which suggested two independent reaction paths are operative [50] as shown in steps 5) and 6). Successfully PHE HDO reactions on oxide catalysts are possible [46]. Ni-W/AC was employed in a fixed bed reactor for PHE HDO at 1.5 MPa, temperatures ranging from 150°C-300°C, and WHSV of 0.5 g_{phenol}/(g_{catalyst} h). PHE HDO occurs via two direction pathways (as same as sulfided CoMo/Al₂O₃) in parallel, which lead to formation of cylohexane, cyclohexene, cyclohexanol,

methylcyclopentane and benzene. Moreover, cyclohexanol formation is favored at the lowest temperature (150°C), which is due to the free hydrogen attacks to large π bond of phenol as tungsten sites are not activated at such a low temperature. Oxide tungsten species are proposed for the activation of oxy-group in PHE molecules. However, monometallic catalysts show different selectivity in products. Ni/AC only allows for cyclohexanol formation, while W/AC allows for cyclohexene but not cyclohexane at 300°C and 1.5MPa.

In case of Pt/HY zeolite catalysts at 200°C and 4 MPa, hydrogenation-hydrogenolysis was the major reaction pathway due to catalyst bifunction (metallic function for hydrogenation and the presence of acidic protons for dehydration) though a small amount of benzene was formed [63]. However, at the same conditions, Pt/Al₂O₃ and Pt/SiO₂ produced mainly cyclohexanol with no further hydrogenolysis due to the catalyst monofunction (metallic function). Similarly, Cyclohexane was formed by dehydration of cyclohexanol and subsequently hydrogenation of cyclohexene over Pd/C with H₃PO₄ at 80°C and 5 MPa [64]. Direct hydrogenolysis of PHE to benzene is inhibited, and direct hydrogenolysis of cyclohexanol to cyclohexane is also suppressed. However, direct hydrogenolysis of cyclohexanol to cyclohexane was reported over Pt/AC at 280°C and 4 MPa [65]. Cyclohexane was primarily produced by the hydrogenation of phenols and the hydrogenolysis of the resulting cyclohexanols. The combination of metals and Brønsted acids can be expanded to more complex bio-derived phenols [66] such as 2-methoxy-4-n-propylphenol, 4-n-propylphenol, and 4-allyl-2-methoxyphenol at 300°C with 4 MPa H₂. Cycloalkane can be produced with high selectivity (99% for 4-n-propylphenol) over the Raney Ni and Nafion/SiO₂ catalysts. RANEY Ni acts as the hydrogenation sites, while Nafion/SiO₂ acts as the Brønsted solid acid sites for hydrolysis and dehydration.

3.5 Furfural (FAL)

Furfural HDO proceeds mainly via two major routes as shown in Figure 7.

1) Decarbonylation to produce furan, followed either by hydrogenation to tetrahydrofuran (THF) or ring opening to butanal, butanol or butane;

2) Hydrogenation of FAL to FOL, and further dehydroxylation to 2-methyl furan (MF).

The addition of Cu to Pd/SiO₂ for the furfural HDO was investigated at 230°C and atmospheric pressure in a fixed bed reactor [69]. Decarbonylation to furan is the dominant reaction due to the preferential formation of an acyl intermediate at higher temperatures even at low W/F, and furan is further hydrogenated to THF. However, Cu addition greatly reduces the decarbonylation but increases the hydrogenation of furfural to furfuryl alcohol (FOL) due to the formation of Pd-Cu alloys, FOL is further hydrogenated to tetrahydro furfuryl alcohol (HFOL). Cu/SiO₂ was found to by deoxygenation with the route 2) at 270°C and in a tubular reactor [67], but only a small amount of MF is formed.

Cu, Pd and Ni supported on SiO₂ were studied in a continuous-flow reactor at atmospheric pressure and 210-290°C [68]. The reaction pathways are strongly related to the metals used. Cu/SiO₂ favors route 2) in Figure 7, which produces FOL with a small amount of MF; both Pd/SiO₂ and Ni/SiO₂ favor route 1) in Figure 7. However, Pd/SiO₂ mainly produces furan by decarbonylation, which is further converted to THF; Ni/SiO₂ favors ring opening of furan and the production of butanal, butanol and butane. The strength of interaction of the furan ring with the metal surface, and the type of surface intermediates are responsible for the different product distributions.

4. Catalysts and reaction mechanisms

An active and stable catalyst plays a crucial role during HDO process. The development of catalysts for bio-oil HDO has been focused on the new active phases or multi-phases and supports with modifications. Up to now, transition metal sulfides, carbides, nitrides, oxynitrides, phosphides, noble metals, non-precious metals and metal oxides have been used as active

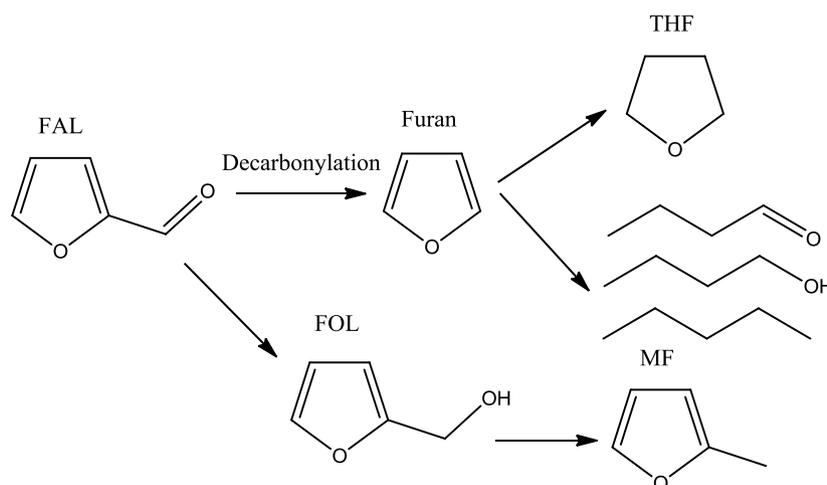


Figure 7. Main reaction pathways for FAL HDO on the basis of Ref [67-69].

phases for HDO of model compounds or mixtures from pyrolysis bio-oils. Though researchers test the catalysts under different reaction conditions including temperature, pressure, reaction time, reactor types, liquid hourly space velocity, and etc., it is meaningful to summarize the common nature of catalysts required for HDO of model compounds or mixtures from pyrolysis bio-oils to understand the reaction mechanisms. For this purpose, the reported catalysts are discussed separately by group or common features.

4.1 Transition metal sulfides (TMSs)

4.1.1 Sulfided NiMo and CoMo catalysts

The conventional HDS and HDN catalysts such as CoMo/Al₂O₃ and NiMo/Al₂O₃ have been the most commonly used catalysts in HDO studies.

Mo serves as an active element while Co [37,51,53,55,70-84] or Ni [51,53,70,72-76,78,79,85-94] as a promoter supported on γ -Al₂O₃ or without support [95] in these HDO catalysts. It is generally believed that sulphur vacancies (coordinatively unsaturated sites) which are located at the edges of MoS₂ nanoclusters, are the active sites in sulfided catalysts [96]. These sites exhibit Lewis acid character and can absorb atoms with unpaired electrons. Therefore, sulphur anion vacancies play an important part in scission of carbon-heteroatom bond [78]. Ni and Mo atoms occupy the edge of MoS₂ phases forming the so-called Co-Mo-S and Ni-Mo-S structures at the interface [97] which through d-electron donation causes the Mo to mimic a noble metal catalytic material [98]. Ni or Co does not apparently

increase the number of vacancies, but it did appreciably increase the activity of the vacancies by weakening the bond between sulphur and molybdenum. In addition, the sulfiding catalysts show Brønsted acid character since groups such as H⁺ and SH⁻ existed in the catalyst surface. Thus, they provided hydrogen for HDO reactions, for example, SH⁻ donates a proton to the attached molecule, and then forms a carbocation, followed by generating a deoxygenated compound (Figure 8). Meanwhile, hydrogen from S-H and Mo-H groups can be donated to C=C bonds to form C-C bonds (Figure 9).

