A Review on Required Catalysts Composition and its Effective Preparation Method for Hydrodeoxygenation of Bio-oil

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Abstract

The hydrodeoxygenation of bio-oil performance is dependent on the efficiency and effectiveness of the applied catalyst. The effectiveness of a catalyst in hydrodeoxygenation reaction heavily depends on its composition. In this review, an overview of hydrodeoxygenation catalyst composition and its effective preparation methods are highlighted and discussed. Various catalyst compositions such active metals, promoters, and catalyst supports used for hydrodeoxygenation of bio-oil to saturated hydrocarbon fuels are discussed. Furthermore, effective synthesis methods for nickel-based catalysts as well as factors that can enhance better distribution and dispersion of active nickel species over catalyst support at various developmental stages, i.e. during deposition, drying and activation (which involve calcination and reduction of catalysts synthesis) are discussed.

Keywords: Hydrodeoxygenation, Bio-oil, Nickel-based catalyst, Synthesis

1. Introduction

The role of catalyst in hydrodeoxygenation (HDO) reactions is tremendous. It is even believed that the future and prospect of HDO processes rely heavily on the efficiency and effectiveness of the applied catalyst [1,2]. Based on structure-activity relationship, as demonstrated by previous works on HDO of lignin derived bio-oil particularly with prototype compounds [3], bi-functional catalyst systems have been recognised as one of the best catalysts for HDO of lignin derived bio-oil [4,5].

The bi-functional catalyst systems consist of an active metal (e.g. Pt, Ru, Ni, Fe, Co, Ir, Re, Pd), catalyst support (e.g. transition metal oxides and silica materials), and in most cases with a promoter, either to the active metal or to the catalyst support which either enhance catalytic activity, selectivity or stability [1,5]. The required bi-functional catalyst system should as well allow synergistic role between the active metal and support during the HDO reactions. The role of the metal is primarily to promote hydrogenation of aromatic ring or unsaturated compounds during HDO reaction [4,5]. Furthermore, the metal could also influence deoxygenation process by direct hydrogenolysis [2]. The duty of the catalyst support is to disperse and stabilize the active metal species. However, the catalyst support is also expected to provide functional sites for activation of C-O bonds during HDO reactions [4,6]. Therefore, acidic supports with Lewis acidity or Bronsted acidity or the presence of both are preferred for HDO reactions [7,8]. Acidic

supports have also been noticed to influence the state and stability of the active phase through metal-support interactions during the activation process [9,10].

For most HDO reactions, catalyst promoters such as Cu, Mo e.t.c. are usually employed to enhance activity, selectivity, or stability of the active metal. It has been observed experimentally that the synergy between promoter and active metal exert great influence on the catalytic activity, selectivity, and stability. Hence, bimetallic catalysts are more active than mono metallic catalysts for HDO of lignin derived bio-oil [7,11,12].

2. Catalyst Composition

Various types of materials such as sulphides, noble metals and non-noble metals have been investigated as active components in catalysts for HDO of lignin derived bio-oil. The conventional CoMoS and NiMoS catalysts used for hydrodesulphurization (HDS) process in petroleum refinery were initially investigated for the HDO reactions [13,14]. The catalytic activity of these catalysts mainly depended on the sulphide region of the catalyst, since loss of sulphur generates vacancies that serves as the active sites for the HDO reaction [15]. The generated vacancies located at the edges of WS_2 and MoS_2 exhibit Lewis acid properties with ability to adsorb heteroatoms resulting to C-O cleavage [16]. The catalysts also exhibit Bronsted acid properties, which comes from molecular hydrogen (H_2), alcohols, thiols, or water activation into SH^- and H^+ over the catalysts surface. The SH^- promotes deoxygenation while H^+ per takes in multiple bond saturation [14,16-18].

The promoters (e.g. Ni and Co) enhance the catalytic activity of the process by controlling the bond strength between molybdenum and sulphur during hydrogenation and deoxygenation processes [10,17,18]. However, there are many challenges associated with these catalysts: (i) the active sites require sulphiding agent to keep it catalytically active, which results to high cost of operations (ii) The excessive use of sulphiding agent (H_2S) contaminates the products and (iii) the unconverted sulphur gets oxidised to sulphur oxides (SO_2) and pollutes the environment [19,20]. The formation of sulphur containing intermediates as unwanted by-products during HDO reactions has also been reported [21, 22].

In order to obtained more effective catalysts, noble metal based-catalysts have gained interest as potential catalyst for HDO process [21,23]. The noble metal catalysts appeared to be more advantageous than sulphide catalyst since they do not require sulphiding agent for their activities to be maintained and, hence no product contamination is expected [14]. Additionally, they become more attractive because of their high hydrogenating ability to activate H_2 under mild conditions [13,14]. The potential activities of a number of noble metals such as Pt [21,24,25], Ru [24,26-28], Pd (21,24,29,30], and Rh [21,26,30] for HDO of bio-oil and its model compounds have been investigated. The outcome of their findings revealed that these catalysts are more catalyti active than the previously applied sulphide catalysts. For instance, Wildschutet et al. [31] compared Ru/C and CoMo/Al_2O_3 and also NiMo/Al_2O_3 catalysts for HDO of bio-oil in a batch reactor at mild (250 °C and 100 bar) and high (350 °C and 200 bar) reaction conditions. They reported that, the Ru/C catalyst gave higher catalytic performance both in terms of yield and degree of deoxygenation. However, the challenges of expensiveness and less availability make it difficult for commercial application. Additionally, noble metals are less resistant to coking and sintering which resulted to their rapid deactivations during HDO reactions [10,13,14].

