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In situ hydrodeoxygenation of guaiacol using magnetic catalysts and heterogeneous hydrogen producer

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This research aims to figure out the effect of nickel, cobalt, iron powders and alumina-supported nickel catalyst on the hydrodeoxygenation (HDO) of guaiacol using zero-valent Zn as heterogenous hydrogen producer. The HDO tests are conducted at hydrothermal conditions in a batch micro reactor using equal amount of Zn and guaiacol feedstock, water to guaiacol ratio of 10, and catalyst load of 40 and 20 wt.% for metal powders and supported catalyst, respectively, with respect to the mass of guaiacol. Reaction time and temperature were set at 60 min and 300 ºC. The fresh and exhausted supported catalysts were characterized by the XRD and SEM-EDX analyses. Among the tested commercial metal powders, Ni has the highest guaiacol conversion rate 51.3%, significantly higher than 11.8% of Fe and 20.0% of Co. Compared with metal powders, the alumina-supported nickel catalyst showed superior performance in terms of high conversion rate of 99.3% and high hydrodeoxygenation (HDO) and hydrodearomatization (HDA) efficiencies.

1. Introduction

Searching for renewable and sustainable fossil fuel alternatives has been increasingly critical in recent years since the explosion of energy demand and environmental concerns (Nurariffudin, Hashim & Tin, 2018; Poolsawat & Wongsapai, 2018; Guan et al., 2020). Bio-oil as a product obtained from the thermochemical treatments of lignocellulosic biomass is drawing more attention due to the worldwide availability and carbon neutral properties of biomass (de Caprariis et al., 2020; Scarsella et al., 2020). However, the straight utilization of crude bio-oil in the current engineering infrastructures still faces some challenges. The presence of high oxygen content compounds like phenols, acids, ketones and aldehydes results in the corrosive, low heating value and thermal instability properties of the crude bio-oil which restrains its implementation. Therefore, the upgrading process is needed to improve the quality of bio-oil approaching the properties of commercial diesel product. Hydrodeoxygenation (HDO) process is a promising upgrading technique typically conducted at mild temperature (200-400 °C) with high pressure hydrogen gas (1-15 MPa) in which oxygen atom is removed as water. The preparation of high efficiency catalyst and exploitation of economic hydrogen source are two hot research topics about HDO technique. Guaiacol as an informative model compound due to its multiple functional groups (methoxy group and phenol) is widely adopted in the HDO reactions. However, most previous guaiacol HDO studies used organic solvent and high hydrogen pressure causing potential environmental and security risk (Mao et al., 2017; Feitosa et al., 2019; Gutiérrez-Rubio et al., 2020; Xu et al., 2020). Zero-valent metals like Zn, Al and Mn are readily oxidized by water at hydrothermal conditions and can generate hydrogen in situ (Yavor et al., 2015), besides that subcritical water due to its low dielectric constant is a good green solvent for organic reactions. Therefore, using water as solvent combined with metal-water redox reaction as hydrogen source is a promising technique for bio-oil HDO. Since now, the hydrothermal technique was mainly adopted in the bio-crude production from various biomass materials such as agricultural and forestry wastes. The use of hydrothermal technique to the upgrading process of bio-fuel is of great significances, making possible the coupling of the two processes in a single device: the bio-oil production and its upgrading. Additionally, the utilization of magnetic metal catalysts ensures easily separation of exhausted catalyst from the metal oxides solid residues. Magnetic elements such as Fe, Ni and Co are commonly used as active sites in the HDO reaction of guaiacol (Blanco et al., 2020; Li et al., 2020; Xu et al., 2020). However, few researchers investigated guaiacol HDO reactions with synthesized magnetic catalyst and heterogeneous hydrogen producer. In this research, first the selection of suitable active catalyst was conducted by adopting Ni, Fe and Co commercial metal powders as catalysts with the in situ hydrogen generated from zinc-water redox reaction. Then high-efficiency Ni supported Al_2O_3 catalyst was prepared. The possible reaction pathway was also proposed. All the tests were done in a micro batch reactor.

2. Materials and methods

2.1 Materials

Fe (purity > 99.5%; particle size < 10 μm), Ni (purity > 99.9%; particle size < 7 μm), Co (purity > 99.8%; particle size < 2 μm), Zn (purity > 99.9%; particle size < 10 μm), nickel (II) nitrate hexahydrate, guaiacol and ethyl acetate were purchased from Sigma-Aldrich. γ-Al_2O_3 was provided from Merck. All the materials were used as received.

