Hydrodeoxygenation of prairie cordgrass bio-oil over Ni based activated carbon synergistic catalysts combined with different metals

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Abstract Bio-oil can be upgraded through hydrodeoxygenation(HDO). Low-cost and effective catalysts are crucial for the HDO process. In this study, four inexpensive combinations of Ni based activated carbon synergistic catalysts including Ni/AC, Ni-Fe/AC, Ni-Mo/AC and Ni-Cu/AC were evaluated for HDO of prairie cordgrass(PCG) bio-oil. The tests were carried out in the autoclave under mild operating conditions with 500 psig of H₂ pressure and 350°C temperature. The catalysts were characterized by X-ray Diffraction (XRD), Brunauer–Emmett–Teller (BET) and Transmission electron microscope (TEM). The results show that all synergistic catalysts had significant improvements on the physicochemical properties (water content, pH, oxygen content, higher heating value and chemical compositions) of the upgraded PCG bio-oil. The higher heating value of the upgraded bio-oil (ranging from 29.65MJ/kg to 31.61MJ/kg) improved significantly in comparison with the raw bio-oil (11.33MJ/kg), while the oxygen content reduced to only 21.70-25.88% from 68.81% of the raw bio-oil. Compare to raw bio-oil (8.78% hydrocarbons and no alkyl-phenols), the Ni/AC catalysts produced the highest content of gasoline range

hydrocarbons (C6-C12) at 32.63% in the upgraded bio-oil, while Ni-Mo/AC generated the upgraded bio-oil with the highest content of gasoline blending alkyl-phenols at 38.41%.

Keywords Prairie cordgrass; Bio-oil; Hydrodeoxygenation; Synergistic catalyst; Nickel; Activated carbon

Introduction

The world's energy consumption is increasing due to population growth and economic developments. More than 80% of the world primary energy consumption is derived from the utilization of depleting fossil fuels [1]. However, the massive application of fossil fuels causes many global problems such as global warming [2]. Renewable biomass, which is carbon neutral, is a reasonable and promising energy source which can reduce the world's dependence on fossil fuels [3]. Fast pyrolysis is an effective method to convert biomass to liquid bio-oil, and it is the thermochemical process in which biomass is heated to 400–600 °C in the absence of air at a short vapor residence time [4, 5]. However, the bio-oil produced has a high water and oxygen content. As a result, it exhibits acidic and corrosive properties and has a relatively low higher heating values compared with conventional petroleum-derived fuels, making it unusable as transport fuels [6]. Consequently, bio-oil upgrading is needed to reduce its water and oxygen content. Hydrodeoxygenation (HDO) is considered an effective method for bio-oil upgrading, and it involves the stabilization and selective removal of oxygen from untreated bio-oil through its catalytic reaction with hydrogen [6, 7]. Catalysts play a critical role in bio-oil HDO, and many catalysts have been investigated. For instance, hydrosulfurization (HDS) catalysts such as sulfided Co-Mo and Ni-Mo supported on alumina have been tested [8, 9]. But the sulfided catalysts are less suitable for bio-oil HDO due to the economic factors of using sulfur, product contamination and the poor stability of alumina support (deactivation by water) [10]. Also, noble metal catalysts, such as Pd/C, Rh/ZrO₂, Pt/C, and Ru/C were used for in bio-oil upgrading studies [11-14]. However, the availability and high cost of noble metals are main challenges for their application. Recently, non-noble catalysts such as metallic Ni, Cu, Fe or their bimetallic combination supported on Al₂O₃ were tested, and they are very active in bio-oil HDO [15, 16]. However, the problem of alumina's poor tolerance to water still existed in these tests, which can easily cause catalyst deactivation [17].

