



## A Critical Review on Bimetallic Nickel Based Catalysts and Its Catalytic Stability during Hydrodeoxygenations of Bio-Oil

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### ABSTRACT

The catalytic hydrodeoxygenation (HDO) reactions which remove chemically bonded oxygen in the form of water have been considered as a promising technique for bio-oil upgrading to various types of Fuel. In this regard many researchers' attention focused toward nickel-based catalysts for HDO reaction by considering its cheapness, availability and good catalytic activity, which resulted to huge literature accumulation. We earlier provided a review on mono-metallic nickel-based catalysts for hydrodeoxygenation which were found to have lower catalytic activity compared with bimetallic catalysts for this type of reaction. Therefore, in this review we focused toward bimetallic nickel-based catalysts for hydrodeoxygenation reactions and we further extended outlook on deactivation of nickel-based catalysts and finally recommendation for future work.

### 1.0 INTRODUCTION

The prospect and potential displayed by nickel based supported catalysts for hydrodeoxygenation of lignin derived biooil generate a lot of motivation to many researchers to search for more improved hydrodeoxygenation nickel-based catalysts by incorporating various promoters to yield more active, selective and stable nickel-based catalysts for hydrodeoxygenation of lignin derived bio-oil toward transportation fuels. In this regard, many promoted nickel-based catalysts such as Cu-Ni, Ni-Fe, Ni-Pd, Ni-Re, Ce-Ni-W-B, etc. have been investigated (Ambursa, Sudarsanam, Voon, Hamid, & Bhargava, 2017; Gonçalves et al., 2017; Y. Li, Zhang, Zhang, Chen, & Smith, 2017; Mortensen, Gardini, et al., 2016; Rodríguez-Aguado et al., 2017). On the other hand, several factors such as coke formations, poisoning of active sites, sintering and leaching affect the stability of nickel-based catalysts. So, and this section presents the most recent review for promoted nickel-based catalysts.

On the other hand, the stability of nickel-based catalysts is of great concern in hydrodeoxygenations of lignin derived bio-oil since, it will have a major influence on the economic considerations for bio-refinery catalytic processes upon commercialisations. While it has been noticed that, catalysts stability

remains paramount for this process, many factors influencing catalysts deactivation remain inevitable for this hydrodeoxygenation processes. The major causes of catalysts deactivation in hydrodeoxygenations of lignin derived bio-oil includes coking, poisoning, sintering and leaching of the active components of the catalysts (Argyle & Bartholomew, 2015; Bartholomew & Argyle, 2015; Lup, Abnisa, Daud, & Aroua, 2017; Saidi et al., 2014).

### 2.0 Cu-NI BIMETALLIC CATALYST

The motivating interests for the choice of Cu species as promoter to Ni metal for hydrodeoxygenation of lignin derived bio oil was due to its potential to electronically interact with d-orbital of Ni metal and result to its partial filling, hence change in catalytic activity and stability of nickel based catalysts in hydrodeoxygenation of lignin derived bio oil (Guo, Wu, Wang, Zhang, & Xu, 2015; Izadi, Rashidi, Zeraatkar, Varmazyar, & Rashtchi, 2014). According to electron band theory, the group 1B metal such as Cu has free d-electron and that of group VIII such as Ni has free d-orbital delocalised in the conduction band. Therefore, the interaction between the two might result to filling of the d-zone of nickel species leading to relatively low adsorption strength compared to mono-metallic Ni species (Guo et al., 2015; Khromova et al., 2014). In line with