Additives like P [99], K [83] or Pt [83] were added to CoMoS or NiMoS catalysts for HDO. The promotion effect of P in HDO is generally accepted [99-101] as the following: 1. Formation of new Lewis and Brønsted acid sites on the catalyst surface; 2. Formation of compounds that are more easily reducible and sulfidable; 3. Increase in Mo dispersion due to enhanced solubility of molybdate by the formation of phosphomolybdate complexes; 4. Increase in the stacking in MoS₂ crystallites and change of their morphology. Both Pt and K additions to CoMo/Al₂O₃ catalysts enhance the activity of 4-methylacetophenone conversion [83]. The reason for the former is due to high hydrogenation activity of noble metals [102,103], while for the latter is because of changes in molybdenum dispersion and structure.

Richard and co-workers [76] proposed a mechanism for HDO of 2-ethylphenol over a CoMoS/Al₂O₃ catalyst by direct deoxygenation and HDO as indicated in Figure 8 and Figure 9. In the mechanism for direct deoxygenation, vacancy sites are created by the removal of hydrogen sulphide in presence of H₂.

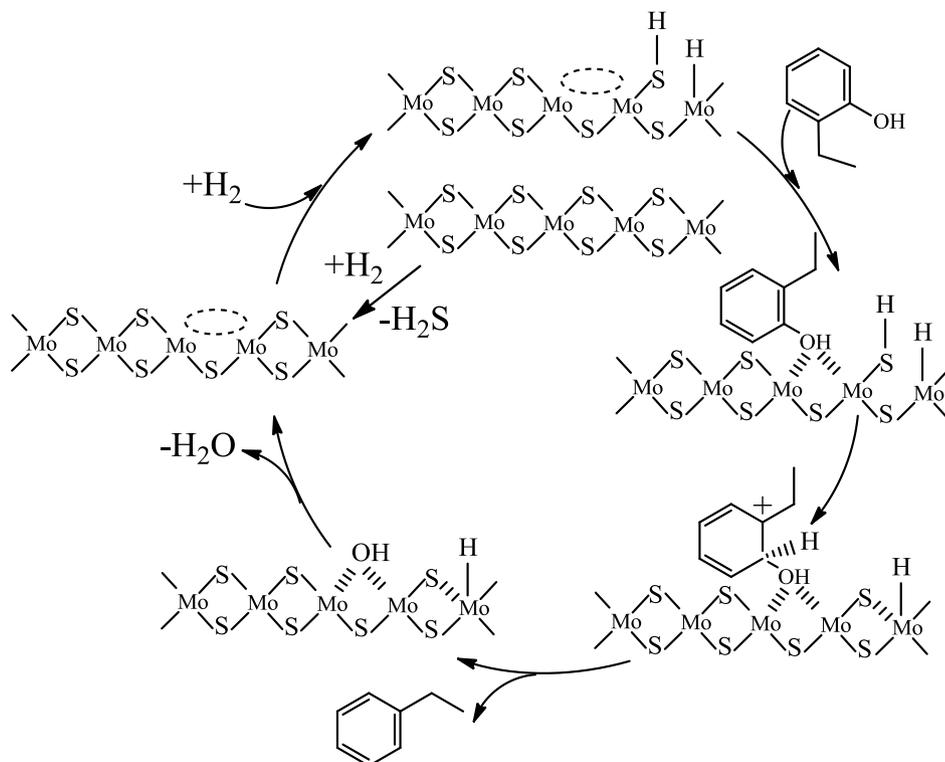


Figure 8. Mechanism of HDO pathway of 2-ethylphenol over a CoMoS/Al₂O₃ catalyst, adapted from Ref [76] with permission from Elsevier.

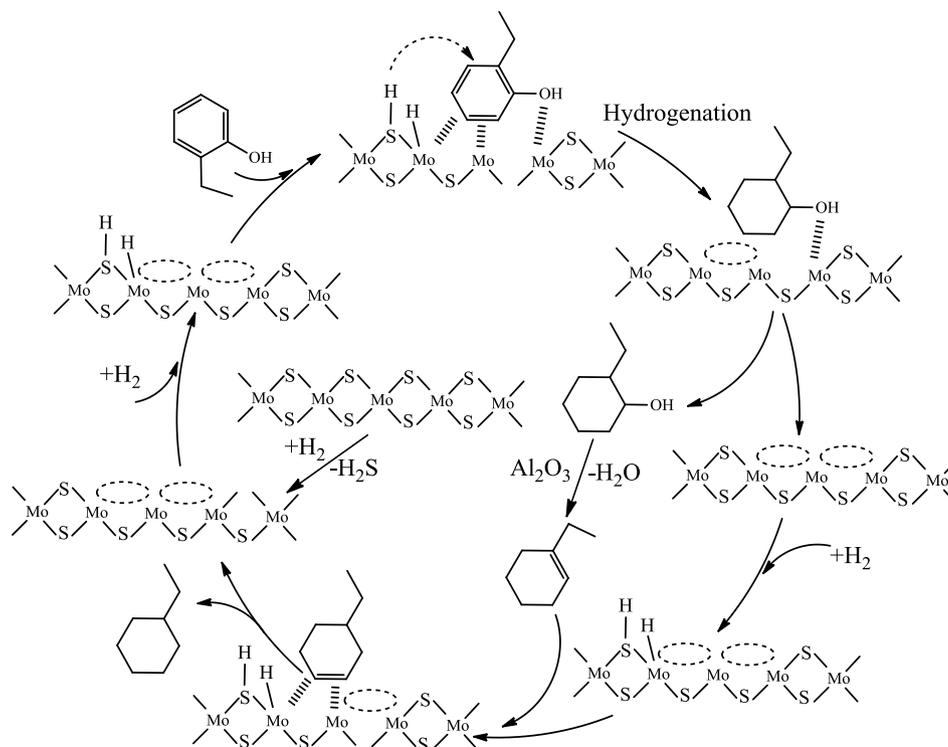


Figure 9. Mechanism of HDO pathway of 2-ethylphenol over a CoMoS/Al₂O₃ catalyst, adapted from Ref [76] with permission from Elsevier.

H₂ is activated by heterolytic dissociation forming one S-H and one Mo-H groups; oxygen in 2-ethylphenol adsorbs on the vacancy sites. An adsorbed carbocation is formed after the donation of a proton from S-H group. This intermediate undergoes direct C-O bond cleavage and generates a deoxygenated product. The vacancy site is recovered by the formation of H₂O from the adsorbed OH and H groups. 2-ethylphenol undergoes a HDO pathway when benzene ring is adsorbed on the vacancies. The benzene ring is fully hydrogenated first by hydrogen from S-H and Mo-H groups forming 2-ethylcyclohexanol, and this alcohol undergoes dehydration on acidic support producing cycloalkenes which is re-hydrogenated into ethylcyclohexane. The whole pathway is shown in Figure 9.

4.1.2 Sulfided W and Re catalysts

Sulfided NiW [74,93,104,105] were studied for HDO processes. WS₂ is generally accepted as the active phase for HDO activity over sulfided NiW catalysts while Ni is used as the promoter. Similar to sulfided NiMo catalysts, multi-layered Ni-W-S phase is also found in sulfided NiW catalysts. The high dispersion of WS₂ phase and the increased number of coordinatively unsaturated sites present in the sulfided catalysts are critical to the HDO activity. ReS₂/ZrO₂ is reported by Escalona [61] for guaiacol HDO. The activity of ReS₂/ZrO₂ was 2.8 times more active than NiMoS/Al₂O₃ catalysts (based on amount of metal atoms: Re or Mo), producing catechol and phenol as primary products. The mechanism for HDO of oxy-compounds over sulfided NiW and ReS₂ catalysts was similar to those shown in Figure 8 and Figure 9.