In continuation of search for new, effective, and promising catalyst, non-noble transition metals have also been considered in the form of mono and bi-metallic catalysts because they are cheap and readily available. These non-noble metal catalysts tend to have superior advantages over noble metal catalysts. Many of mono-metallic catalysts such as Ni [32-34], Fe [35], Cu [32], and Co [33,35] have been explored for HDO reactions. The investigations revealed their activity for HDO reactions. Other non-noble metal based catalysts such as phosphides (Ni$_2$P, Co$_2$P, Fe$_2$P, WP Ni$_2$P, MoP and NiMoP) [30,34,36,37], carbides (Mo$_2$C and W$_2$C) and MoO$_3$ [37,38], metal nitrides (MoN and Mo$_2$N) [38,39] have been investigated for HDO reactions. Bimetallic non-noble metal-based catalysts such as Ni-Cu, Ni-Fe, Ni-La, Ni-Co, and Ni-W were also reported [40-43].

2.2 HDO Catalyst Support

The catalyst support (also known as carrier) is a key player in HDO reactions. Besides its function in dispersing and stabilizing the promoter and active phase of the catalyst, it also provides additional functional sites (Bronsted and Lewis acids) for deoxygenation reaction. Some supports also interact with the metal active phase thereby forming new active phase on the surface or at the active metal-support interface [44]. Al_2O_3 was initially considered as catalyst support for HDO of lignin derived bio-oil considering its high performance in HDS and hydrodenitrogenation (HDN) reactions [36]. However, the performance of Al_2O_3 in HDO reactions has been hindered by many factors: i.e., Al_2O_3 supports deactivate quickly due to presence of H_2O in bio-oil. As by-product of HDO, H_2O undergoes competitive adsorption on the Al_2O_3 active sites leading to its strong adsorption thereby preventing subsequent reactions from taking place [18]. Also, the presence of H_2O vapour causes recrystallization of Al_2O_3 to boehmites and partial oxidation of nickel sulphide to nickel oxide, which causes deactivation of the catalyst [13,45]. As an alternative to Al_2O_3, SiO_2 support has been investigated [32,46-49] for HDO reactions. The inner characteristics and small interactions of silica with supported active phase have been the main attracting features affiliated to silica supports [35,50]. Additionally, compared to Al_2O_3-based catalysts, SiO_2-based catalysts show superior advantages of higher selectivity and weaker interactions with oxygenated-compounds. During HDO reactions, the SiO_2 selectively interacts with oxygenated compounds via hydrogen-bonding and less affinity for aromatics compounds, thus making its stable for HDO reactions [18,30]. However, lack of acidity in SiO_2 was the main challenge with these supports since acidity is necessary for HDO reactions. Hence, transition metal oxides such as CeO_2, ZrO_2, TiO_2 and La_2O_3 were explored [6,51-53]. ZrO_2 has been reported to have high resistivity to coking due to amphoteric character. Moreover, ZrO_2 has been shown to possess good textural properties to strongly enhance adsorption and redox attributes of the supported catalyst [51,54,55]. TiO_2 has been shown to enable good dispersion of MoS_2 due to small crystallites, reducibility, favourable morphology as well as high activity in HDS reactions [55,56]. The HDO of guaiacol was investigated by Yakovlev [57] and Schimming [58] over CeO_2–ZrO_2 and CeO_2 as catalysts without active metal. The conclusion from these previous studies was that both CeO_2–ZrO_2 and CeO_2 possessed greater ability to activate H_2 and generate oxygen vacancies in a similar fashion to sulphide catalysts. The general explanation is that metal oxides such as TiO_2, ZrO_2 and CeO_2 possess suitable acidity to activate C=O bond during HDO reactions and the order of their acidity are TiO_2 > ZrO_2 > CeO_2 [9]. However, some of the drawbacks which tend to diminish their catalytic activity in HDO

reactions include their smaller surface area, lack of porosity and deactivation at high operating conditions.

In order to enhance surface area, acidity and provide porosity necessary for HDO reactions, microporous supports such as zeolites (Alumino-silicate) [9-64,65] and mesoporous based supports such as MCM-41, Ti-MCM-41 [4,66], SBA-15, Ti-SBA-15, Al-SBA-15 [7,60,67,68], Al-MCM-41 [8,69], KIT-6 and Ti-KIT-6 [7] have been evaluated. The textural properties and generated acidity greatly influenced the catalyst performance in terms of both activity and selectivity in HDO of bio-oil and its model compounds. A detailed discussion on the performance of mesoporous supports for HDO of bio-oil has been reviewed [2].