modern catalytic theory that, catalysts species with moderate adsorption strength possess higher catalytic activity and possess more prefer attributes for catalysis hence wide consideration for Cu-Ni bimetallic catalysts for hydrodeoxygenation of lignin derived bio oil (Ambursa et al., 2016; Ambursa et al., 2017; Bykova, Zavarukhin, Trusov, & Yakovlev, 2013; Hamid, Ambursa, Sudarsanam, Voon, & Bhargava, 2017) Cresol (Kannapu, Mullen, Elkasabi, & Boateng, 2015) Anisole (Khromova et al., 2014). The comparative studies of catalytic activity between mono-metallic Ni based and bimetallic Cu-Ni based catalysts for hydrodeoxygenation of lignin derived bio oil model compounds revealed that, the synergy between copper and nickel in Cu-Ni bimetallic catalysts greatly enhance its selectivity to saturated hydrocarbons above mono-metallic Ni based catalysts (Bykova et al., 2014). For example, Ni/SiO<sub>2</sub> and Cu-Ni/SiO<sub>2</sub> were compared for hydrodeoxygenation of Guaiacol at 320°C, 17MPa and 1h reactions time and they reported that, bimetallic Cu-Ni/SiO<sub>2</sub> displayed high cyclohexane selectivity of ~64% than Ni/SiO<sub>2</sub> with lower cyclohexane selectivity of ~3% (Bykova et al., 2012). Due to Ni-Cu synergy between the two (Cu and Ni metals), more favourable catalytic attributes would be achieved which influence hydrogen adsorption with moderate strength making it easier to activate and desorb highly active hydrogen species from Cu-Ni bimetallic surface. Therefore, a greater number of activated hydrogens could promote reduction of aromatic ring and hydrodeoxygenation of methoxy or hydroxyl groups from guaiacol molecules either through direct hydrogenolysis or dehydrations leading to formations of more saturated hydrocarbons over Cu-Ni bimetallic surface than mono metallic nickel-based catalysts. The proof of more catalytic activity for bimetallic Cu-Ni based catalysts than mono-metallic nickel based catalysts interest more researchers to explored it potential for hydrodeoxygenation reactions (Bykova et al., 2014; Dongil, Bachiller-Baeza, Rodriguez-Ramos, Fierro, & Escalona, 2016; Hamid et al., 2017; Kannapu et al., 2015; Khromova et al., 2014; Zhang et al., 2013) For example, Bykova et al. (Bykova et al., 2014)

investigated hydrodeoxygenation of guaiacol at 320°C, 17MPa and 1h reactions time over Cu-Ni catalysts in batch reactor and reported high catalytic activity and selectivity to cyclohexane. Also at mild temperature condition, Ambursa et al., (Ambursa et al., 2017) studies hydrodeoxygenation of Guaiacol at 260°C, 10MPa and 6 hours of reaction time obtained high catalytic activity and cyclohexane. Also in another study, Dickinson and Savage (Dickinson & Savage, 2014) investigate hydrodeoxygenations of O-cresol in a fixed bed reactor over Ni-Cu/Al<sub>2</sub>O<sub>3</sub> and Reney Ni-Cu/Al<sub>2</sub>O<sub>3</sub> catalysts at 380°C and 30.05MPa for 24h it was found that, both catalysts possessed high catalytic activity and selectivity to hydrocarbons under the tested conditions. Both catalysts showed O-cresol conversion of 100% with Ni-Cu/Al<sub>2</sub>O<sub>3</sub> hydrocarbons selectivity of 80% and that of Reney Ni-Cu/Al<sub>2</sub>O<sub>3</sub> with corresponding hydrocarbons selectivity of 60%. The high catalytic activity was due to synergistic role between metal and acids sites in these catalysts. The synergy between Cu and Ni as well have been reported to lower reduction temperature of nickel oxides to nickel metal in bimetallic catalysts hence facilitating reductions, control sintering and improve dispersion of nickel and Bimetallic copper- nickel species during activations processes (Ambursa et al., 2016; Bykova et al., 2014). For examples, Bykova et al. (Bykova et al., 2014) in their comparative study between mono-metallic Ni and bimetallic Cu-Ni based catalysts for Guaiacol hydrodeoxygenation tried to correlate catalysts physico-chemical properties with catalytic activity. During temperature programme reductions it was found that, the reductions temperature of NiO/SiO<sub>2</sub> is much high than CuO-NiO/SiO<sub>2</sub> reductions temperature. Reason being that, Cu as a promoter influence moderate Ni-support interactions through synergistic relationship hence, low thermal energy requirement to overcome the attractions (Ambursa et al., 2016). Several catalytic reactions pathways leading to saturated hydrocarbons have been inferred depending on the reaction's conditions and dominant catalysts functions.

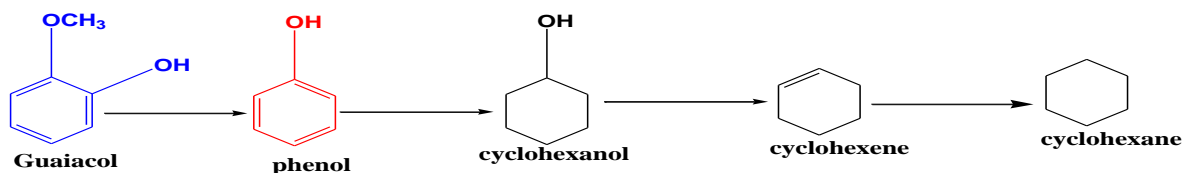


Figure 1 :- Proposed reactions pathways for hydrodeoxygenation of Guaiacol to cyclohexane over Cu-Ni/Ti-MCM-41 as adopted from (Ambursa et al., 2017).