2.2 Catalyst preparation and characterization

The Ni/Al_2O_3 catalyst with 20 wt% Ni loading was prepared by wet impregnation method. A certain amount of $Ni(NO_3)_2.6H_2O$ and Al_2O_3 was added in 50 ml deionized water. The resulted suspension was stirred for 4 h and then dried overnight at 100 °C. Then, the obtained powder was calcinated at 550 °C for 4 h in the air atmosphere. Prior to the HDO reaction, the catalyst was reduced ex-situ at 550 ºC for 4 h under hydrogen and nitrogen flows. The prepared Ni/Al_2O_3 catalyst was characterized by X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM) along with Energy Dispersive X-Ray (SEM-EDX) analyses. The XRD patterns were obtained with a Philips X'Pert X-ray device (PANalytical B.V., The Nedeands) operating at 40KV and 40mA with CuKα1 radiation. The samples were scanned with a scan range of 0°-90°, step size of 0.02° and counting time of 2 s. The micrographs were obtained with a FE-SEM Tescan Mira-3 with the SE detector at 15keV in order to observe the morphology of the zeolite powders. Also EDX analysis were performed to identify the elements present in the powders. Before the observations, zeolites were graphitized in order to obtain conductive samples.

2.3 Catalytic Hydrodeoxygenation of Guaiacol

In a typical test, 0.5 g guaiacol, 0.5 g Zn powder, 5 g water and 0.2 g commercial Ni, Fe and Co powder catalyst or 0.1 g synthesized catalyst were fed in a 10 ml stainless steel micro batch reactor. After purged with N_2 for 3 times to displace air, the sealed reactor was fixed in a shaft connected on a mechanical stirrer, then was immersed in a sand bath preheated to 300 °C. The mean heating rate was 60 °C/min. Once the set temperature was reached, the reactor was maintained for 60 min reaction time with 130 rpm stirring velocity. Finally, the reactor was taken out from the sand bath and rapidly quenched in cold water. After cooled down to ambient temperature, the reactor was opened and the gas product was released. Then 2 g of ethyl acetate was introduced in the reactor to extract the organic chemicals. The reactor was vigorously shaken for at least 2 minutes to ensure a good extraction effect. The crude products were transferred from micro reactor to a centrifugal tube. After centrifugation (5000 rpm, 5 min), three phases were separated, the upper phase is ethyl acetate solution with a majority of organic products, the middle phase is an aqueous solution including some polar compounds, and the bottom phase is sediment containing exhausted catalyst, metal oxides and small amount of coke. The qualitative and quantitative analyses of liquid products in ethyl acetate phase and aqueous phase were respectively conducted on a gas chromatograph with mass spectrometer detector (GC-MS) and a gas chromatograph with flame ionization detector (GC-FID). Isobutanol and undecane were adopted as internal references in the aqueous product and ethyl acetate phase product, respectively. Finally, the organic substances in these two parts were aggregated, the molar balance of identified products was closed at 95-100% in all the tests. The guaiacol conversion rate, product yield and selectivity, hydrodeoxygenation (HDO) and hydrodearomatization (HDA) efficiencies were calculated according to the following formulas:

$$X_{gua}(\%) = \frac{n_{gua}^0 - n_{gua}}{n_{gua}^0} \times 100\% \tag{1}$$

$$Y_i(\%) = \frac{n_i}{n_{gua}^0} \times 100\% \tag{2}$$

$$S_i(\%) = \frac{n_i}{n_{gua}^0 - n_{gua}} \times 100\% \tag{3}$$

$$HDO(\%) = \frac{2 \times (n_{gua}^{0} - n_{gua}) - \sum n_i b_i}{2 \times n_{gua}^{0}} \times 100\% \qquad (4)$$

$$HDA(\%) = \frac{n_{gua}^{0} - n_{gua} - \sum n_i c_i}{n_{gua}^{0}} \times 100\% \qquad (5)$$

Where n_{gua}^{0} and n_{gua} are initial and final moles of guaiacol, n_i is the moles of product i in the final mixture, b_i and c_i are the number of oxygen atoms and aromatic rings per molecule of product i.

The recovery ability of synthesized Ni/Al_2O_3 magnetic catalyst was also tested. After centrifugation, the solid residue was washed with acetone for two times to totally remove the organic substance. Then a magnet was used to separate the magnetic exhausted catalyst from the solid residue suspension in acetone under ultrasonic bath. Finally, the separated exhausted catalyst was dried in the oven at 80 °C.