3. Synthesis of Nickel-Based Catalyst for HDO of Bio-oil

A suitable catalyst synthesis method and synthesis conditions are very crucial for the activity, selectivity, and stability of the catalyst system for HDO of bio-oil towards transportation fuels. With regards to synthesis of nickel-based catalysts, impregnation, precipitation, ion exchange and sol gel methods have been utilized [4-6, 70-74]. However, impregnation and precipitation are the most considered methods due to several advantages associated with them such as high reproducibility, simplicity and economical, as compared to other methods [70, 71, 74]. Impregnation methods are of two types: wet impregnation and dry impregnation. The wet impregnation involves contacting porous support with excess metal solution to be deposited into the pores through diffusion mechanism [71, 72, 75-77]. In the case of dry impregnation method, the volume of the metal solution used is equal to the pore volume of support, and metal deposition into the pores occurred mainly through capillary actions [5]. Studies revealed that a large number of mesoporous supported nickel-based catalysts have been prepared by impregnation methods [75, 78-81]. Therefore, the rest of this review is focused towards factors influencing good distribution and dispersion of active nickel species over mesoporous supports for improved catalytic activity during HDO of bio-oil.

3.1 Influence of Precursor-Support Interactions on Dispersion

The major goal of impregnation is to produce highly disperse and uniformly distributed Ni or Ni-based species on the external and internal surface of mesoporous supports, which has been found to be influenced by precursor-support interactions [74,76,77,81,82]. It has been shown experimentally that weak or moderate precursor-support interaction leads to better distribution and hence good dispersion of the supported nickel species [75,78,82]. It was reported that good distribution and dispersion of Nickel based supported catalyst was associated to weak interaction between the silica support and $[Ni(OH_2)_6]^{2+}$ complex in $Ni(NO_3)_2.6H_2O$ solution

[74,76]. Due to the weak precursor-support interaction, there was high migration of this complex into the pores, which led to homogenous distribution and consequently better dispersion [78]. However, when precursor-support interactions are high, there was slow mobility of this complex ions into the pores [75,78,82]. This was also demonstrated using $[Ni(NH_3)_6]^{2+}$ when it was used to introduce nickel species into porous silica support at high pH ($\approx$ 8). There was poor distribution of the resulting dispersion of the supported nickel-based catalyst due to strong interactions with silica support body [75,76,78]. It has also been found that the mobility of' the complex ions such as $[Ni(NH_3)_6]^{2+}$ and $[Ni(OH_2)_6]^{2+}$ during synthesis can be enhanced by adjusting the pH of the solution [73, 75]. This is because pH affects the distribution and dispersion of the resulting nickel-based supported catalysts [74,76,77,82]. Therefore, regulating the pH during preparation of nickel-based catalysts with various types of supports or nickel precursors could also be used to enhance the distribution and dispersion.

3.2 Influence of Drying Process on Dispersion

Drying process has been reported to affect the distribution of nickel precursors, which directly affect the dispersions of the resulting active Ni species [75,83,84]. During the drying process, solvent removal, temperature, and air flow rate significantly affect the redistribution of the supported nickel precursors, especially in the case of weak-precursor-support interaction [75,77]. High air flow rate during drying may lead to redistribution of Ni precursor species having weak interaction with the support. This has been demonstrated in a recent study by Sietsma *et al.* [75] who investigated the influence of drying on the distribution and dispersion of NiO supported catalyst using mesoporous SBA-15 as a model support. The authors reported that redistribution occurred because of high air flow rate during the drying processes.

Generally, the drying processes begins with solvent evaporation from the larger pores, with slight delay of that in the smaller pores at the periphery of support's body [75,82]. The evaporation of the solvent in the smaller pores is delayed due to additional solution received from the larger pores. The excess solution flowing may result to migration and accumulation of the complex precursors at the periphery of the support's body. Due to high concentration of complex precursors, there could be existence of back-diffusion of precursor complexes toward the centre of the support's body leading the formation of various isolated patches inside the mesopores, and hence redistribution and poor dispersion can occur inside and outside of the mesopores [75,83-85]. However, redistribution of nickel precursors has been reported to be minimal with strong precursor-support interactions, particularly with moderate air flow rate.

Drying temperature should be controlled in a way to avoid rigorous evaporation and to allow gentle loss of

evaporating solvent in order to ensure better mechanical properties and to prevent sintering of the supported NiO during activation process [75,82]. Therefore, preferable temperature should be below the boiling point of evaporating solvents and the air flow rate during drying should be moderate [75,78,86].