4.2 Noble metals

Sulfided catalysts have been the most popular ones reported in the literature for HDO process. However, these conventional industrial hydrotreating catalysts are less suitable for bio-oil HDO due to the economy of using sulphur, product contamination, and poor stability in the presence of H₂O. Therefore, the development and study of sulphur-free catalysts for bio-oil upgrading process is environmentally and economically favourable.

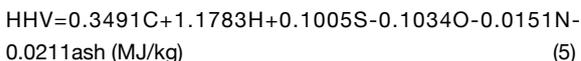
Noble metals are particularly efficient catalysts in activating molecular hydrogen [106] under mild conditions since hydrogen is easily activated and split on interface or surface to react with other reactants. Thus, it is expected that on noble metal catalysts better activity can be achieved and stability can be improved on supports other than alumina (deactivation by water) [107]. As reported by literature, Rh[39,49,53,108-110], Pt[108-113], Pd[49,68,69,108-110], Ru [28,39,49,109] or bimetallic metals with two of them were studied in HDO process and exciting results were achieved.

Concerning the HDO over noble metal supported catalysts, it is generally accepted that H₂ is adsorbed and activated on noble metal sites, while oxy-compounds can be adsorbed and activated on either noble metal sites or at the metal-support interface (exposed cations/oxygen vacancies). Adsorbed H atoms on noble metals spill over and react with the adsorbed oxy-compound intermediates, leading to the cleavage of C-O bond and formation of deoxygenated products and H₂O subsequently. The mechanism is proposed on the basis from literature [114,115] as shown in Figure 10 (a).

If reducible metal oxides are used as supports, such as MoO_3 , WO_3 , Fe_2O_3 , and SnO_2 , the Mars and Van Krevelen mechanism is involved [116]. In this mechanism, lattice oxygen reacted with H_2 and oxygen vacancies are created, which afterwards are refilled with the oxygen from the oxy-compounds. The intermediate species undergoes C-O cleavage and forms a final product as shown in Figure 10 (b). In the reactions of HDO, if the metal-oxygen bond is too weak, it would be difficult for the catalysts to abstract oxygen from oxy-compounds, but if metal-oxygen bond is too strong, it is difficult to create surface vacancies to adsorb oxy-compound [117]. It follows the Sabatier rule that oxides with intermediate metal-oxygen bond strength are the best better supports [118]. The metal-oxygen bond strength in (2) is summarized from Ref [115].



Two typical studies of noble metal catalysts were done by Gutierrez [108] with guaiacol and by Heeres [110] with fast pyrolysis oils. The activity of guaiacol HDO on noble metal supported on ZrO_2 catalysts at 100°C and 8 MPa (5 h) in a batch reactor followed the sequence shown in (3). The activity of pyrolysis oil HDO reported by Heeres at 350°C and 20 MPa (4 h) followed the trend in (4). Though the sequence of the activity for supported noble metal supported catalysts is not consistent from these two studies due to different reaction conditions (temperature, pressure, feedstocks, and etc.), supported noble metal supported catalysts exhibit much higher activity as compared with commercial sulfided CoMo catalysts. The profiles of O/C vs. H/C are shown in Figure 11. Noble metals show very good activity for oxygen removal. The H/C value after HDO is 1.0-1.5, indicating that the products are partially or highly aromatic due to different metals. The ratios of O/C and H/C are related to higher heating value (HHV) of upgraded products. According to the correlation of the calculation of HHV with elemental composition [119] as shown in (5), lower O/C and higher H/C lead to higher HHV.



In brief, supported noble metal supported catalysts are very active in HDO process. However, the main challenges for noble metal application are the availability, cost and higher sensitivity towards poisoning such as iron and sulphur [113] than sulfide catalysts [107].

4.3 Transition-metal phosphides (TMPs)

TMPs are generally prepared by the temperature programmed reduction (TPR) of phosphorus source. TMPs were studied for HDO reactions only recently, including Ni_2P [62,120-122],

CoP [62], WP [62], MoP [62,120,123], FeP [62], Ru_2P [124] and RuP [124]. The main active phases for TMPs during HDO are $\text{M}^{\delta+}$ (M stands for a transition metal and bearing small positive charges) and Brønsted sites [120]. $\text{M}^{\delta+}$ acted as Lewis acid sites and participated in hydrogenation, hydrogenolysis and demethylation reactions [125]. Incomplete reduction of phosphate species results in Brønsted sites (PO-H) [123] that donate active hydrogen species, but they are less active as compared to metal sites. The higher d electron density is beneficial for a better activity. MoP displays bifunctional acidic and metallic properties similar to noble metals supported on acidic supports [126]. The mechanism of HDO over TMPs is proposed in Figure 12 based on the literature [120,123] and without considering the support contribution. Oxy-compounds and adsorbed H_2 are activated on the $\text{M}^{\delta+}$ sites, and H atoms

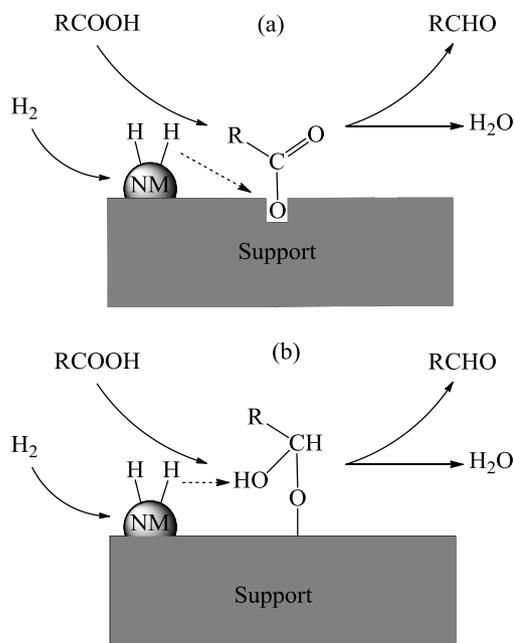


Figure 10. HDO mechanisms over noble metal (NM) supported catalysts. The figures are drawn based on Refs [114,115].

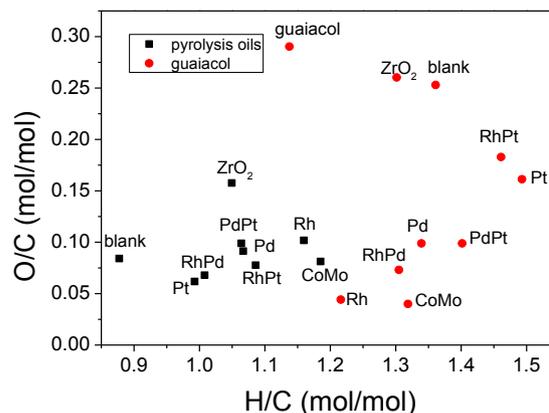


Figure 11. Van Krevelen plot of the upgraded pyrolysis oils at $T = 350^\circ\text{C}$, $P = 20 \text{ MPa}$, 4 h and guaiacol at 300°C , 8 MPa and 3 h over ZrO_2 -supported noble metal catalysts.

from both M^{b+} sites and Brønsted PO-H sites react with the adsorbed oxy-intermediate species producing deoxygenated products.

The HDO activity of guaiacol over typically phosphides supported on SiO_2 was investigated by Oyama [62] in a fixed bed at $300^\circ C$ and atmospheric pressure. The results are shown by the sequence (6). Lower cost than supported noble metal catalysts and high activity make TMPs attractive for bio-oil HDO process. However, one of the primary dilemmas currently using TMPs involves the oxidation of phosphides by H_2O and may result in the formation of metal oxide or phosphates. The presence of H_2O which is a product of deoxygenation would cause catalyst deactivation.