3. Results and discussion

3.1 Catalysts characterization

The X-ray powder diffraction spectrum of fresh and exhausted Ni/Al_2O_3 catalysts is displayed in Figure 1. The peaks at 2θ degree of 37.4, 43.38 and 63.02° are belonged to the γ-Al_2O_3. The peaks at 44.5, 51.8 and 76° are attributed to the crystalline phase of Ni (JCPDS no. 00-004-0850). The peaks at 37.3, 43.38 and 63.02 are assigned to the NiO (JCPDS no. 01-073-1519). Also, the reflection peaks at 2θ= 31.7, 34.4, 47.53, 56.6 and 62.8° are attributed to the ZnO (JCPDS no. 00-036-1451). The results indicated that the deposited nickel on the alumina surface is well crystallized, and the presence of ZnO in the spectrum of the exhausted sample confirms that the catalyst is not completely separated from Zn after the recovery.

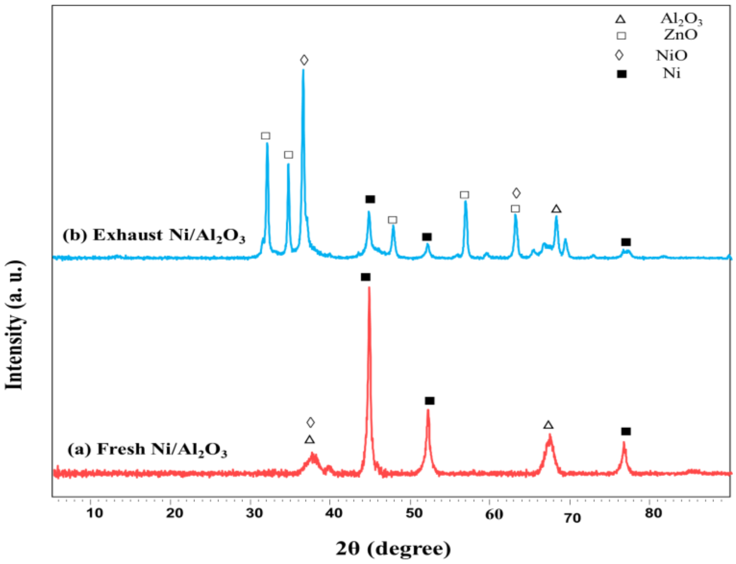

Figure 1: XRD patterns of fresh and exhausted Ni/Al_2O_3 catalyst

The morphology of the nickel supported catalyst along with EDX analysis before and after HDO reaction is shown in Figure 2. Similar to the observation of Kiyohara (Kiyohara et al., 2000) on the alumina morphology, the particles of alumina powder are composed of agglomerates of platy crystals. As seen, in the fresh catalyst, the distribution of nickel particles on the alumina support is almost uniform, while some large blocks and aggregation of spherical shapes were observed in the morphology of the catalyst after the reaction. The presence of all elements (Ni, Al and O) is confirmed by the EDX analysis. Compared with fresh catalyst, two other elements (Zn and C) exist in the EDX spectrum of the exhausted sample. The presence of zinc is attributed to the incomplete separation of catalyst from the solid residue after the reaction, which was also confirmed by XRD analysis. The presence of C is related to the coke deposition on the catalyst surface during the reaction. Since the inevitable impurity of Zn and coke in the recycled catalyst, in the industrial application, partial addition of fresh catalyst to the reused one will be of benefit to maintain stable catalytic performance.