### 3.0 OTHER NICKEL BASED CATALYSTS

Other nickel based catalysts have recently been explored for hydrodeoxygenation of lignin derived bio oil and its model compounds. It was also observed experimentally that, nickel other active metal synergy such as Fe, Pd, Pt were observed enhance catalytic activity of nickel based catalysts (Lai, Zhang, & Holles, 2016; Shafaghat, Rezaei, & Daud, 2016; Yang et al., 2017). Bimetallic nickel based catalysts such as Ni-Fe (Fang et al., 2017), Ni-W-P-B (Wang et al., 2015), NiB (LIU, LIU, Xiang, ZHANG, & ZHAI, 2017) and Ni-Ru (Luo, Zheng, Li, Cui, & Zhao, 2017) Ni-Pd and Ni-Pt (Lai et al., 2016) were found to be active for hydrodeoxygenation of lignin derived bio oil prototypes compounds with high selectivity to saturated cyclic hydrocarbons such as cyclohexane and methylcyclohexane.

For examples Fang et al., investigated hydrodeoxygenation of Guaiacol at 300°C, 3MPa, and 2 hours of reactions time in a fixed bed reactor using NiFe/CNT, the final products analysis revealed high Guaiacol conversion of 96.8% with good cyclohexane selectivity of 83.4%. In both cases the high selectivity was affiliated to hydrogenations and deoxygenation potential of these catalysts. However, some bimetallic nickel based catalysts such as were found to exhibit good activity but low selectivity saturated hydrocarbons for example Hong et al. (Hong, Lee, Eom, & Lee, 2014) obtained 100% conversion with low cyclohexane selectivity of 16% in hydrodeoxygenation of Guaiacol over Sulphided Ni/W/TiO<sub>2</sub> at 300°C, 7MPa and 2.5 reaction time in batch reactor. Also low hydrocarbons selectivity of 21.66% was reported by Shafaghat et al. (Shafaghat et al., 2016) in hydrodeoxygenation of lignin derived bio oil model compounds mixtures as simulated phenolic bio oil at 300°C, 4MPa and 16 hours over NiFe/Hbeta in batch reactor. They further reported that, with modification of water to methanol as reaction medium, there was shift of selectivity from saturated hydrocarbons to

aromatic hydrocarbons in this reaction. Also noble metal promoted nickel based catalysts such as Ni-Pd and Ni-Pt, Ni-Re/SiO<sub>2</sub> influence selectivity of nickel based catalysts towards aromatic hydrocarbons as observed (Lai et al., 2016; Yang et al., 2017).

In this regards the aromatic selectivity to aromatic hydrocarbons increases with increase of reaction temperature. For examples Yang et al. (Yang et al., 2017) conducted studies at 300°C for hydrodeoxygenation of cresol in fixed bed reactor over Ni-Re/SiO<sub>2</sub> there was low selectivity to toluene of 23.7% but, when Lai et al. (Lai et al., 2016) carried out hydrodeoxygenation of Guaiacol at 450°C in a fixed bed reactor over Ni-Pd and Ni-Pt, the selectivity of aromatic hydrocarbons was observed to reached 80%. Besides the crystalline phase of nickel-based catalysts, amorphous nickel-based catalysts such as Ce-Ni-W-B, La-Ni-W-B and Ni-W-P-B were reported to manifest high hydrogenation and deoxygenation activity (Wang et al., 2014; Wang et al., 2015; Wang, Yang, Luo, Peng, & Wang, 2011). For example, hydrodeoxygenations of phenol over La-Ni-W-B amorphous catalysts, at temperature of 225°C, hydrogen pressure of 4MPa and reactions time of 4h in batch reactor was conducted and finding revealed selectivity to oxygen free products of 79.10%. In this type of catalysts, Ni species was observed to promote hydrogenation activity, W<sup>6+</sup> species provide Bronsted acidity as effective sites for deoxygenations, B increase hydrogenating activity of amorphous Ni site through electron transfer (which make Ni species more unsaturated and hence facilitate activation and desorption of hydrogen over the catalysts surface). Besides enhancing B<sup>0</sup> to Ni<sup>0</sup> electronic transfer, the La species also promotes Bronsted acidity of WO<sub>3</sub> and therefore influence more deoxygenation activity (Wang et al., 2014; Wang et al., 2015; Wang et al., 2011).