Cu can retard the catalyst deactivation caused by coking and prevent methanization of oxygen-containing compounds in bio-oil hydrodeoxygenation process [18]. Fe had a high selectivity for the formation of hydrocarbons

without much aromatic ring hydrogenation in the HDO of guaiacol [19]. Mo served as an active element in the hydrodeoxygenation of bio-oil model compound (2-ethylphenol) [20], and Mo catalysts were more active supported on activated carbon (AC) than on alumina or silica due to the weak acidity [21,22].

Catalyst supports played a crucial role in dispersing and stabilizing active phases of catalysts, decreasing the cost of catalysts [23]. The alumina (Al_2O_3) support can partially transform into boehmite ($\text{AlO}(\text{OH})$) in presence of water [24,25]. The alumina can also oxidize active metals such as Ni to metal oxides [26], which caused catalyst deactivation [27]. In comparison, activated carbon (AC) can be utilized as a support for catalysts due to its low affinity for carbon deposition and economical features [28]. Besides, activated carbon (AC) support can provide an increasing selectivity for direct oxygen removal at low hydrogen consumption [29]. Moreover, the hydrophobic nature of activated carbon support can resist the deactivation of metal catalysts from water produced in the hydrodeoxygenation reaction [29]. Furthermore, AC could be produced from bio-char, one of the main products generated in biomass fast pyrolysis process [30]. To our best knowledge, few studies have been reported to use bimetallic Ni based (Ni combined with Fe, Mo and Cu) catalysts supported on activated carbon (AC) for bio-oil hydrodeoxygenation.

Existing bio-oil hydrodeoxygenation methods suffered from serious drawbacks such as the requirement of extreme reaction conditions (high pressure ranging from 1088 to 4351 psig), which resulted in high hydrogen consumption and severe design standard of HDO reactors [31]. However, the monometallic and bimetallic Ni catalysts were found to be highly selective for oxygen removal under mild HDO conditions [32, 33], which can reduce the hydrogen consumption and equipment cost.

In this study, non-precious monometallic (Ni) and bimetallic (Ni combined with Fe, Mo and Cu) catalysts supported on activated carbon were utilized for PCG bio-oil HDO process to produce upgraded biofuels under low operating pressure (500 psig). The objective of the study is to investigate the catalyst selectivity of oxygen removal at lower catalysts cost (non-noble metals), lower operating cost (low hydrogen pressure) and lower coke formation (AC support).

The PCG bio-oil upgrading experiments were conducted in the autoclave in order to identify catalytic effects of different catalysts on product yields and quality. The catalysts are evaluated with focus on their ability to reduce the

oxygen content of the bio-oil, while maintaining the organic fraction yield at acceptable levels. In order to evaluate the catalysts' selectivity towards desirable gasoline range products including alkyl phenols and hydrocarbons, the composition of the organic fraction was also studied.

Materials and Methods

Feedstock

Prairie cordgrass bio-oil was used as the feedstock, and it was produced from prairie cordgrass (PCG) pyrolysis in a fixed bed reactor at 500°C. The properties of the bio-oil are listed in Table 1. In each test, 100 g of bio-oil was added to the autoclave.

Catalyst

The activated carbon (AC) was provided by Norit Company. The nickel (II) nitrate hexahydrate (crystalline), ammonium molybdate tetrahydrate (81-83wt.%), iron(III) nitrate nonahydrate (98 wt.%), copper (II) nitrate hemi (pentahydrate) (99 wt.%) were purchased from Sigma-Aldrich and used as received. The Ni/AC, Ni-Fe/AC, Ni-Mo/AC and Ni-Cu/AC catalysts were prepared by the wet impregnation method. AC powers were impregnated with aqueous solutions of a given amount of nickel (II) nitrate hexahydrate, ammonium molybdate tetrahydrate, iron(III) nitrate nonahydrate and copper (II) nitrate hemi (pentahydrate). The catalysts were dried in oven at 120°C for 4h, and then calcined in furnace in inert nitrogen at 550°C for 5h. All AC catalysts were based on 6% metal content. 5 g of catalysts was used in each test.