3.3 Influence of Activation on Dispersion

The redistribution of complex precursors and dispersion of the final active metal phase could also be affected by the activation processes (calcination and reduction). The major factors affecting redistribution and sintering during activation process include the type of gaseous environment, temperature and porosity of the mesoporous support [75,82,86]. With regards to gaseous environment, the rate of sintering of nickel species based on supported catalyst decreases with gaseous environment as follows: $NO > O_2 > H_2 > N_2$. The redistribution and sintering of NiO species were observed to occur during calcination in air [75,86]. It was further revealed that the degree of sintering of NiO species at the interior and exterior of the mesopores increased with formation of NO_2 species and O_2 from decomposition of the complex species $((Ni_3(NO_3)_2(OH)_4))$ of Ni precursor during thermal treatment [86]. However, water vapour was observed to control migration and particles growth of NiO species during decomposition of $Ni_3(NO_3)_2(OH)_4$. Further studies on redistribution and sintering control found that the presence of H_2 or NO during decomposition of $Ni_3(NO_3)_2(OH)_4$ could inhibit the formation of NO_2 and O_2, which resulted into the formation of water vapour and thus preventing redistribution and sintering of the active NiO species during thermal treatment [75,78,86].

The temperature of activation affects redistribution and particle growth. In general redistribution and migration as well as particle growth of the active nickel species can be promoted at high temperature. Lowering the activation temperature of nickel-based catalysts can be achieved with the use of promoters such as Cu metal during the synthesis processes [4,6,75,87]. Pore size in porous supports may significantly decreases the rate of sintering of nickel-based catalysts, particularly when the active nickel species growth approaches the pore diameter [88]. In another study, it was revealed that to obtain good dispersion and small particles size of the supported nickel-based catalyst, porous supports with high surface area such as mesoporous silica (MCM-41, SBA-15, KIT-6 etc.) and an atmosphere containing hydrogen (e.g., 5% H_2/He) should be employed [75,78,86]. Therefore, good dispersion of nickel species could be obtained using appropriate gaseous environment, moderate temperature, and porosity.

4. Conclusion

Based on the literatures reviewed, it can be concluded that metallic sites promote hydrogenation while acidic sites play an important role in deoxygenation. It has been found that good catalyst promoters greatly improve catalyst performance in terms of activity, selectivity, and stability during HDO of bio-oil. Also, good performing catalytic materials, which are less expensive such as noble metals, could greatly enhance economical value of the HDO reactions. Therefore, less expensive catalyst composition, with active metallic and acidic sites as well as a suitable promoter are the required catalyst composition for HDO of bio-oil to transportation fuels with moderate metal-support interaction, suitable gaseous environment such as H_2/He mixture, moderate drying and activation temperature and appropriate porosity of porous supports during catalyst synthesis by impregnation, could yield highly disperse nickel-based catalysts for HDO of bio-oil.

References

1. Saidi M, Samimi F, Karimipourfard D, Nimmanwudipong T, Gates BC, Rahimpour MR. Upgrading of lignin-derived bio-oils by catalytic hydrodeoxygenation. Energy & Environmental Science. 2014;7(1):103-29.
2. Li X, Chen G, Liu C, Ma W, Yan B, Zhang J. Hydrodeoxygenation of lignin-derived bio-oil using molecular sieves supported metal catalysts: A critical review. Renewable and Sustainable Energy Reviews. 2017;71:296-308.
3. Abd Hamid S, Ambursa MM, Sudarsanam P, Voon LH, Bhargava SK. Effect of Ti loading on structure-activity properties of Cu-Ni/Ti-MCM-41 catalysts in hydrodeoxygenation of guaiacol. Catalysis Communications. 2017;94:18-22.
4. Ambursa MM, Sudarsanam P, Voon LH, Hamid SBA, Bhargava SK. Bimetallic Cu-Ni catalysts supported on MCM-41 and Ti-MCM-41 porous materials for hydrodeoxygenation of lignin model compound into transportation fuels. Fuel Processing Technology. 2017;162:87-97.
5. Lup ANK, Abnisa F, Daud WMAW, Aroua MK. A review on reactivity and stability of heterogeneous metal catalysts for deoxygenation of bio-oil model compounds. Journal of Industrial and Engineering Chemistry. 2017;56:1-34.
6. Ambursa MM, Ali TH, Lee HV, Sudarsanam P, Bhargava SK, Hamid SBA. Hydrodeoxygenation of dibenzofuran to bicyclic hydrocarbons using bimetallic Cu–Ni catalysts supported on metal oxides. Fuel. 2016;180:767-76.
7. Selvaraj M, Shanthi K, Maheswari R, Ramanathan A. Hydrodeoxygenation of guaiacol over MoO3-NiO/mesoporous silicates: Effect of incorporated heteroatom. Energy & Fuels. 2014;28(4):2598-607.
8. Tran NT, Uemura Y, Ramli A. Hydrodeoxygenation of guaiacol over Al-MCM-41 supported metal catalysts: A comparative study of Co and Ni. Procedia Engineering. 2016;148:1252-8.

9. Zanuttini M, Peralta M, Querini C. Deoxygenation of m-Cresol: Deactivation and Regeneration of Pt/γ-Al$_2$O$_3$ Catalysts. Industrial & Engineering Chemistry Research. 2015;54(18):4929-39.

10. He Z, Wang X. Hydrodeoxygenation of model compounds and catalytic systems for pyrolysis bio-oils upgrading. Catalysis for sustainable energy. 2012;1:28-52.