Table 1: Bimetallic Nickel-Copper Based Catalysts for Hydrodeoxygenation of Lignin Derived Bio Oil Model Compounds

Authors	Catalysts	model compound	Temp.°C	Pressure	Time	Reactor	major products	Conversion (%)	Selectivity (%)
(Ambursa et al., 2017)	Ni-Cu/Ti-MCM-41	Guaiacol	260	10 MPa	6h	Batch	cyclohexane	90.49	50.09
(Hamid et al., 2017)	Ni-Cu /Ti-MCM-41	Guaiacol	260	10 MPa	6h	Batch	cyclohexane	74.20	48.8
(Dongil et al., 2016)	Ni-Cu/CNT	Guaiacol	573	5MPa	4h	Batch	cyclohexanol	100.00	60
(Kannapu et al., 2015)	Ni-Cu/Al <sub>2</sub> O <sub>3</sub>	cresol	300	5MPa	4h	Batch	4-Methyl-cyclohexanol	95	95
(Dickinson & Savage, 2014)	Ni-Cu/Al <sub>2</sub> O <sub>3</sub>	O-Cresol	380	30.05MPa	24h	Fixed-Bed	saturated hydrocarbon	~100	~80
(Dickinson & Savage, 2014)	Reney-Ni-Cu/Al <sub>2</sub> O <sub>3</sub>	O-Cresol	380	30.05MPa	24h	Fixed-Bed	saturated hydrocarbon	~100	~60
(Bykova et al., 2014)	Ni-Cu/SiO <sub>2</sub> -ZrO <sub>2</sub>	Guaiacol	320	17MPa	1h	Batch	Cyclohexane	95	67
(Bykova et al., 2014)	Ni-Cu -Mo/SiO <sub>2</sub> -ZrO <sub>2</sub>	Guaiacol	320	17MPa	1h	Batch	Cyclohexane	92	62
(Bykova et al., 2014)	Ni-Cu -P/SiO <sub>2</sub> -ZrO <sub>2</sub>	Guaiacol	320	17MPa	1h	Batch	Cyclohexane	81	67
(Bykova et al., 2014)	Ni-Cu-Mo-P/SiO <sub>2</sub> -ZrO <sub>2</sub>	Guaiacol	320	17MPa	1h	Batch	Cyclohexane	81,	67
(Zhang et al., 2013)	Ni/SiO <sub>2</sub> -ZrO <sub>2</sub>	Guaiacol	300	5MPa	8h	Batch	cyclohexane	100	96.8
(Bykova et al., 2013)	Ni-Cu /SiO <sub>2</sub> -ZrO <sub>2</sub> -La <sub>2</sub> O <sub>3</sub>	Guaiacol	320	17MPa	1h	Batch	Cyclohexane	~78	~ 40
(Bykova et al., 2011)	Ni/SiO <sub>2</sub>	Guaiacol	320	17MPa	1h	Batch	Cyclohexane	96.7,	~3
((Bykova et al., 2011)	Ni-Cu/SiO <sub>2</sub>	Guaiacol	320	17MPa	1h	Batch	Cyclohexane	87	~64
(Bykova et al., 2011)	Ni-Cu/ZrO <sub>2</sub> -SiO <sub>2</sub>	Guaiacol	320	17MPa	1h	Batch	Cyclohexane	85.6	~65
(Bykova et al., 2011)	Ni-Cu/CeO <sub>2</sub> -ZrO <sub>2</sub>	Guaiacol	320	17MPa	1h	Batch	Cyclohexane	94.2	~2
(Bykova et al., 2011)	Ni-Cu/Al <sub>2</sub> O <sub>3</sub>	Guaiacol	320	17MPa	1h	Batch	Cyclohexane	80.2	~50

Our literature search from table 7 show that, amorphous Ce–Ni–W–B catalysts was adopted for hydrodeoxygenation of phenol at 225°C, 4MPa and 1h in batch reactor exhibit greater performance with 100% conversion and 100% selectivity to cyclohexane. The mechanisms for hydrodeoxygenation of phenol over was reported by Wang et al. (Wang et al., 2011). as given in figure 12 below. According to stated mechanisms, phenol was adsorbed on Bronsted acids sites via lone electron pair from oxygen which caused polarization of C-O bond and the

activated hydrogen from amorphous nickel sites attacked and hydrogenate aromatic ring instead of C-O bond (more energy demanding) to produce cyclohexanone which later reduced by adsorbed hydrogen from neighbouring Ni sites to cyclohexanol. Dehydration of cyclohexanol to yield cyclohexene was shown to took place on Bronsted acids sites at slower rate (representing rate determining step) and hydrogenations of cyclohexene to produced cyclohexane occurred on amorphous Ni sites.