Apparatus

The 500ml Parr 4575 autoclave reactor was used to carry out batch PCG bio-oil hydrodeoxygenation experiments. The reactor's allowable maximum pressure and temperature were 5000psi and 500°C respectively. The Parr controller was used to control the vessel temperature and impeller mixing speed, and it also monitored the vessel pressure. The impeller mixing speed was set at 1000 rpm through all tests. Hydrogen was supplied from a hydrogen cylinder via a pressure regulator.

Experiment Design

Catalyst Reduction

Water and catalyst slurry was used to reduce the catalysts [34]. 5g catalysts (6%Ni/AC, 6%Ni-6%Fe/AC, 6%Ni-6%Mo/AC and 6%Ni-6%Cu/AC) and 150g deionized water were firstly loaded into the autoclave vessel. The vessel was then shut completely and flushed with hydrogen at 40psig for 3 times to remove the air inside. After charging the vessel with hydrogen at 500 psig, the catalyst and water slurry was stirred at 1000 rpm, and the vessel was heated to the temperature of 350 °C by a furnace at a heating rate of 5°C /min. After 3.5h, the heater was removed and the vessel was cooled to room temperature at 20 °C. Then the autoclave vessel with reduced catalysts was dried in vacuum drying oven for 12h.

Bio-oil HDO Test

100g raw PCG bio-oil was added in the vessel which contained the reduced catalysts. After installing the vessel and purging the air with hydrogen as shown in the reduction of catalyst, the vessel was charged with 500 psig hydrogen and heated to 350°C at the heating rate of 4°C /min. 5h later, the heater was shut down and the reactor was gradually cooled to room temperature. Then non-condensable gases (NCG) were collected in sample bags for further analysis. The aqueous phase (AP) and oil phase (OP) of upgraded products were poured to the sample bottles. The targeted oil phase (OP) was subjected to further analysis. The suspended catalysts with char in AP and OP was separated by filtration (using 0.2µm PTFE filter), and then dried in the drying oven at 110°C for 3h. The catalysts left in the vessel were washed with ethanol and then dried at 110°C for 3h. Experiments were conducted in duplicate for each catalyst. The weight difference between the used catalysts and fresh catalysts was the mass of char generated in the bio-oil HDO process. The yield of char, aqueous phase and oil phase were defined using the following equations:

$$Y_{\text{product}}(\%) = \frac{M_{\text{product}}(\text{g})}{M_{\text{bio-oil}}(\text{g})} \times 100 \quad (1)$$

$$Y_{\text{gas}}(\%) = 100 - (Y_{\text{char}} + Y_{\text{aqueous phase}} + Y_{\text{oil phase}}) \quad (2)$$

where Y_{product} and M_{product} are the yield of the upgraded products (char, aqueous phase and oil phase) and the mass of the products, respectively.

In order to evaluate the HDO effect of each catalytic treatment, the degree of deoxygenation (DOD) was defined as follows:

$$\text{DOD} = \left(1 - \frac{\text{wt\%O oil phase}}{\text{wt\%O bio-oil}}\right) \times 100 \quad (3)$$

where wt%O oil phase and wt%O bio-oil are the weight percent of oxygen in the upgraded oil phase and raw PCG bio-oil, respectively.

Catalyst Characterization

After catalyst reduction, the catalysts samples in the autoclave vessel were cooled to room temperature (20°C). Then the catalysts were flushed with N₂ for 30 minutes. Prior to exposure to air, the catalysts were passivated by purging autoclave vessel with 1% O₂/N₂ for 5 h at room temperature [35-37].

The passivated catalysts were disassembled from the autoclave vessel, and transferred to black plastic sample bags (The air in the sample bags was removed before usage). Then the sample bags were stored in a vacuum desiccator immediately. The catalyst samples were transferred to the characterization instruments (XRD, BET and TEM), where the catalysts were quickly taken out from sample bags for characterization.