4.4 Transition-metal nitrides and carbides

Transition-metal carbides (TMCs) are commonly prepared by carbothermal hydrogen reduction or TPR. Transition-metal nitrides (TMNs) are often prepared by TPR with NH_3 . Similarity in activities to noble metals for hydrogenation [127-129] was reported with TMCs and TMNs in early studies [112,113]. TMCs

and TMNs also show good activity in HDO, HDS and HDN, and are resistant to sulphur, nitrogen and oxygen [18].

TMCs such as Mo_2C [18,113,130], WC [18], NbC [18], VC [18], and NiMo carbide [131] were used for HDO. TMCs exhibit similar catalytic performance to NMs, involving hydrogenation and hydrogenolysis reactions. The reason why TMCs are active for HDO might be the permeation of carbon atoms into the lattice of transition metals which lengthens the distance of metal-metal and thus increases the d-band electron density at Fermi level of transition metals [130,132].

TMNs such as Mo_2N [18,30,38,41,133,134], VN [18,30], TiN [18], and WN [30] were investigated for HDO. The activity of TMNs depends on the surface structure: metal oxidation state and N deficiency. The unsaturated metal sites and oxynitride species available from support surface or on the subsurface of nitride species are related to the HDO activity [38]. Different crystalline planes also possess different activities for hydrogen activation. For instance, the (111) and (200) planes of Mo_2N are associated with the hydrogen adsorption capacities while the (111) plane might be the most active sites for HDO [135].

Oyama [18] investigated the benzofuran HDO with various TMCs and TMNs catalysts in a trickle-bed reactor

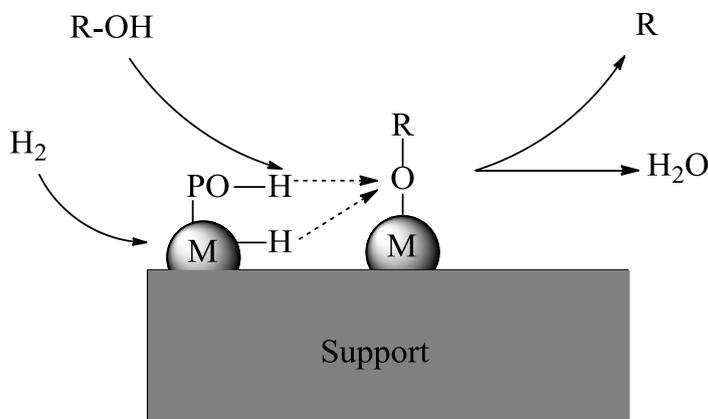


Figure 12. Proposed HDO mechanisms over TMPs catalysts based on Refs [120,123], M stands for metals.

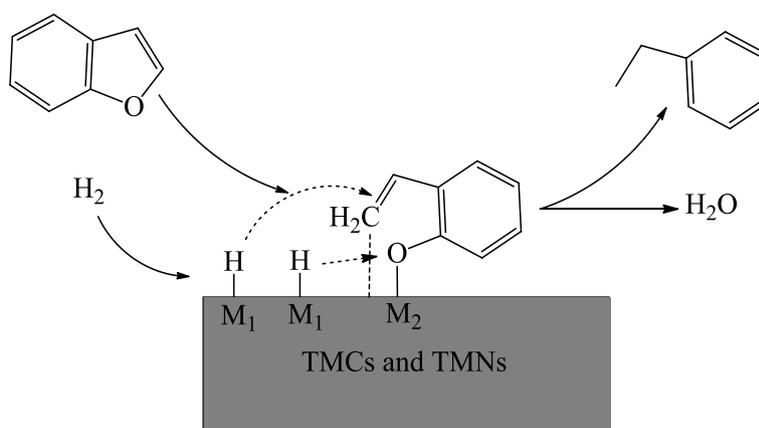


Figure 13. Proposed HDO mechanisms over TMNs and TMCs catalysts (M_1 : unsaturated metals, M_2 : C or N) based on Refs [18,38].

at 3.1 MPa and 370°C. The main products are ethylphenol, ethylcyclohexane and ethylbenzene. VN shows the best activity among the TMCs and TMNs catalysts due to the optimal binding energy for HDO. However, commercial NiMoS/Al₂O₃ shows much higher activity than the TMCs and TMNs catalysts. The activity of benzofuran HDO is shown in Figure 14. Noticeably, VN shows better selectivity to ethylbenzene, while NiMoS yields more ethylcyclohexane, indicating alkyl benzene products are selectively form over VN with less H₂ assumption during oxygen removal from benzofuran [18].

4.5 Non-precious metal catalysts

4.5.1 Fe-based catalyst

Fe/SiO₂ for HDO of guaiacol was reported by Dufour [57] in a fixed bed reactor at 350-450°C and atmosphere pressure. Metallic Fe activates H₂ whereas guaiacol is activated by acidic OH sites from SiO₂. Benzene and toluene are selectively produced over this catalyst. However, reduced Co/Kieselguhr catalyst shows high selectivity for methane formation. For metallic metal supported catalyst, a mechanism for HDO is proposed with

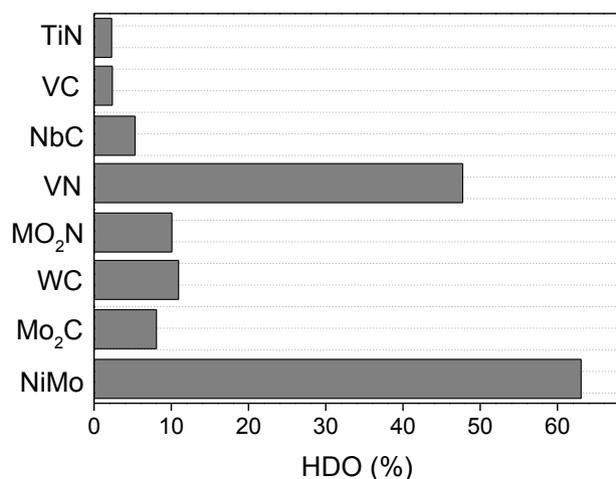


Figure 14. Comparison of steady state HDO activities of the carbides and nitrides with the commercial sulfided Ni-Mo/Al₂O₃ catalyst at 370°C and 3.1 MPa, adapted from Ref [18] with permission from the ACS.

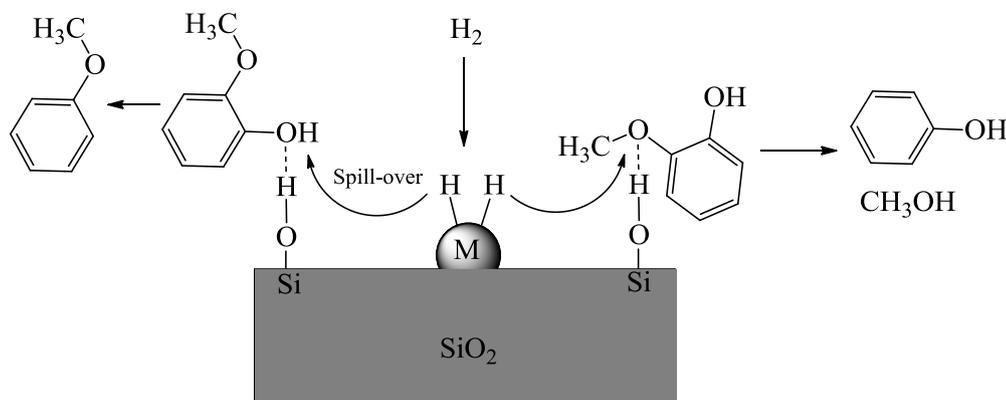


Figure 15. Proposed mechanism of guaiacol HDO into aromatic hydrocarbons over non-precious catalysts based on Refs [57, 136], M stands for metals

GUA as a demonstration in Figure 15. Acidic OH sites interacted with oxygen atoms from oxy-compound (n-electrons from the oxygen atoms are more basic compared with π-electrons from aromatic ring), while H₂ is activated by metallic metals and spills over to adsorbed oxygen atoms and causes C-O bond cleavage instead of C-C bond cleavage. An oxy-compound with more than one oxygen atom may have different adsorption sites on the supports [136].