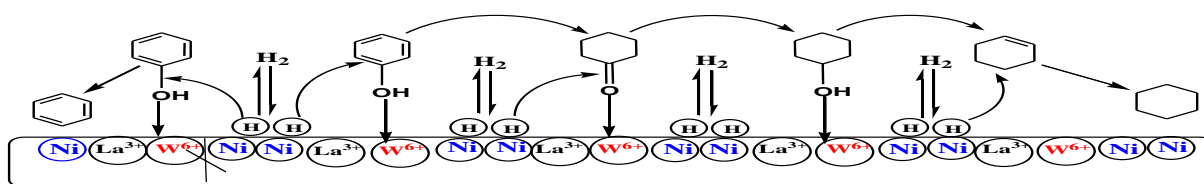


Figure 2. Reactions mechanisms of hydrodeoxygenation of phenol over La-Ni-W-B amorphous catalysts as adopted from Wang et al. (Wang et al., 2011).

## 4.0 CATALYSTS DEACTIVATION

### 4.1 Catalysts Deactivation Due To Coking

Coking involved deposition of carbonaceous material on the catalysts surface. Coke are usually form on catalysts surface through unsaturated hydrocarbons polymerization or condensation of oxygenated compounds (Argyle & Bartholomew, 2015; Bartholomew, 2001). The formed coke may cover the catalysts active sites or block pores of the supports leading to catalytic activity lost in hydrodeoxygenation reactions. In hydrodeoxygenation of lignin derived bio oil and its prototypes compounds, formation of coke on nickel based catalysts surface can be significantly influence by the nature of catalysts, types of bio oil compounds / model compounds and resulted intermediates species, as well as applied reaction conditions such as temperature, pressure and time (Argyle & Bartholomew, 2015; Saidi et al., 2014). Although, supports acidity due to presence of either Bronsted or Lewis acids sites greatly enhance the rate of hydrodeoxygenation reactions through C-O bonds activations, it also influences coke formation on nickel-based catalysts surface (Bartholomew & Argyle, 2015; Lup et al., 2017; Saidi et al., 2014). For examples, Li et al. (Yu Li et al., 2017) investigated hydrodeoxygenation of lignin derived bio oil over Ni and promoted Cu-

Ni supported on HZSM-5 between 250-330°C and 20 bar of hydrogen pressure and a long progress of the reactions, they noticed drastic decreased in catalytic performance as a consequence of coke formation on the catalysts surface which was affiliated to high acidity of HZSM-5 zeolites. Availability of excessive amount of unsaturated hydrocarbons and oxygenated compound during hydrodeoxygenation reactions could also serve as the precursor to coke formation (Bartholomew & Argyle, 2015; Lup et al., 2017). For example, in hydrodeoxygenation of Guaiacol, reaction pathway associated with methyl lost leading to formation of catechol as reactant intermediate has been inferred to be more prone to coke formation than phenol formation pathway. The produced catechol species was founds to strongly adsorbed on the surface acidic sites and through polycondensation coking mechanism is converted to sensitive coke on the catalysts surface (Argyle & Bartholomew, 2015; Bartholomew, 2001).

Table 2: Other Ni based catalysts for hydrodeoxygenation of lignin derived bio oil model compounds