X-ray diffractometer (XRD, SmartLab, Rigaku Corporation) with Cu Kα radiation was used for the determination of catalyst crystallinity[38]. The X-ray tube was set as 40 kV (tube voltage) and 44 mA (tube current). The X-ray pattern was scanned from 5° to 90° (2θ) with a scan speed of 4°/min and a step of 0.02°.

Tristar 3000 micropore analyzer was employed to analyze BET specific surface area and porosity texture of catalysts. The nitrogen adsorption was measured at 77.2 K. The catalysts were first degassed at 573 K for around 6 h and then studied by a static volumetric technique. The specific surface area of catalysts was calculated according to the Brunauer–Emmett–Teller (BET) method, and the total pore volume was confirmed at a relative pressure P/P₀ = 0.995. Density functional theory (DFT) was utilized to determine the micropore, mesopore and pore size distribution [39,40].

Transmission electron microscope (TEM, JEOL JEM-2100 LaB6) was performed with 200 kV of the accelerating voltage. A few micrograms of catalyst samples was dispersed in isopropyl alcohol (0.5–1.0 mL) and shaken in ultrasonic for about 2 min. Then, a few drops of suspension were dropped on a carbon-coated 200-mesh copper grid and allowed to dry [41].

Physicochemical Characterization

The properties (pH, water content, higher heating value, elemental compositions and chemical components) of raw bio-oil and upgraded bio-oil were characterized. The pH value of the bio-oil was tested by a pH meter (AB15, Accumet Company). Water content was analyzed using a Karl Fischer Titrator V20 (Mettler Toledo Company) in accordance with ASTM E1064. The higher heating value (HHV) of samples was determined using a Calorimeter System (C2000, IKA-Works, Inc.) which is based on ASTM D4809. The samples' elemental analysis (carbon, hydrogen and nitrogen) was measured by the CE-440 elemental analyzer.

The major components of liquid products (oil phase) were analyzed by gas chromatography–mass spectrometry (GC–MS) (Agilent GC-7890A and MSD-5975C). Hydrogen was used as carrier gas with a flow rate of 1 mL/min. The injection temperature was 300°C, and the injection volume was 1 µL. The initial column temperature was 60 °C and this temperature was held for 1 min. Then, the increase of column temperature followed ramp 1 at 3°C/min to 140°C, ramp 2 at 10°C/min to 180°C, ramp 3 at 3°C/min to 260°C, and ramp 4 at 10°C/min to 300°C. The temperature was kept for an additional 2 min after each ramp. Major compositions of samples were identified based on the NIST Mass Spectral library and literature [42].

The gas chromatography system (Agilent GC 7890A) with a 50 m × 0.53 mm × 15 µm column was used to determine compositions of non-condensable gas. The thermal conductivity detector (TCD) was used for the analysis of H₂ and CO₂. The flame ionization detector (FID) was used for the identification of light hydrocarbons (C1–C5). Standard gas mixtures were used for calibration, and argon was employed as the carrier gas.

Results and Discussion

Catalyst Characterization

XRD

X-ray Diffraction (XRD) was employed to identify the crystalline phases in the investigated catalysts. The XRD patterns of different metal loaded AC catalysts are shown in Fig. 1. The specific pattern of AC support maintained in all catalysts, since the small sharp peak (26.6°) of graphitic carbon existed in all catalysts [43]. There are two peaks (44.2° and 51.7°) identified in all metal AC catalysts, corresponding to the presence of metallic Ni particles on the

crystalline structure of impregnated catalysts [44]. In the Ni-Cu/AC catalyst, the existence of Cu particles can be detected from peaks at around 43° and 50°. However, they overlapped the reflection peaks of the metallic Ni phase, which is due to the segregation of some of the metallic Cu particles from the Ni-Cu alloy particles formed after the thermal treatment [44]. The diffraction peaks at 35.5°, 43.1° and 62.6° associated to cubic iron oxide phases (Fe_2O_3) are determined in Ni-Fe/AC catalysts [45, 46]. MoO_2 crystallites along with α - NiMoO_4 and β - NiMoO_4 mixed phases are identified in Ni-Mo/AC catalysts [43].