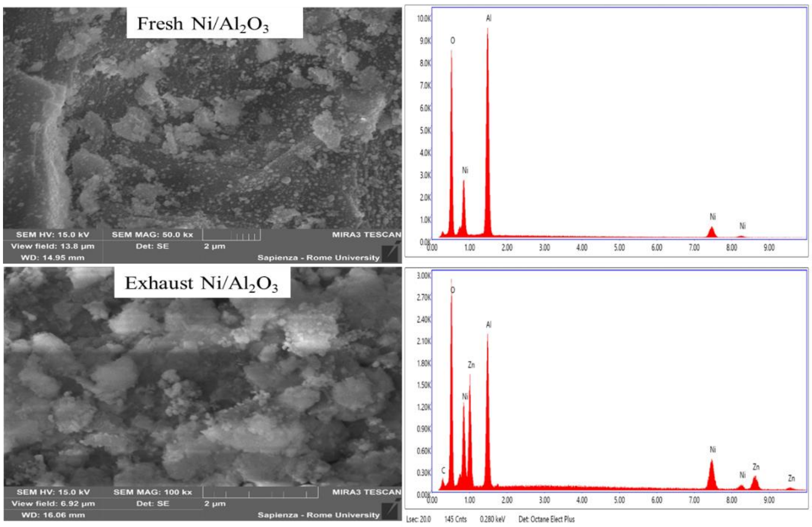

Figure 2: SEM-EDX analysis of fresh and exhausted catalyst

3.2 Catalytic activity

Guaiacol conversion rate, product selectivity, HDO and HDA efficiencies were shown in Table 1. Ni powder has the highest guaiacol conversion rate 51.3%, significantly higher than 11.8% of Fe and 20.0% of Co. The main products of Ni catalytic test are cyclohexanol and phenol. Phenol is generated from the demethoxylation of guaiacol, and after further hydrogenation of aromatic ring, phenol could convert into cyclohexanone and cyclohexanol. HDO and HDA efficiencies of Ni powder catalyst are 25.9% and 33.4% respectively. In the test with Fe powder, benzene, 1,2-dimethoxy- and 1,2-Benzenediol are dominant compounds, taking account of 61.6% of the product selectivity. The main chemical reaction is the methyl transfer between guaiacol molecules, however the Fe does not contribute to HDO and HDA of guaiacol. Co catalyst promotes the transformation of guaiacol into 1,2-cyclohexanediol,trans- (cis-), phenol and benzene, 1,2-dimethoxy-, its HDO and HDA efficiencies are slightly higher than that of Fe powder reaching 5.3% and 10.9%. Among the tested metallic catalysts, Ni shows the best performance, and thus Ni was chosen as the active metal in the preparation of the supported catalyst. This result is consistent with the finding of Zhao (Zhao et al., 2011), they synthesized transition metal phosphide catalysts for the gas phase HDO of guaiacol on a packed bed reactor, observing the activity order: $Ni_2P > Co_2P > Fe_2P$.

Table 1: Guaiacol conversion, product selectivity and, HDO and HDA efficiency under different commercial metal powder catalysts.

Product selectivity	Ni powder	Fe powder	Co powder
Cyclohexane	6.62%	-	-
Cyclohexanone	8.47%	-	-
Cyclohexanol	32.19%	-	1.62%
1-Methyl-1,2-cyclohexanediol	4.61%	-	5.81%
Cyclohexanone, 2-hydroxy-	-	3.42%	0.54%
1,2-Cyclohexanediol,trans- (cis-)	6.85%	7.50%	32.66%
Phenol	34.99%	1.23%	22.62%
Phenol, 2-methyl-	-	13.38%	1.50%
Benzene, 1,2-dimethoxy-	-	37.53%	17.91%
1,2-Benzenediol	-	24.03%	3.65%
Guaiacol conversion	51.31%	11.80%	20.05%
HDO	25.90%	2.39%	5.32%
HDA	33.36%	2.81%	10.89%

As shown in Figure 3, the synthesized Ni/Al_2O_3 has a superior catalytic effect than the commercial Ni powder. The guaiacol conversion rate is 99.3%, twice the value reached with Ni powder. The HDO and HDA efficiencies of Ni/Al_2O_3 are 50.3% and 82.4%, respectively equal to the 1.9 and 2.5 folds those achieved with Ni powder, notwithstanding the much lower amount of Ni present in the Ni/Al_2O_3 with respect to Ni powder. The principal final products are cyclohexanone, cyclohexanol and phenol, with the yield of 36.8%, 32.4% and 14.4% respectively. The other generated compounds are cyclohexane, 2-methyl-cyclopentanone, 1-methyl-1,2-cyclohexanediol, 2-methoxy-cyclohexanone and benzene.

From the guaiacol HDO products, two main hydrodeoxygenation reaction routes are proposed. One of them starts with the demethoxylation of guaiacol and generates phenol, which then further goes through the benzene ring hydrogenation or deoxygenation producing cyclohexanone, cyclohexanol and benzene, respectively. The other reaction pathway includes first the saturation of the aromatic structure of guaiacol obtaining 1-methyl-1,2-cyclohexanediol and 2-methoxy-cyclohexanone as intermediates, and then the deoxygenation to cyclohexanol.