Authors	Catalysts	model compounds	Temperature °C	Pressure	Time	Reactor	Conversions	Selectivity	major products
(Fang et al., 2017)	Ni-Fe/CNT	Guaiacol	300	3MPa	2h	fixed bed	96.8	83.4	Cyclohexane
(Hong et al., 2014)	Sulphided Ni/W/TiO <sub>2</sub>	Guaiacol	300	7MPa	2.5h	batch	100%	16%	Cyclohexane
(Lai et al., 2016)	Ni-Pd and Ni-Pt	Guaiacol	450	1 atm.	1h	fixed bed	~90	80	Aromatics
(LIU et al., 2017)	NiB/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	Guaiacol	260	5MPa	3h	batch	98.7	57.1	Cyclohexane
(LIU et al., 2017)	NiB/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	Anisole	260	5MPa	3h	batch	90.6	33.5	Cyclohexane
(Yang et al., 2017)	Ni-Re/SiO <sub>2</sub>	cresol	300	1 Atmos	0.5h	fixed bed	47.6	23.7	Toluene
(Wang et al., 2015)	Ni-W-P-B	p-cresol	225	4MPa	5h	batch	99.6	92.6	methylcyclohexane
(Shafaghat et al., 2016)	NiFe/Hbeta	mixture	300	1.6MPa	4h	batch	—	21.66	Cycloalkane
(Valdés-Martínez, Suárez-Toriello, de los Reyes, Pawelec, & Fierro, 2017)	NiRu/Al <sub>2</sub> O <sub>3</sub> , TiO <sub>2</sub> , ZrO <sub>2</sub>	Phenol	320	5.4MPa		batch	80	55	cyclohexane
(Wang et al., 2014)	Ce-Ni-W-B	Phenol	225	4MPa	1h	batch	100	100	cyclohexane
(Wang et al., 2014)	Ce-Ni-W-B	p-cresol	225	4MPa	1.5h	batch	100	98.9	methylcyclohexane
(Wang et al., 2014)	Ce-Ni-W-B	Guaiacol	225	4MPa	6h	batch	100	85	cyclohexane
(Luo et al., 2017)	Ru-Ni/HZSM-5	Guaiacol	240	0.2MPa	1h	batch	~70	88	phenol
(Mortensen, Grunwaldt, Jensen, & Jensen, 2013)	Ni-V <sub>2</sub> O <sub>5</sub> /ZrO <sub>2</sub>	Phenol	275	1 Atmos	4h	batch	100	70	cyclohexane
(Mortensen et al., 2013)	Ni-V <sub>2</sub> O <sub>5</sub> /SiO <sub>2</sub>	Phenol	275	1 Atmos	4h	batch	100	54	cyclohexane
(Wang et al., 2011)	La-Ni-W-B	Phenol	225	4MPa	4h	batch	97.3	37.2	cyclohexane
(Pichaikaran & Arumugam, 2016)	RuO <sub>2</sub> -NiO/Al-SBA-15	Anisole	400	1 Atmos	24h	fixed- bed	46	61.60%	Benzene
(Pichaikaran & Arumugam, 2016)	RuO <sub>2</sub> /Al-SBA-15	Anisole	400	1 Atmos	24h	fixed- bed	19.80%	38 %,	Benzene

Also literature survey revealed that, high reaction temperature particularly with low reaction pressure and high catalysts-reactant contact time influence coke formation over the catalysts surface and result to catalysts deactivation during reactions progress (Lup et al., 2017; Saidi et al., 2014). For instance, He et al. (He et al., 2017) reported catalysts deactivation due to coke formation in hydrodeoxygenation of Anisole over Ni-Mo/SiO<sub>2</sub> at 410 °C and 1 atmosphere. The formations of coke was due to high reaction temperature of 410°C since, many studies in the literature indicated high stability of Ni-Mo as well as resistivity of SiO<sub>2</sub> support to coke formation due to weak acidity (Smirnov et al., 2016). Table 9 below show data on recent catalysts deactivation due to coke formations which reflected to various influential factors as discussed in this section.

#### 4.2 Catalysts Deactivation Due To Poisoning Of active Sites

Poisoning of active sites on the catalysts surface is depend on the strength of adsorption of chemical species competing with reactant for catalytic sites over the catalysts surface (Argyle & Bartholomew, 2015). Also poisoning of active sites was observed with nickel-based catalysts in hydrodeoxygenation of lignin derived bio oil and its prototypes compounds (Argyle & Bartholomew, 2015; Lup et al., 2017; Saidi et al., 2014). Poisoning of active sites occur due to strong chemisorption of chemical species (reactant, intermediates, products or impurities) on catalytic sites over catalysts surface and some observed poisons in hydrodeoxygenation of lignin derived bio oil includes oxygen containing compounds such as water, CO etc. water is produced in hydrodeoxygenation process and tend to competes with reactant for adsorption on the catalysts active sites. A number of recent studies reported detrimental effect of water poisoning on the catalytic sites some studies even showed that, water in hydrodeoxygenation reactions not to only adsorbed active sites but modified the chemical structures of the active sites. For examples, Kelun et al., in hydrodeoxygenation of Anisole over NiP/SiO<sub>2</sub> and NiMoP/SiO<sub>2</sub> and the water was generated as a by-products. generated water molecules in the reactions led to oxidation of NiP there by forming nickel oxides and nickel phosphates which is less active compounds compared to phosphides.

Water as well have been reported by Mortensen et al. (Mortensen, Grunwaldt, Jensen, & Jensen, 2016) to caused deactivations of Ni-MoS<sub>2</sub>/ZrO<sub>2</sub> due to in habiting effect of water. In their deactivations studies for hydrodeoxygenation of phenol and octanol, Water undergo competitive adsorption of water on the active sites there by converting sulphide to sulphate on the edge of MoS<sub>2</sub> catalysts.