4.5.2 Ni-based catalysts

Anisole HDO over Ni-based catalysts at 300°C and 1 MPa was reported by Yakovlev [137]. Metallic Ni supported catalysts are found to be very active, such as Ni/Al₂O₃ (HDO degree of 95%). Bimetallic Ni-Cu supported catalysts are even more active than Ni, such as Ni-Cu/Al₂O₃ (HDO degree of 99.2%). The activity data of anisole HDO is shown in sequence (7). Cu is found to facilitate hydrogen spillover, thus promoting nickel oxide reduction and forming substitution solid solution with CeO₂ support.

$$\text{Ni-Cu/CeO}_2 > \text{Ni-Cu/Al}_2\text{O}_3 > \text{Ni/Al}_2\text{O}_3 > \text{Ni/ZrO}_2 > \text{Ni-Cu/ZrO}_2 > \text{Ni/SiO}_2 > \text{Ni/Cr}_2\text{O}_3 \quad (7)$$

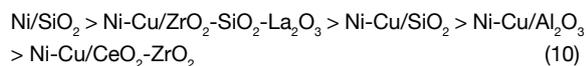
Bimetallic Ni-Mo and Ni-Fe supported on Al₂O₃ are reported for acetic acid HDO at 200-280°C and 4 MPa in a fixed bed reactor by Ren [27]. Above 95% conversion is achieved over these catalysts. Mo and Fe are found to facilitate both the reduction (by hydrogen spillover) and dispersion of NiO, promoting C-O activation while inhibiting the C-C breaking. The catalyst activity follows the trend as shown in (8).

$$\text{Ni-Mo} > \text{Ni-Fe} > \text{Ni} \quad (8)$$

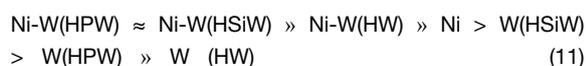
Butanone HDO over Ni-based bimetallic catalysts supported on Al₂O₃ at 200-300°C and 4 MPa in a fixed bed reactor was also reported by Ren [138]. The activity data at 240°C follows the order in (9).

$$\text{Ni-Cu} > \text{Ni-Fe} > \text{Ni-La} > \text{Ni-Co} > \text{Ni} \quad (9)$$

More recently, guaiacol HDO with Ni-based catalysts were investigated in an autoclave at 300°C and 17 MPa by Bykova [40]. The HDO degree of the deoxygenated products follows sequence (10).

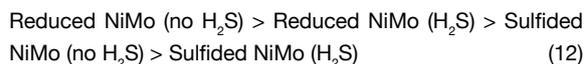


Ni-W (synthesized by different precursors) and W oxides on active carbon were used for phenol HDO in a fixed bed reactor at 150-300°C and 1.5 MPa [46]. These catalysts are very active in phenol HDO especially on Ni-W catalysts over 200°C. The phenol conversion at 150°C follows the trend in (11), W precursors are shown in brackets.



HDO of phenolic monomers (phenols, guaiacums and syringes) over Raney® Ni (nickel-alumina alloy) and Nafion/SiO₂ in a batch reactor at 200°C and 5 MPa was studied by Lercher [66]. 100% yields are achieved with formation of hydrocarbons and methanol. Raney® Ni serves as the hydrogenation catalyst while Nafion/SiO₂ acts as the Brønsted solid acid for hydrolysis and dehydration.

It is interesting to investigate the activity between sulfided catalysts and corresponding reduced catalysts for HDO process. Benzofuran HDO over sulfided NiMo and reduced NiMo supported on Al₂O₃ with and without H₂S (0.03%) in the feed was studied by Ozkan [94]. The activity of benzofuran HDO over the reduced and sulfided catalyst at 200-300°C and 500 psig in a fixed bed reactor is shown in (12). Reduced catalysts show higher activity compared with sulfided catalysts due to more active sites [139]. The competitive adsorption of H₂S and benzofuran on coordinatively unsaturated sites causes activity drop for both catalysts. For the sulfided NiMo, HDO proceeds through a hydrolysis route, while for reduced NiMo catalyst, hydrogenation of aromatic ring is followed by heteroatom removals.



4.5.3 Bimetallic amorphous boron-based catalysts

Amorphous catalysts are famous for their high concentration of coordinative unsaturated sites and unique isotropic which are responsible for catalytic activity.

Using amorphous catalysts for HDO process was reported by Yang in recent years, including Ni-Mo-B for phenol [140], Ni-Mo-B for phenol with addition of Co and La [141], Co-Mo-B for Phenol, benzaldehyde and acetophenone [142], and Ni (Co)-W-B for cyclopentanone [143]. These catalysts show excellent activity (*i.e.*, close to 100% conversion) and deoxygenation rate (*i.e.*, higher than 90%). The studies confirm that HDO required two types of active sites in these amorphous catalysts during reactions: (i) hydrogen activation sites are metal sites such as Ni and Co; (ii) oxy-group activation sites are Brønsted acid sites such as MoO₂ in the form of Mo-OH [123,144] and WO₃. B⁰ donates partial electrons to Ni species, which makes Ni electron-rich and benefits the formation of dissociated hydrogen. A mechanism for HDO over amorphous Ni(Co)-Mo(W)-B with phenol is proposed in Figure 16. H₂ is activated by Ni or Co, while oxy-compound is activated on Brønsted acid MoO₂ or WO₃ (polarization of C-O bond) sites, followed by C-O breaking with spilt hydrogen atoms (nucleophilic attack on the carbon atom in C-O group by dissociated hydrogen). Brønsted acid sites benefit dehydration, while B⁰ donates partial electrons to Ni or Co, stabilizing them as metallic state. Investigations of the activity and stability of these amorphous catalysts as compared with noble metal supported catalysts and sulfided NiMo or CoMo catalysts will be interesting topics in this area.

4.5.4 Reduced metal oxide bronzes

Pretreatments of WO₃ and MoO₃ in H₂ produce active phases as H_yWO_{3-z} (x is in the range of 0.9-1.3) [145] and H_xMoO_{3-y} (x is in the range of 1.1-1.2) [117]. This new class of heterogeneous catalysts for HDO of allyl alcohol and acrolein was reported by Frederick. A mechanism similar to the Mars-van Krevelen cycle

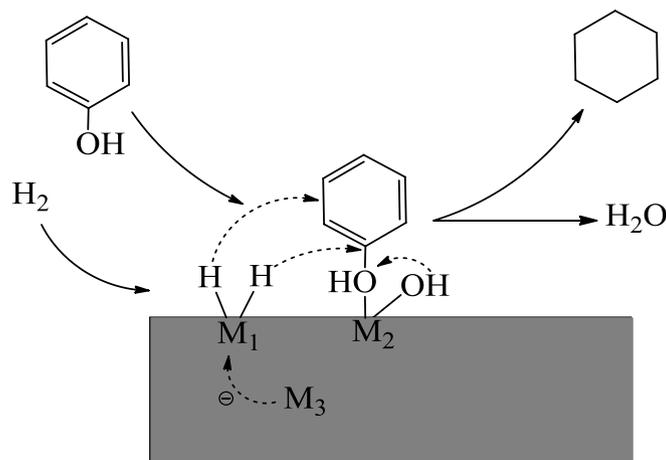


Figure 16. Proposed mechanism for the phenol HDO of acrolein over amorphous Ni(Co)-Mo(W)-B. (M₁: Ni or Co, M₂: MoO₂ or WO₃, M₃: B⁰), based on Refs [140-143].

is proposed in which oxy-compounds adsorbed on oxygen vacancies, forming a metal-oxygen bond, followed by splitting the carbon-oxygen bond and forming the final product. Surface hydroxyl groups are important for oxygen vacancy formation and function as Brønsted acids. The mechanism is proposed in Figure 17 [145].