BET

The textural properties of the AC support catalysts with different metals are listed in Table 2. Surface areas of metal loaded AC catalysts are lower than the surface area of the activated carbon. The addition of the metals (Ni, Fe, Mo and Cu) on the AC support resulted in a decrease of the surface area and total pore volumes for all metal loaded catalysts, which is probably due to the filling or blocking of the metal and metal oxides (Ni, Cu, Fe_2O_3 , MoO_2 , α - NiMoO_4 and β - NiMoO_4) in the pores of the corresponding AC support [47].

TEM

Fig. 2 shows the bright field high resolution TEM images of catalysts. As seen in Fig. 2a, there were no dark spots shown for pure AC, because there was no metal loading on it. However, fresh 6%Ni/AC showed obvious dark spots in Fig. 2b, which was attributed to the presence of Ni particles. As was shown in Fig. 2c, TEM images of Ni-Cu/AC also showed obvious dark spots due to the presence of Ni-Cu alloy particles. Dark spots were also found in the TEM images of Ni-Fe/AC (Fig. 2d), which indicated the existence of metal Ni or Fe_2O_3 . Ni, MoO_2 , α - NiMoO_4 or β - NiMoO_4 crystallites are also detected as dark spots in the TEM images of Ni-Mo/AC (Fig. 2e).

The histograms on the particle size distribution were calculated by counting particles appeared in the TEM images of prepared catalysts [48]. The histograms on the particles distributions in the four prepared catalysts were built towards a random selection of particles (from 711 to 882 depending on the catalyst samples). The histograms in Fig. 3 show the particle size distribution of the four prepared catalyst. The 6%Ni/AC catalyst (Fig. 3a) has a narrow particle size distribution with a maximal size ranging from 6 nm to 7 nm, and there are a very few large particles or agglomerates with size above 28 nm. The 6%Ni-6%Cu/AC (Fig. 3b) also has a narrow size distribution with a maximum at 8 nm - 9 nm, and some large particles or aggregates were found with size larger than 28 nm. The

6%Ni-6%Fe/AC (Fig. 3c) has a wider size distribution with a maximum between 10 nm and 11 nm, and some large particles or aggregates were detected with size above 36 nm. The 6%Ni-6%Mo/AC (Fig. 3d) has the widest size distribution with a maximum at 8 nm - 9 nm, and there are even some large particles or aggregates with size over 72 nm. Besides, the average particle sizes of the bimetallic Ni based catalysts are larger than the monometallic Ni based catalyst.

The metal dispersion (D_M (%)) was defined as the ratio of the number of metal atoms at the catalyst surface to the total number of metal atoms in the catalyst sample [49, 50]. The dispersion D_M was calculated according to the following equation [51]:

$$D_M = \frac{N_{(S)M}}{N_{(T)M}} \times 100\% = \frac{6 \times \alpha_M}{d \times V_M} \times 100\% = \frac{6 \times \alpha_M \times M_w}{d \times \rho_M \times N_0} \times 100\% \quad (4)$$

where $N_{(S)M}$ is the number of metal atoms at the catalyst surface, $N_{(T)M}$ is the total number of metal atoms in the catalyst sample, α_M (m⁻²) is the number of surface atoms per unit area, d (nm) is the average metal particle size, V_M (cm³) is the volume per metal atom in the bulk, M_w (g • mol⁻¹) is the metal atomic weight, ρ_M (g • cm⁻³) is the metal density and N_0 (mol⁻¹) is the Avogadro's number. The average particle size and metal dispersion are shown in the Table 3. The dispersions of the four prepared catalysts were varying in a range of 6.39%-10.68%. Compared to monometallic 6%Ni/AC, the addition of Cu, Fe and Mo reduced metal dispersions of bimetallic 6%Ni-6%Cu/AC, 6%Ni-6%Fe/AC and 6%Ni-6%Mo/AC. This might be due to the larger average particle sizes of bimetallic catalysts, which might result from the higher proportion of metal particles or aggregations with larger sizes on the surface of the bimetallic catalysts [52, 53]. Similar results were found by Duvenhage DJ et al [54-58].