#### 4.3 Catalysts Deactivation Due To Sintering and Leaching

Sintering is regarded as loss of catalytic surface area of the active phases due to its crystallites growth, pores collapses on crystallites of the catalytic phases or loss of support area due to degradation and collapses (Argyle & Bartholomew, 2015). It should be noted that, data concerning sintering of nickel-based catalysts is limited in the literature. Reason being that, most of the recent work related to nickel-based catalysts focused toward promoted acidic supports and mesoporous support particularly metal doped mesoporous supports under mild reaction conditions. nickel based catalysts supported on acidic supports such as transition metal oxides (Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>) showed high thermal stability than non-acidic or weakly acidic supports such as SiO<sub>2</sub> due to Ni support interactions in the former one. For examples sintering of active nickel in Ni<sub>2</sub>P/SiO<sub>2</sub> have been reported by Lan et al., (2018), in hydrodeoxygenation of Guaiacol at 300°C. Such sintering effect results to loss of activity from 100 to 10% conversion within 8h of reaction time. Those nickel based catalysts supported on metal doped mesoporous support such Al-SBA-15, Ti-SBA-15, Al-MCM-41 and Ti-MCM-41 up hold double advantages of (1) Nickel supports interaction and (2) pore size confinements which restrict crystallites and atomic migration as well as decreases crystallites growth rate as it approach diameter of the pores (Argyle & Bartholomew, 2015).

For examples Selvaraj et al. investigated catalytic stability of Mo-Ni supported on mesoporous aluminosilicate promoted by alumina support in hydrodeoxygenation of Guaiacol 300°C and 10 hours of reaction time by conducting reusability study for up to 4 cycles and they found that, high catalytic performance was maintained for the entire runs and even

indicating catalytic surface area was merely on altered. However, some recent studies showed that, sintering of nickel based catalysts occurred (Dickinson & Savage, 2014; Lan et al., 2018). For examples, for hydrodeoxygenation of O-Cresol over Ni/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> at 380°C and 305 bars, Sintering of Nickel phase have been reported to occur with Ni crystallites growth from 3.8 to 36nm. Since it has been reported that, sintering increases with temperature (Argyle & Bartholomew, 2015; Bartholomew & Argyle, 2015) hence, catalytic activity at moderate temperature reduces sintering effect. For example, Long et al. (Long et al., 2015) carried out recyclability study at 160°C in hydrodeoxygenations of Guaiacol for up to 4 cycles using Ni/MgO catalyst and they found high stability of this catalysts with good conversion and selectivity.

Leaching of the active sites from nickel based catalysts during hydrodeoxygenation of lignin derived bio oil to transportations fuels molecules have been reported (Zhao, Yu, Jentys, & Lercher, 2013). For examples Zhao et al., (Zhao et al., 2013) have reported leaching of nickel species from Ni/Al<sub>2</sub>O<sub>3</sub>-HZSM-5 catalysts for hydrodeoxygenation of phenol at 200°C and 5MPa of hydrogen pressure. The leached of this Ni species led to lost of hydrocarbons selectivity from 70 to 25%. Also according to Dickinson et al. (Dickinson & Savage, 2014) leaching of Al species was observed along with Ni particle growth from 3.8 to 36nm from Ni/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts in hydrodeoxygenation of cresol at 380°C and 30.5MPa. The observed Al leaching and sintering of Ni species resulted to greater lost of activity and deoxygenation degree during the reactions.

## 5.0 CONCLUSION

The catalytic activity and selectivity of bimetallic nickel-based catalysts for saturated hydrocarbons were found to be good due to metal-metal synergy. mild reactions temperature with moderate hydrogen pressure influence selectivity to saturated hydrocarbons due to dominant

hydrogenation activity than hydrogenolysis of C-O bond of Nickel species. Catalyst deactivation due to coking, poisoning, sintering and leaching of the active components of the catalysts could be greatly reduced in the presence of Bimetallic Nickel-based catalysts. Therefore, Bimetallic Nickel based catalysts displayed greater potential for hydrodeoxygenation of lignin derived bio-oil to transportation fuels.

## 6.0 RECOMMENDATIONS FOR FUTURE WORKS

Considering the vast literature so far, the development of Nickel based catalysts for hydrodeoxygenation of bio-oil is still on going. In this review some recommendation can be forwarded as follow -: We recommend for further optimizations of Nickel, Supports and promoter's compositions particularly for mesoporous supported nickel-based catalysts to come up with optimized various catalysts functions (Such as Acids and Metal sites) needed for hydrodeoxygenation of lignin derived bio oil toward various types of fuel.