5. Supports

Active phases and promoters play crucial roles for the HDO activity. However, supports are also very important including dispersing and stabilizing active phases, decreasing the cost of catalysts [146]. Moreover, some supports provide active sites such as Brønsted acid sites, and interact with supported active phases, forming new active phases on the surface or in the interface of the catalysts.

5.1 Alumina

γ - Al_2O_3 , with excellent crushing strengths and high surface area, has non-negligible activity due to Lewis acid sites [120]. The strong interaction between MoS_2 and alumina causes a single slab monolayer of this phase on alumina and an electronic transfer through Mo-O-Al linkages [147]. The latter would be one of explanations to the low activity of alumina supported catalysts. Moreover, coke may form and interact with acidic Al_2O_3 support from both oxygen-containing reactants and intermediate products (especially for molecules with two or more oxygen atoms), leading to activity loss and/or catalyst deactivation

[70,136]. Poor tolerance to water is another challenge to use Al_2O_3 -based supports. As reported in literature, Al_2O_3 could turn to boemite ($\text{AlO}(\text{OH})$) [15,86,148] in presence of a lot of water, and oxidize active metal to metal oxide such as Ni [15], causing catalyst deactivation [12].

Al_2O_3 is not a suitable support for bio-oil upgrading since it contains up to ~30 wt% water and a number of oxy-molecules with two or more than two oxygen atoms. For these reasons, new catalysts have been developed on the basis of CoMo- or NiMo- catalysts by changing Al_2O_3 to mesoporous supports such as MCM-41 (Mobil Crystalline Materials) [149] and SBA (Santa Barbara Amorphous type material) [150] or silica [83], or to neutral supports such as activated carbon [83,151-153] or to simple oxides like ZrO_2 [71,110,137], TiO_2 [71], CeO_2 [40,137] or even a basic support like MgO [99]. Active phases other than CoMoS and NiMoS supported on these alternative supports have also reported to form less coke than that on Al_2O_3 in HDO reactions [40,46,108].

5.2 Mesoporous materials

Mesoporous materials, such as SBA and MCM, unlike active carbon that is full of micropores, have a relatively large apertures and pores, which improves molecular diffusion speed [150], especially for large organic molecules, such as dibenzofuran [112], triglycerides [150], benzaldehyde [31]. Mesoporous supports also show compelling character since they have much higher surface area [154] and more active acid sites as compared with γ - Al_2O_3 , and even twice amount of active phase.

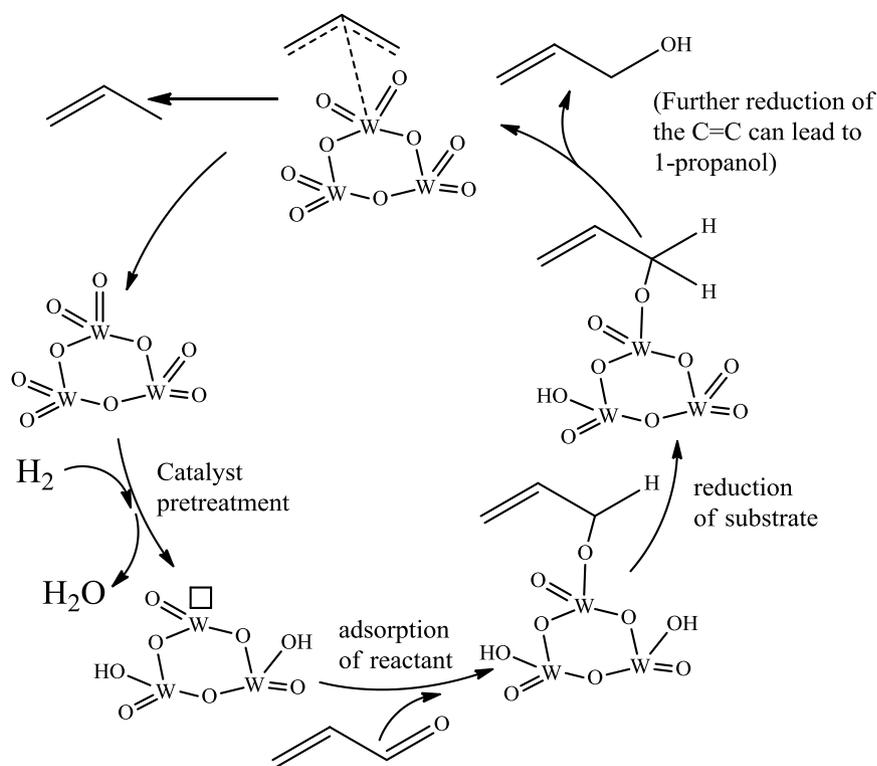


Figure 17. Proposed mechanism for the HDO of acrolein over reduced metal oxide bronzes, adapted from Ref [145] with permission from Elsevier.

For instance, molybdena can be supported without decreasing its dispersion [155].

5.3 Silica

SiO₂ alone is considered as “inert” support to Co and Mo [156], sulfided CoMo/SiO₂ was indicated to be a less active catalyst compared with sulfided CoMo/ γ -Al₂O₃ [83]. However, SiO₂ is often used due to its inert character and smaller interaction with sulfide phase, which allows for a better characterization. Moreover, SiO₂-based catalysts show better selectivity and activity than Al₂O₃-based catalysts when metal-support interactions and support acidity are detrimental to the activity [57,157]. SiO₂ has a weaker interaction with oxygen from oxy-compounds as compared with Al₂O₃. The oxygen in hydroxyl group interacts only with H bonds from SiO₂ support [136], but strongly adsorbed phenates species is found on Al₂O₃ [158]. Due to the very weak acidity nature of SiO₂, relatively low affinity for carbon formation was observed [62]. Thus, SiO₂-based supports should be considered as potential candidates for HDO of bio-oils with better stability.

5.4 Activated carbon (AC)

Mo-based catalysts have been suggested to be more active supported on activated carbon than on alumina or silica due to the weak acidity and low cost and coking tendency [159,160]. Even though the interaction between molybdenum oxide and AC is weak, the high surface area of activated carbon still allows for a high dispersion and a complete sulfidation of the oxide species. However, increasing metal loading favors sintering due to weak interaction with supported phases, agglomeration and micropore blocking could also take place. The extensive microporosity of carbon materials is a drawback in hydrotreating reactions since part of metals deposited in micropores is wasted in the catalytic reactions involving large molecules. Additionally, how to improve low bulk density and poor crushing strengths is another challenge issue in the utilization of carbon.

5.5 Zirconium, ceria and titania

ZrO₂ and TiO₂ were reported to be beneficial for dispersion of MoS₂ in HDS [161]. Several explanations are proposed for high activity obtained with TiO₂, such as the formation of small crystallites of MoS₂, a higher sulfidability, the reducibility or a favourable morphology [71]. The amphoteric character of ZrO₂ is suggested to be important especially in preventing coke formation [71,110]. Moreover, ZrO₂ exhibits properties of p-type semiconductor, strongly interacting with active species and influencing the adsorption and redox properties of the catalysts. The morphology of MoS₂ is considered to be salient to the reactivity behaviour of ZrO₂ supported Mo catalysts [162]. The acidic-basic properties of TiO₂ and ZrO₂ are pointed out to play an important role during GUA HDO [71]. CeO₂ and ZrO₂ were suggested by Yakovlev [137] as suitable supports for HDO because of possible additional activation of oxy-compounds on the support surface.

Overall, ZrO₂, TiO₂ and CeO₂ have weak acidity which would benefit oxy-compound activation. According to the literature [71,163], the acidity decreases in the order as shown in (13).