11. Gutierrez A, Turpeinen E-M, Viljava T-R, Krause O. Hydrodeoxygenation of model compounds on sulfided CoMo/γ-Al$_2$O$_3$ and NiMo/γ-Al$_2$O$_3$ catalysts; Role of sulfur-containing groups in reaction networks. Catalysis Today. 2017;285:125-34.

12. Mortensen PM, Gardini D, Damsgaard CD, Grunwaldt J-D, Jensen PA, Wagner JB, et al. Deactivation of Ni-MoS$_2$ by bio-oil impurities during hydrodeoxygenation of phenol and octanol. Applied Catalysis A: General. 2016;523:159-70.

13. Honkela ML, Viljava T-R, Gutierrez A, Krause AOI. Hydrotreating for bio-oil upgrading. Thermochemical Conversion of Biomass to Liquid Fuels and Chemicals 2010. p. 288-306.

14. Ruddy DA, Schaidle JA, Ferrell III JR, Wang J, Moens L, Hensley JE. Recent advances in heterogeneous catalysts for bio-oil upgrading via "ex situ catalytic fast pyrolysis": catalyst development through the study of model compounds. Green Chemistry. 2014;16(2):454-90.

15. Tropsoe H, Clausen B, Massoth F. Hydro treating catalysis: Science and Technology. Berlin; 1996.

16. Badawi M, Paul J-F, Payen E, Romero Y, Richard F, Brunet S, et al. Hydrodeoxygenation of Phenolic Compounds by Sulfided (Co) Mo/Al2O3 Catalysts, a Combined Experimental and Theoretical Study. Oil & Gas Science and Technology–Revue d'IFP Energies nouvelles. 2013;68(5):829-40.

17. Romero Y, Richard F, Brunet S. Hydrodeoxygenation of 2-ethylphenol as a model compound of bio-crude over sulfided Mo-based catalysts: promoting effect and reaction mechanism. Applied Catalysis B: Environmental. 2010;98(3):213-23.

18. Popov A, Kondratieva E, Goupil JM, Mariey L, Bazin P, Gilson J-P, et al. Bio-oils hydrodeoxygenation: adsorption of phenolic molecules on oxidic catalyst supports. The Journal of Physical Chemistry C. 2010;114(37):15661-70.

19. Furimsky E. Catalytic hydrodeoxygenation. Applied Catalysis A: General. 2000;199(2):147-90.

20. Viljava T-R, Komulainen R, Krause A. Effect of H$_2$S on the stability of CoMo/Al$_2$O$_3$ catalysts during hydrodeoxygenation. Catalysis Today. 2000;60(1):83-92.

21. Gutierrez A, Kaila R, Honkela M, Slioor R, Krause A. Hydrodeoxygenation of guaiacol on noble metal catalysts. Catalysis Today. 2009;147(3):239-46.

22. Şenol O, Ryymin E-M, Viljava T-R, Krause A. Effect of hydrogen sulphide on the hydrodeoxygenation of aromatic and aliphatic oxygenates on sulphided catalysts. Journal of Molecular Catalysis A: Chemical. 2007;277(1):107-12.

23. Lin Y-C, Li C-L, Wan H-P, Lee H-T, Liu C-F. Catalytic hydrodeoxygenation of guaiacol on Rh-based and sulfided CoMo and NiMo catalysts. Energy & Fuels. 2011;25(3):890-6.

24. Wang L, Li C, Jin S, Li W, Liang C. Hydrodeoxygenation of dibenzofuran over SBA-15 supported Pt, Pd, and Ru catalysts. Catalysis letters. 2014;144(5):809-16.

25. Wang L, Wan H, Jin S, Chen X, Li C, Liang C. Hydrodeoxygenation of dibenzofuran over SiO$_2$, Al$_2$O$_3$/SiO$_2$ and ZrO$_2$/SiO$_2$ supported Pt catalysts. Catalysis Science & Technology. 2015;5(1):465-74.

26. Lee CR, Yoon JS, Suh Y-W, Choi J-W, Ha J-M, Suh DJ, et al. Catalytic roles of metals and supports on hydrodeoxygenation of lignin monomer guaiacol. Catalysis Communications. 2012;17:54-8.

27. Zhang W, Chen J, Liu R, Wang S, Chen L, Li K. Hydrodeoxygenation of lignin-derived phenolic monomers and dimers to alkane fuels over bifunctional zeolite-supported metal catalysts. ACS Sustainable Chemistry & Engineering. 2014;2(4):683-91.

28. Zhou X-F. Conversion of kraft lignin under hydrothermal conditions. Bioresource technology. 2014;170:583-6.

29. Hong Y-K, Lee D-W, Eom H-J, Lee K-Y. The catalytic activity of Pd/WO x/γ-Al$_2$O$_3$ for hydrodeoxygenation of guaiacol. Applied Catalysis B: Environmental. 2014;150:438-45.

30. Zhao C, He J, Lemonidou AA, Li X, Lercher JA. Aqueous-phase hydrodeoxygenation of bio-derived phenols to cycloalkanes. Journal of Catalysis. 2011;280(1):8-16.