The Stability of nickel-based catalysts in hydrodeoxygenation of lignin derived bio oil need to be enhance and therefore more investigations of the appropriate catalysts compositions and reactions conditions to yield highly stable nickel-based catalysts that, could resist deactivation especially, due to coking and sintering during hydrodeoxygenation reactions is highly required. Deactivation due to coking could be effectively improved if high catalytic performance could be achieved at moderate reactions temperature and hydrogen pressure particularly with involvement of stable supports and promoters and therefore, its highly encourage to consider these factors in designing hydrodeoxygenation catalysts. The resistance to sintering of nickel-based catalysts could as well be increased with appropriate metal-support interactions especially at moderate reaction temperature hence it will be taking into consideration when designing hydrodeoxygenation catalysts.

**Table 3: Deactivations Of Nickel Based Catalysts In Hydrodeoxygenation Of Lignin Derived Bio Oil And Its Model Compounds**

Authors	model compounds	Catalysts	Temperature °C	Pressure	Causes of deactivations	Effect of deactivations
(Lan et al., 2018)	Guaiacol	Ni <sub>2</sub> P/SiO <sub>2</sub>	300	1 atm.	Due to coking and sintering of the active components as well as change in structural properties of Ni and P species.	Loss of catalytic activity from 100 to 10% within 8h of reaction time.
(Shafaghat et al., 2016)	Guaiacol, Phenol, cresol	Ni/Hbeta, NiFe/Hbeta	300	1.6MPa	Blocking of catalysts active sites by coke depositions on the catalysts surface.	Selectivity lost from 53.59 to 9.36 (wt.%) after the 5th run of Reusability studies
(He et al., 2017)	Anisole	Ni-Mo/SiO <sub>2</sub>	410	1 atm.	The catalysts deactivation has been reported to occur due to coke deposit.	Loss of activity and shift of selectivity to phenol and heavier products
(Yu Li et al., 2017)	Bio oil	Ni/HZSM-5	250-330	2MPa	Coking formations on the catalysts surface.	Lost of Activity and deoxygenation degree over reaction time
(Dickinson & Savage, 2014)	O-Cresol	Ni/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	380	30.5MPa	Activity lost due to supports degradations and sintering of Ni species with particle growth from 3.8 to 36nm. In additions there was Al leaching from the support.	Activity lost to about 10% couple with lost of deoxygenation degree to about 20%
(Zhang, Tang, Zhang, Wang, & Ma, 2017)	mixture	Ni/Al <sub>2</sub> O <sub>3</sub>	300	5MPa	Coking on the catalysts surface with 9% weight lost as suggested by TGA analysis.	affiliated to significant decreased in conversion and hydrocarbon yield

(Zhao et al., 2013)	Phenol	Ni/HZSM-5	200	5MPa	Sintering (average Ni particle growth from 41-94 nm) as well as Leaching of Ni particles from support	Lost of hydrocarbons selectivity from 30 to 10% after the 4th cycle of re-run.
(Zhao et al., 2013)	Phenol	Ni/Al <sub>2</sub> O <sub>3</sub> -HZSM-5	200	5MPa	Sintering with Ni particle growth from 8.8 -17 nm as well as Leaching of Ni particles from supports.	Decreased of hydrocarbons selectivity from 70 to 25% after the 4th cycle of re-run.
(Mortensen et al., 2014)	Guaiacol	Ni/ZrO <sub>2</sub>	250	100 bar	Poisoning of active sites by sulphur, and potassium as well as Sintering of Ni particles	Lost of stability from 100h to 20h
(K. Li et al., 2011)	anisole	NiP/SiO <sub>2</sub> , MoP/SiO <sub>2</sub> and NiMoP/SiO <sub>2</sub>	300	1.5MPa	Coking and poisoning of active sites by H <sub>2</sub> O adsorptions as well as oxidation of Ni <sub>2</sub> P by H <sub>2</sub> O molecules	lost of conversion and degree of deoxygenations along the reactions time
(Mortensen, Grunwaldt, et al., 2016)	phenol	Ni-MoS <sub>2</sub> /ZrO <sub>2</sub>	280	100 bars	Poisoning of active sites by H <sub>2</sub> O due to replacement of sulphur on the edge of MoS <sub>2</sub> catalyts.	Resulted to decrease in conversion from 56% to 21% after 110h of reaction time.

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