5.6 Magnesium oxide

The roles of MgO in Mo-based catalysts for HDO are very limited [99]. As a basic support, MgO shows superior resistance to coke formation on MgO supported catalysts due to two reasons: The basicity allows for high dispersion of acidic species such as MoO₃ and sulfided Mo species. Besides, the basic support promotes formation of short edge-bonded MoS₂ slabs (with Lewis acid on each edge plane) and thus increases the edge plane area suitable for the promotion by Ni or Co [99].

5.7 Active phases other than CoMoS and NiMoS

Noble metals (Pt, Rh, Pd, and Ru) supported on acidic matrices of Al₂O₃, SiO₂-Al₂O₃, and nitric-acid-treated carbon black (NAC) for GUA HDO were studied by Cho Rim *et. al.* [39] at 250°C and 4 MPa in a batch reactor. Noble metals supported on Al₂O₃ allow for formation of cyclohexane, cyclohexanol, and 2-methoxycyclohexanol with no or a small amount of cyclohexanone. However, only cyclohexane is produced when these noble metals are supported on SiO₂-Al₂O₃ except that Ru gives a small amount of cyclohexanol. In addition, 2-methoxycyclohexanol is the major product when NAC is used as the support. The hydrodeoxygenation activity is more dependent on acid supports not the number of metal's active sites, which can be confirmed by (i) Rh/Al₂O₃ shows much less hydrodeoxygenation activity than Rh/SiO₂-Al₂O₃, but Rh/Al₂O₃ has ~ 10 times the number of active sites (metal sites) as compared to Rh/SiO₂-Al₂O₃; (ii) Pt/Al₂O₃ and Pd/Al₂O₃ exhibit better hydrodeoxygenation activity than Pt/NAC and Pd/NAC, and Pt/Al₂O₃ and Pd/Al₂O₃ have ~ 4 times the number of active sites as compared to Pt/NAC and Pd/NAC.

Acidity and metal-oxygen bond strength in oxide support are also important for the product distribution over Pt supported transition metal oxides for HDO of acetic acid [29]. Stronger acidity with proper metal-oxygen bond strength in the support favors ethane production such as on Pt/TiO₂, while Pt/CeO₂ and Pt/ZrO₂ favor production of ethane and ethyl acetate due to weak acidity and improper metal-oxygen bond strength. He *et. al.* [54] investigated GUA HDO over Pt/TiO₂, Pt/Al₂O₃ and NiMo/Al₂O₃ at 285°C and 4 MPa in a fixed bed reactor, Pt/TiO₂ shows much less active coke formation as compared with Pt/Al₂O₃. Non-sulfided NiMo/Al₂O₃ is more active than the other two catalysts, but has graphitic carbon formation on the surface. Thus, both Pt/Al₂O₃ and NiMo/Al₂O₃ deactivate as a function of time, while Pt/TiO₂ is stable during the HDO reactions.

HDO of propanoic acid over Ru/C and Ru/ZrO₂ and Ru/Al₂O₃ was studied by Chen *et. al.* [28]. The C-C bond cleavage is favored in the order of Ru/C > Ru/ZrO₂ > Ru/Al₂O₃, which is correlated to the surface acidity, electronic state of Ru species and metal-support interaction of catalyst. The stronger

metal-support interaction, the more electron deficient Ru species (Ru^{II}) and the more acidity sites on the catalyst result in the higher extent of C=O hydrogenation or lower extent of C-C bond cleavage.

Ni is much less expensive than noble metals but it is very active in the hydrogenation reactions [164]. Ni (loading of 37wt% - 58wt%) and/or Cu supported on $\gamma\text{-Al}_2\text{O}_3$, SiO_2 , $\text{SiO}_2\text{-ZrO}_2$, and $\text{CeO}_2\text{-ZrO}_2$ for GUA HDO was investigated at 320 °C and 17 MPa H_2 in an autoclave by Bykova *et. al.* [40]. High loading of Ni can be stabilized by SiO_2 and/or ZrO_2 , producing much more cyclohexane in the liquid products than on other two supports. However, More 1-methylcyclohexane-1,2-diol and cyclohexanone are produced when NiCu is supported on $\gamma\text{-Al}_2\text{O}_3$ and $\text{CeO}_2\text{-ZrO}_2$, leading to a poor deoxygenation activity. In addition, more coke formation is observed on NiCu/ Al_2O_3 as compared with NiCu/ $\text{CeO}_2\text{-ZrO}_2$, NiCu/ SiO_2 and NiCu/ $\text{ZrO}_2\text{-SiO}_2\text{-La}_2\text{O}_3$.

Ni and W phases supported on AC benefits the activity of PHE HDO due to the lower coke formation on the surface of AC with respect to Al_2O_3 [46], and these Ni and W oxides location is limited mainly on the external surface. However, coke formation is not the main factor for the catalyst deactivation as a function of time at 200°C and 1.5MPa.

The surface chemistry and porosity of the support over Mo_2N supported on activated carbon is found to be critical in the HDO activity [42]. High concentration of oxygen surface groups on the support and high support mesoporosity promotes better dispersion of Mo oxynitride. The importance of support mesoporosity is also confirmed over the Mo_2N /Norit catalyst in [38], which facilitates reactant diffusion to the internal surfaces where the active sites are primarily located.

Mo nitride supported on Al_2O_3 and SBA-15 silica in GUA HDO was studied at 300°C and 5 MPa [58]. $\text{Mo}_2\text{N}/\text{Al}_2\text{O}_3$ favors catechol production, while $\text{Mo}_2\text{N}/\text{SBA-15}$ silica favors phenol production. The less production of catechol using SBA-15 silica support is beneficial for minimizing coke and also opens up possibilities for utilizing silica supports with highly controlled pore sizes in HDO processes. The similar trend is observed on $\text{ReS}_2/\text{Al}_2\text{O}_3$ and $\text{ReS}_2/\text{SiO}_2$ catalysts [60]. ReS_2 supported on Al_2O_3 allows for catechol formation, while no catechol is formed on the $\text{ReS}_2/\text{SiO}_2$ catalyst at 300°C and 5 MPa in a batch reactor.

As discussed above, the supports influence the activity, coking formation, and product distribution through different reaction pathways involved during the HDO reactions. The effect of supports on the catalyst performance may be ascribed to these factors of the catalysts, *i.e.*, water tolerance, surface acidity, porosity, interaction with supported metals by modification the electronic state of metal species, and etc. In brief, the supports should be carefully selected by considering the following aspects: (i) Weak acidity to limit the coking formation on the catalyst surface; (ii) Ability to stabilize the active phases such as noble metals and to keep them in highly dispersed state to activate H_2 ; (iii) Ability to activate oxy-compounds (defects such as oxygen vacancies and Brønsted acid sites) especially for metal supported catalysts.

6. Deactivation

A great challenge in HDO process is the catalyst deactivation. In general, coking, sintering, attack from water, loss of sulphide from the catalyst [108] could cause decrease in activity and deactivate the catalysts [165]. 100 h lifetime of Pd/C for bio-oil HDO was reported by Elliott [166], and 192 h test of bio-oil HDO over $\text{CoMoS}/\text{Al}_2\text{O}_3$ but with substantial deterioration in activity was reported by Bridgwater [167]. TMSs, TMPs and Al_2O_3 -based catalysts are sensitive to H_2O during HDO process. H_2O could cause the oxidation of phosphide sites (Lewis acid) to phosphate sites (Brønsted acid) and/or metal oxides, leading to the catalyst deactivation [120]. The water formed during the HDO reactions could result in the formation of inactive nickel sulfate layer covering the active sulphide phases or the formation of nickel aluminate, leading to the structure change of sulfided catalysts and caused the decrease of activity [86]. Water attack to supports, such as Al_2O_3 could turn alumina to boemite ($\text{AlO}(\text{OH})$) as reported in Refs [14,84].