31. Wildschut J, Mahfud FH, Venderbosch RH, Heeres HJ. Hydrotreatment of fast pyrolysis oil using heterogeneous noble-metal catalysts. Industrial & Engineering Chemistry Research. 2009;48(23):10324-34.

32. Bykova M, Ermakov DY, Khromova S, Smirnov A, Lebedev MY, Yakovlev V. Stabilized Ni-based catalysts for bio-oil hydrotreatment: Reactivity studies using guaiacol. Catalysis Today. 2014;220:21-31.

33. Sankaranarayanan S, Shankar VH, Jayalakshmi S, Bau NQ, Gupta M. Development of high performance magnesium composites using Ni$_{50}$Ti$_{50}$ metallic glass reinforcement and microwave sintering approach. Journal of Alloys and Compounds. 2015;627:192-9.

34. Yang Y, Ochoa-Hernández C, Víctor A, Pizarro P, Coronado JM, Serrano DP. Effect of metal–support interaction on the selective hydrodeoxygenation of anisole to aromatics over Ni-based catalysts. Applied Catalysis B: Environmental. 2014;145:91-100.

35. Olcese R, Bettahar M, Petitjean D, Malaman B, Giovanella F, Dufour A. Gas-phase hydrodeoxygenation of guaiacol over Fe/SiO$_2$ catalyst. Applied Catalysis B: Environmental. 2012;115:63-73.

36. Li K, Wang R, Chen J. Hydrodeoxygenation of anisole over silica-supported Ni2P, MoP, and NiMoP catalysts. Energy & Fuels. 2011;25(3):854-63.

37. Whiffen VM, Smith KJ. Hydrodeoxygenation of 4-Methylphenol over Unsupported MoP, MoS$_2$, and MoO$_x$ Catalysts†. Energy & Fuels. 2010;24(9):4728-37.

38. Santillan-Jimenez E, Perdu M, Pace R, Morgan T, Crocker M. Activated carbon, carbon nanofiber and carbon nanotube supported molybdenum carbide catalysts for the hydrodeoxygenation of guaiacol. Catalysts. 2015;5(1):424-41.

39. Ghampson IT, Sepúlveda C, Garcia R, Radovic LR, Fierro JG, DeSisto WJ, et al. Hydrodeoxygenation of guaiacol over carbon-supported molybdenum nitride catalysts: Effects of nitriding methods and support properties. Applied Catalysis A: General. 2012;439:111-24.

40. Yang Y-n, Zhang H-k, En-jing L, Zhang C-h, Ren J. Effect of Fe, Mo promoters on acetic acid hydrodeoxygenation performance of nickel-based catalyst. Journal of Molecular Catalysis (China). 2011;25:30-6.

41. Bykova M, Ermakov DY, Kaichev V, Bulavchenko O, Saraev A, Lebedev MY, et al. Ni-based sol–gel catalysts as promising systems for crude bio-oil upgrading: Guaiacol hydrodeoxygenation study. Applied Catalysis B: Environmental. 2012;113:296-307.

42. Wang J. Carbon-nanotube based electrochemical biosensors: A review. Electroanalysis. 2005;17(1):7-14.

43. Echeandia S, Arias P, Barrio V, Pawelec B, Fierro J. Synergy effect in the HDO of phenol over Ni–W catalysts supported on active carbon: Effect of tungsten precursors. Applied Catalysis B: Environmental. 2010;101(1):1-12.

44. Stakheev AY, Kustov L. Effects of the support on the morphology and electronic properties of supported metal clusters: modern concepts and progress in 1990s. Applied Catalysis A: General. 1999;188(1):3-35.

45. Bu Q, Lei H, Zacher AH, Wang L, Ren S, Liang J, et al. A review of catalytic hydrodeoxygenation of lignin-derived phenols from biomass pyrolysis. Bioresource technology. 2012;124:470-7.

46. Wang L, Ye P, Yuan F, Li S, Ye Z. Liquid phase in-situ hydrodeoxygenation of bio-derived phenol over Raney Ni and Nafion/SiO$_2$. International Journal of Hydrogen Energy. 2015;40(43):14790-7.

47. Berenguer A, Sankaranarayanan T, Gómez G, Moreno I, Coronado J, Pizarro P, et al. Evaluation of transition metal phosphides supported on ordered mesoporous materials as catalysts for phenol hydrodeoxygenation. Green Chemistry. 2016;18(7):1938-51.

48. Bykova M, Bulavchenko O, Ermakov DY, Lebedev MY, Yakovlev V, Parmon V. Guaiacol hydrodeoxygenation in the presence of Ni-containing catalysts. Catalysis in Industry. 2011;3(1):15-22.

49. Zhang X, Tang W, Zhang Q, Wang T, Ma L. Hydrodeoxygenation of lignin-derived phenoic compounds to hydrocarbon fuel over supported Ni-based catalysts. Applied Energy. 2017.

50. Jasik A, Wojcieszak R, Monteverdi S, Ziolek M, Bettahar M. Study of nickel catalysts supported on Al$_2$O$_3$, SiO$_2$ or Nb$_2$O$_5$ oxides. Journal of Molecular Catalysis A: Chemical. 2005;242(1):81-90.