Product Yield

The yield of the bio-oil HDO products (aqueous phase, oil phase, char and gas), based on the weight of the raw bio-oil, are shown in Table 4. Compared with Ni/AC treatment, the Ni-Fe/AC catalyst obtained the lowest oil phase yield and char yield, and produced the highest gas yield. This trend may result from the further decomposition of organic compounds in the liquid phase due to the addition of Fe, such as deoxygenation to form carbon dioxide in the gas (20.01% in further gas analysis). The addition of Mo to Ni/AC generated the higher oil phase yield and lower char yield, and it indicated that Ni-Mo/AC slightly reduced the formation of polyaromatic species due to the

polymerization and polycondensation reaction, which result in the lower char forming (8.78%) [59]. The addition of Cu also improved the HDO effect of Ni/AC in terms of increasing oil phase yield and decreasing char yield. The aqueous phase yield of all treatments is similar at around 50%, this might be the result of the de-moisturization of the organic compound in the oil phase to the aqueous phase with high water content (around 90%) [60].

Bio-oil analysis

The physicochemical properties of different upgraded bio-oils, such as water content, pH, elemental compositions and higher heating values, are measured and listed in Table 5. The water content of the oil phase reduced significantly from 48.91% in the raw bio-oil to the figure ranging from 6.12% to 11.98% through hydrodeoxygenation and transferring water to aqueous phase. The HHV of the oil phase (ranging from 29.65 MJ/kg to 31.61 MJ/kg) also improved greatly in comparison with the raw bio-oil (11.33MJ/kg), which is due to its much lower water and oxygen content. The pH of oil phase is slightly higher than raw bio-oil, which may result from the transformation of acids to esters in the upgraded products.

Compared to the carbon and oxygen contents in raw bio-oil (20.01% and 68.81% separately), the carbon content in the upgraded bio-oil (64.29-67.64%) increased significantly, while the oxygen content decreased to only 21.70-25.88%. This was mainly caused by the hydrodeoxygenation and decarboxylation reactions of oxygenated compounds that remove oxygen in the form of H₂O and CO₂, which were then transferred to aqueous phase and gas respectively. The decrease of oxygen levels also lead to the high degree of deoxygenation (DOD), which ranged from 62.39% to 68.46%. This DOD is comparable to the DOD of noble Pt/C catalysts (64%) for the HDO of bio-oil [31].

One of the major objectives for this study was to explore the effects of different catalysts on the distribution of organic compounds in the upgraded liquid products. Therefore, the chemical compositions of upgraded bio-oil (OP) are determined by GC-MS. The various components present in the original bio-oil were also analyzed for comparison. The main chemical compounds of raw bio-oil and upgraded bio-oils, as analyzed by GC-MS, are shown in Table 6. The compositions were classified into different categories: phenols, ethers, ketones, esters, alcohols, acids and hydrocarbons.

1 In raw PCG bio-oil, the type and proportion of organic components are in agreement with those reported by others
2 [61]. The PCG bio-oil produced was rich in phenols (55.88%), and it also contained undesirable carboxylic acids
3 (3.05%) and ketones (8.55%). The content of hydrocarbons was only 8.78%.