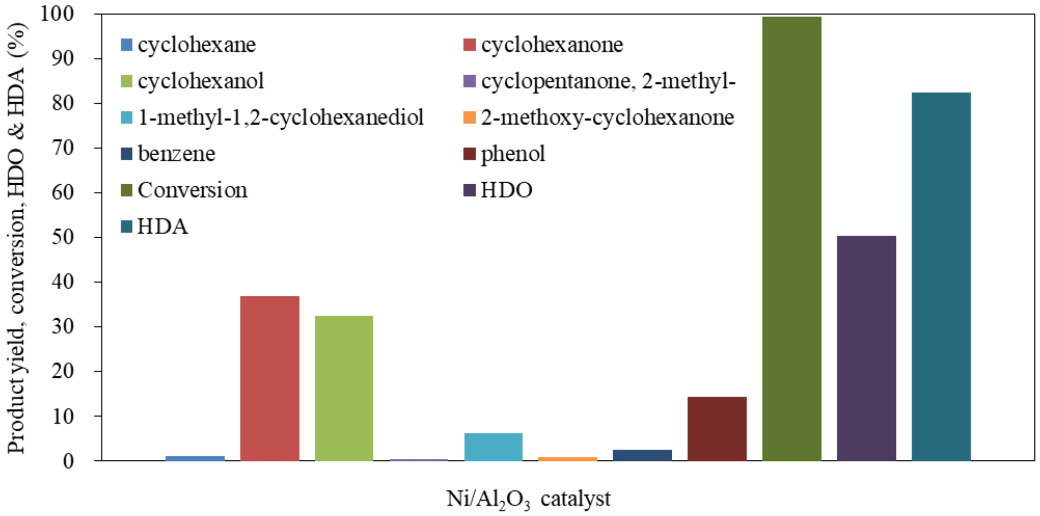

Figure 3: Ni/Al_2O_3 catalytic guaiacol HDO reaction: product yield, conversion rate, HDO and HDA efficiencies

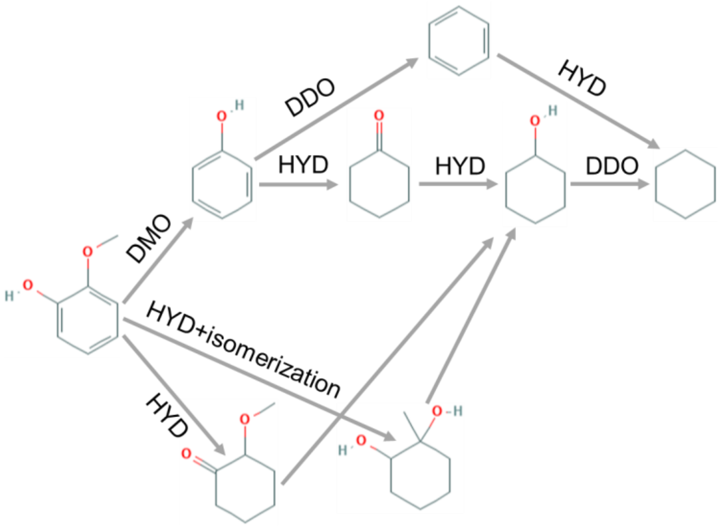

Figure 4: Possible reaction pathway of guaiacol hydrodeoxygenation in hydrothermal condition with heterogeneous hydrogen producer (DMO: demethoxylation, HYD: hydrogenation, DDO: direct deoxygenation)

4. Conclusions

Hydrothermal technique was used in the hydrodeoxygenation of guaiacol using zero-valent Zn as heterogeneous hydrogen producer and Ni, Co and Fe as catalyst. Among the tested metal powder catalysts, Ni showed the best performance with a guaiacol conversion rate of 51.3%, being the dominant products cyclohexanol and phenol. Conversion rates lower than 20 % were found with Co and Fe powder. In the tests with metal powders Ni showed the best performances in the guaiacol HDO reaction, therefore Ni/Al_2O_3 catalyst was synthesized to enhance the catalytic effect of Ni. In the Ni/Al_2O_3 catalytic test, 99.3% guaiacol conversion rate was reached, the guaiacol was mainly converted to cyclohexanone, cyclohexanol and phenol. The high selectivity of cyclohexanone and cyclohexanol with a total yield of 69% makes it a perspective method for producing valuable chemicals, KA oil from guaiacol, which is one of the dominate compounds in bio-oil. The HDO and HDA efficiencies of Ni/Al_2O_3 were 50.3% and 82.4%, respectively equal to the 1.9 and 2.5 folds of the results obtained with Ni powder. The synthesized Ni/Al_2O_3 catalyst shows excellent performance on the deoxygenation and hydrogenation reaction which significantly improves the combustion characteristics of the bio-oil. Thanks to the magnetic properties, the synthesized Ni/Al_2O_3 catalyst was easily separated and recovered although there still is some Zn and coke impurity in it. This research points out the feasibility of using zero-valent metal as hydrogen producer which avoids the risk of using directly gaseous hydrogen and demonstrates that hydrothermal treatment is a promising bio-fuel upgrading technique using only water as a green solvent.

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