51. Zhang X, Zhang Q, Wang T, Ma L, Yu Y, Chen L. Hydrodeoxygenation of lignin-derived phenolic compounds to hydrocarbons over Ni/SiO$_2$–ZrO$_2$ catalysts. Bioresource technology. 2013;134:73-80.

52. Valdés-Martínez O, Suárez-Toriello V, de los Reyes J, Pawelec B, Fierro J. Support effect and metals interactions for NiRu/Al$_2$O$_3$, TiO$_2$ and ZrO$_2$ catalysts in the hydrodeoxygenation of phenol. Catalysis Today. 2017;296:219-227.

53. Wu S-K, Lai P-C, Lin Y-C, Wan H-P, Lee H-T, Chang Y-H. Atmospheric hydrodeoxygenation of guaiacol over alumina-, zirconia-, and silica-supported nickel phosphide catalysts. ACS Sustainable Chemistry & Engineering. 2013;1(3):349-58.

54. Ardiyanti A, Gutierrez A, Honkela M, Krause A, Heeres H. Hydrotreatment of wood-based pyrolysis oil using zirconia-supported mono-and bimetallic (Pt, Pd, Rh) catalysts. Applied Catalysis A: General. 2011;407(1):56-66.

55. Bui VN, Laurenti D, Afanasiev P, Geantet C. Hydrodeoxygenation of guaiacol with CoMo catalysts. Part I: Promoting effect of cobalt on HDO selectivity and activity. Applied Catalysis B: Environmental. 2011;101(3):239-45.

56. Breysse M, Portefaix J, Vrinat M. Support effects on hydrotreating catalysts. Catalysis today. 1991;10(4):489-505.

57. Yakovlev V, Khromova S, Sherstyuk O, Dundich V, Ermakov DY, Novopashina V, et al. Development of new catalytic systems for upgraded bio-fuels production from bio-crude-oil and biodiesel. Catalysis Today. 2009;144(3):362-6.

58. Schimming SM, LaMont OD, König M, Rogers AK, D'Amico AD, Yung MM, et al.

Hydrodeoxygenation of Guaiacol over Ceria–Zirconia Catalysts. ChemSusChem. 2015;8(12):2073-83.

59. Feng J, Hse C-y, Wang K, Yang Z, Jiang J, Xu J. Directional liquefaction of biomass for phenolic compounds and in situ hydrodeoxygenation upgrading of phenolics using bifunctional catalysts. Energy. 2017; 135:1-13.

60. Sankaranarayanan TM, Berenguer A, Ochoa-Hernández C, Moreno I, Jana P, Coronado JM, et al. Hydrodeoxygenation of anisole as bio-oil model compound over supported Ni and Co catalysts: Effect of metal and support properties. Catalysis Today. 2015;243:163-72.

61. Gamliel DP, Baillie BP, Augustine E, Hall J, Bollas GM, Valla JA. Nickel impregnated mesoporous USY zeolites for hydrodeoxygenation of anisole. Microporous and Mesoporous Materials. 2017;261:18-28.

62. Zhang X, Wang T, Ma L, Zhang Q, Jiang T. Hydrotreatment of bio-oil over Ni-based catalyst. Bioresource technology. 2013;127:306-11.

63. Shafaghat H, Rezaei PS, Daud WMAW. Catalytic hydrodeoxygenation of simulated phenolic bio-oil to cycloalkanes and aromatic hydrocarbons over bifunctional metal/acid catalysts of Ni/HBeta, Fe/HBeta and NiFe/HBeta. Journal of Industrial and Engineering Chemistry. 2016;35:268-76.

64. Berenguer A, Bennett JA, Hunns J, Moreno I, Coronado JM, Lee AF, et al. Catalytic hydrodeoxygenation of m-cresol over Ni2P/hierarchical ZSM-5. Catalysis Today. 2017.

65. Song W, Liu Y, Baráth E, Zhao C, Lercher JA. Synergistic effects of Ni and acid sites for hydrogenation and C–O bond cleavage of substituted phenols. Green Chemistry. 2015;17(2):1204-18.

66. Hamid SA, Ambursa MM, Sudarsanam P, Voon LH, Bhargava SK. Effect of Ti loading on structure-activity properties of Cu-Ni/Ti-MCM-41 catalysts in hydrodeoxygenation of guaiacol. Catalysis Communications. 2017;94:18-22.

67. Hsu P-J, Lin Y-C. Hydrodeoxygenation of 4-methylguaiacol over silica-supported nickel phosphide catalysts: The particle size effect. Journal of the Taiwan Institute of Chemical Engineers. 2017;79:80-87.

68. Yao Y, Goodman DW. Direct evidence of hydrogen spillover from Ni to Cu on Ni–Cu bimetallic catalysts. Journal of Molecular Catalysis A: Chemical. 2014;383:239-42.

69. Tran TTN, Uemura Y, Ramli A. Hydrodeoxygenation of Guaiacol over Al-MCM-41 Supported Metal Catalysts: A Comparative Study of Co and Ni. Procedia Enginering. 2016;148: 1252-1258

70. Prasad R, Singh P. Applications and preparation methods of copper chromite catalysts: a review. Bulletin of Chemical Reaction Engineering & Catalysis. 2011;6(2):63-113.