The improper concentration of sulfiding agents may also lead to activity loss for non-presulfided NiMo and CoMo catalysts. Sulfiding agents such as H_2S , CS_2 or dimethyl sulphide have to be blended in proper concentration to the feed in order to maintain the active sulphide phases. Too low concentration of sulphur cannot boost a high conversion, while the excessive concentration of sulphur in the reaction system caused competitive adsorption to the catalysts and lead to catalyst deactivation by decreasing the surface concentration of coordinatively unsaturated sites [48,168].

Among these deactivation causes, coking formation was proven to be the main reason for catalyst deactivation [15,165]. Table 3 summarized observed carbon formation after HDO reactions. Carbon is mainly formed by polymerization and polycondensation reactions that block the catalyst pores and mask the active sites on the surface. The extent of coking formation depends on the type of oxy-compounds, nature of catalysts, and operation conditions. Overall, a transition metal oxide forms less coke than Al_2O_3 , sulfided CoMo forms more coke than NMs, and bimetallic catalysts have better coke resistance than mono-metallic ones.

Unsaturated hydrocarbons such as alkenes and aromatics have the most potential for carbon formation during the hydrotreating reactions. The strong interaction between C=C bonds and aromatic rings from oxy-compounds with active sites on the catalyst surface lead to the formation of carbon formation instead of hydrocarbon fuels. Phenolic components are observed to adsorb on the support and hinder the accessibility of the active sites [14]. It is generally accepted that oxy-compounds with two O atoms in the benzene ring have higher tendency to coking formation by polymerization reactions on the surface [169,170]. Similarly, catechol is found to result in coking more easily than phenol as reported by Oyama [62].

As we discussed earlier, for metal oxides and sulfides, adsorption and desorption energies of oxy-compounds are controlled by the Lewis acidity of coordinatively unsaturated sites,

while proton donation depends on the Brønsted acidity of the surface -SH or -OH groups on the catalysts forming carbocations [76] during HDO process. Oxy-organics could also be adsorbed on metal sites adjacent to Brønsted sites in bimetallic amorphous boron-based catalysts. Therefore, coking formation is related to the acidity of the catalysts including both Lewis acid sites and Brønsted acid sites, and increases with increasing acidity [8]. However, acidity is responsible for reactant activation but also for deactivation of catalysts. Thus, a proper amount and strength of acidity are important for HDO activity while limiting the coke formation.

Operation conditions also affect the coking formation during HDO process. It is established that hydrogen benefits the coking removal by saturating the carbon precursors especially under high pressure. Elevated temperatures favor polycondensation reactions and thus increase carbon formation [148,165]. From the view of HDO reactions, multi-step processes are beneficial for less coking formation and preventing repolymerization of biomass fast pyrolysis products. Three step process were published by Huber [171] as shown in Figure 18. Ru/C catalyst is used in the first step to remove unstable carbonyl functionalities at 125°C and 98 atm, followed by hydrogenation reactions with Pt/C at 300°C and 98 atm to increase H/C ratios and prevent potential coking, and finally HZSM-5 was used for a dual-stage hydrotreating at 600°C. Overall coke formation is reduced from ~32% (HZSM-5 alone) to 12.6%.

To minimize coke formation, suitable catalysts as discussed in sections 4 and 5 with proper operation conditions such as at moderate temperature and H₂ high pressure with multi-step process will be advantages for pyrolysis bio-oil HDO.

7. Conclusions and future perspectives

The energy crisis and environmental concern have made energy from renewable resources especially from biomass very attractive in recent years. Producing liquid fuels from pyrolysis bio-oils by HDO is feasible for future industrialization. However, poor quality of pyrolysis bio-oils with high oxygen content constitutes a big challenge for catalysis without deactivation. Recently, there has been much progress in HDO of pyrolysis bio-oils over different types of catalysts, including classical sulfided hydrotreating catalysts, noble metals, TMSs, TMPs, TMCs, TMNs, non-precious metals, metal oxides, bimetallic amorphous boron-based catalysts, and reduced metal oxide bronzes. The chemistry, reaction and deactivation mechanisms of model components derived from pyrolysis bio-oils over these catalysts were elucidated in this review.

The achievements suggest that pyrolysis bio-oil upgrading by HDO is still in its infancy and has great potentials for more evaluations before in industrial scale. A robust catalyst that withstands coking, high concentration of water and poisoning, and can be regenerated easily without losing too much activity is highly desired for HDO process. The future tasks concerning catalysts, feedstocks, and operations include:

1) Lower cost for noble metal supported catalysts by higher dispersion via adding promoters such as Mo [28], or better

supports such as tungsten monocarbide [172], or preparation methods such as thermal decomposition of layered double hydroxides precursors [173] and atomic layer deposition [174].

2) New active phases to activate hydrogen such as Ti-doped Al [175].

3) New supports instead of Al₂O₃, which have high surface area and tuneable acidity and porosity.

4) Optimization of operation process such as coupling noncatalytic high pressure thermal treatment process [176] with multi-step [171] HDO for real pyrolysis bio-oils.

5) Improved quality of pyrolysis bio-oils by finding new biomass resources or genetic engineering [4].

Table 3. Carbon formation on different catalysts after reactions. Data in rows 1-7 from Ref [83], experiments performed with 4-methylacetophenone, diethylsebacate and guaiacol in a batch reactor at 280°C, 7 Mpa and 3 h. Data in rows 8-12 from Ref [108], experiments performed with guaiacol in a batch reactor at 100°C, 8 Mpa and 5 h. Data in rows 13-14 from Ref [40], experiments performed with guaiacol in an autoclave at 320°C, 17 MPa and 1 h.

Catalysts	Carbon deposition (wt. %)
γ -Al ₂ O ₃	10.3
CoMoS	2.8
CoMoS/Al ₂ O ₃	8.9
K-CoMoS/Al ₂ O ₃	9.5
Pt-CoMoS/Al ₂ O ₃	9.1
CoMoS/SiO ₂	2.7
CoMoS/C	-
Rh/ZrO ₂	1.8
Pd/ZrO ₂	0.7
Pt/ZrO ₂	0.6
CoMoS/Al ₂ O ₃	6.7
ZrO ₂	0.5
Ni/SiO ₂	15.8
NiCu/SiO ₂	2.3

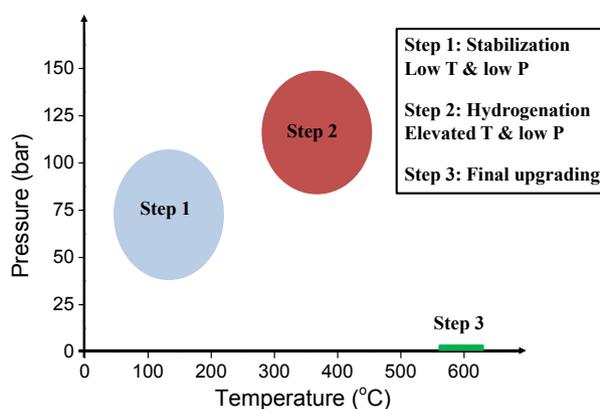


Figure 18. Three-step processes for minimizing coke formation, based on Refs [125,148,171] with permission from the ACS.

Abbreviations

HDO	- hydrodeoxygenation
HDN	- hydrodenitrogenation
HDS	- hydrodesulfurization
HMF	- 5-hydroxymethylfurfural
PHE	- phenol
FAL	- Furfural
THF	- tetrahydrofuran
FOL	- furfuryl alcohol
HFOL	- hydrogenation to furfuryl alcohol

TMSs	- Transition metal sulfides
TMPs	- Transition-metal phosphides
TMCs	- Transition-metal carbides
TMNs	- Transition-metal nitrides
HHV	- higher heating value
TPR	- temperature-programmed reduction

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