71. Srivastava D, Perkas N, Seisenbaeva G, Koltypin Y, Kessler V, Gedanken A. Preparation of porous cobalt and nickel oxides from corresponding alkoxides using a sonochemical technique and its application as a catalyst in the oxidation of hydrocarbons. Ultrasonics Sonochemistry. 2003;10(1):1-9.

72. Sreethawong T, Suzuki Y, Yoshikawa S. Photocatalytic evolution of hydrogen over mesoporous TiO_2 supported NiO photocatalyst prepared by single-step sol–gel process with surfactant template. International journal of hydrogen energy. 2005;30(10):1053-62.

73. Smirnov A, Khromova S, Ermakov DY, Bulavchenko O, Saraev A, Aleksandrov P, et al. The composition of Ni-Mo phases obtained by $NiMoOx-SiO_2$ reduction and their catalytic properties in anisole hydrogenation. Applied Catalysis A: General. 2016;514:224-34.

74. Friedrich H, Sietsma JR, de Jongh PE, Verkleij AJ, de Jong KP. Measuring location, size, distribution, and loading of NiO crystallites in individual SBA-15 pores by electron tomography. Journal of the American Chemical Society. 2007;129(33):10249-54.

75. Sietsma JR, Meeldijk JD, Versluijs-Helder M, Broersma A, Dillen AJv, de Jongh PE, et al. Ordered mesoporous silica to study the preparation of Ni/SiO_2 ex nitrate catalysts: Impregnation, drying, and thermal treatments. Chemistry of materials. 2008;20(9):2921-31.

76. Qiu S, Zhang X, Liu Q, Wang T, Zhang Q, Ma L. A simple method to prepare highly active and dispersed Ni/MCM-41 catalysts by co-impregnation. Catalysis Communications. 2013;42:73-8.

77. Cho YS, Park JC, Lee B, Kim Y, Yi J. Preparation of mesoporous catalyst supported on silica with finely dispersed Ni particles. Catalysis letters. 2002;81(1-2):89-96.

78. Sietsma JR, Meeldijk JD, den Breejen JP, Versluijs-Helder M, Van Dillen AJ, de Jongh PE, et al. The preparation of supported NiO and Co_3O_4 nanoparticles by the nitric oxide controlled thermal decomposition of nitrates. Angewandte Chemie. 2007;119(24):4631-3.

79. Chmielarz L, Kuśtrowski P, Dziembaj R, Cool P, Vansant E. Catalytic performance of various mesoporous silicas modified with copper or iron oxides introduced by different ways in the selective reduction of NO by ammonia. Applied Catalysis B: Environmental. 2006;62(3):369-80.

80. Okamura J, Nishiyama S, Tsuruya S, Masai M. Formation of Cu-supported mesoporous silicates and aluminosilicates and liquid-phase oxidation of benzene catalyzed by the Cu-mesoporous silicates and aluminosilicates. Journal of Molecular Catalysis A: Chemical. 1998;135(2):133-42.

81. Wang Y, Noguchi M, Takahashi Y, Ohtsuka Y. Synthesis of SBA-15 with different pore sizes and

the utilization as supports of high loading of cobalt catalysts. Catalysis Today. 2001;68(1):3-9.

82. Sietsma JR, van Dillen AJ, de Jongh PE, de Jong KP. Application of ordered mesoporous materials as model supports to study catalyst preparation by impregnation and drying. Studies in surface science and catalysis. 2006;162:95-102.

83. Van Dillen AJ, Terörde RJ, Lensveld DJ, Geus JW, De Jong KP. Synthesis of supported catalysts by impregnation and drying using aqueous chelated metal complexes. Journal of Catalysis. 2003;216(1):257-64.

84. Espinosa-Alonso L, de Jong KP, Weckhuysen BM. Effect of the Nickel Precursor on the Impregnation and Drying of γ-Al$_2$O$_3$ Catalyst Bodies: A UV− vis and IR Microspectroscopic Study. The Journal of Physical Chemistry C. 2008;112(18):7201-9.

85. Lekhal A, Glasser BJ, Khinast JG. Impact of drying on the catalyst profile in supported impregnation catalysts. Chemical Engineering Science. 2001;56(15):4473-87.

86. Sietsma JR, Friedrich H, Broersma A, Versluijs-Helder M, Van Dillen AJ, de Jongh PE, et al. How nitric oxide affects the decomposition of supported nickel nitrate to arrive at highly dispersed catalysts. Journal of catalysis. 2008;260(2):227-35.

87. Dongil A, Bachiller-Baeza B, Rodriguez-Ramos I, Fierro J, Escalona N. The effect of Cu loading on Ni/carbon nanotubes catalysts for hydrodeoxygenation of guaiacol. RSC Advances. 2016;6(32):26658-67.

88. Argyle MD, Bartholomew CH. Heterogeneous catalyst deactivation and regeneration: a review. Catalysts. 2015;5(1):145-269.