4 The organic compositions of upgraded bio-oil changed significantly after mild HDO processes over different AC
5 supported catalysts. After the reaction, the content of phenols increased in all catalytic treatments except Ni/AC. The
6 improvement of phenols is due to the formation of alkyl-phenols such as 2-methyl-phenol and 3, 4-dimethyl-phenol
7 (Supplemental Table 1). The Ni/AC was not very active for the hydrogenation of phenol ring, therefore most of the
8 phenol rings were maintained in all treatments [62]. The addition of Fe, Cu and Mo to Ni/AC might promote the
9 alkylation reactions between phenol and alcohols or light olefins, and then the following reactions of
10 demethoxylation, demethylation and hydrogenation lead to the generation of phenolic derivatives such as alkyl-
11 phenols [60]. By comparison, the Ni-Mo/AC generated the upgraded bio-oil with the highest alkyl-phenol content at
12 38.41%. The alkyl-phenols have been found to possess high blending octane numbers. Therefore, it might have
13 potential to be an excellent gasoline blendstock [63].

14 The undesirable acids in bio-oil are significantly reduced by all HDO processes over different AC supported
15 catalysts. The acids may be converted into relatively stable esters through decarbonylation, dehydroxylation and
16 ring opening [60]. In addition, some carboxylic acids may be transferred from the oil phase to the aqueous phase [9].
17 Acids even disappeared totally in Ni-Fe/AC and Ni-Cu/AC treatments. The decreasing of acid content is beneficial
18 for refineries to further processing the upgraded HDO bio-oils in terms of reducing corrosion and materials of
19 construction.

20 Ketones, which are responsible for the low heating value and instability of raw bio-oil, were also reduced in all
21 HDO processes. Micromolecule ketones were decomposed through decarboxylation to form CO₂ and hydrocarbons,
22 while macromolecule ketones were transferred to other ketones [9]. Alcohols were easily transformed to
23 hydrocarbons and phenol derivatives by HDO, which leads to the decrease of alcohol content in all catalytic
24 treatments.

25 The content of hydrocarbons in oil phase increased because of the HDO effect of oxygenated organic compounds in
26 all catalytic treatments, and Ni/AC generated the upgraded bio-oil with the highest hydrocarbon content at 39.42%.

The lower yield of hydrocarbons over Ni-Fe/AC, Ni-Cu/AC and Ni-Mo/AC catalysts might results from the competition reaction to form phenolic derivatives, which reduced the proportion of alcohols that can be used to produce hydrocarbons. The alkylation reactions between phenol and light olefins also consumed partial hydrocarbons. However, the main proportion of hydrocarbons is still light hydrocarbons (C6-C12), which has the potential to be utilized as gasoline additives.

Gas analysis

The composition of non-condensable gas (NCG) provides valuable information on the types of reactions that occurred in the HDO processes. The compositions of syngas are listed in Table 7. As is shown in the table, there are 10 gas compounds detected in the non-condensable gas. As expected, the main component is hydrogen, which was the unreacted hydrogen that fed into the autoclave at the beginning of the experiment. The presence of unreacted hydrogen also indicates that the reactions were not conducted under hydrogen starvation conditions. The second highest composition of gas is always CO₂, which suggested effective decarboxylation of such as ketones and esters followed by water gas shift or disproportionation (Boudouard reaction) over the AC supported catalysts in all bio-oil HDO processes [63]. For each case, small amount of CH₄ were formed as well, which was probably as result of the demethylation of phenolic derivatives [9]. Some light hydrocarbons (C2-C5) were also produced, and this might

Correlation of catalyst composition and bio-oil HDO activity

Ni based catalyst was very active in the hydrogenation reactions [64]. However, monometallic Ni-based catalyst showed higher coking levels in hydrodeoxygenation process [65]. In this study, the coking (char) yield of the Ni/AC treatment was as high as 8.86%.

Compared to the monometallic Ni catalysts, the addition of a second metal such as Mo, Fe and Cu reduced the coke formation and increased catalyst activity.

Bimetallic Ni–Cu catalysts are found to be more active than single Ni catalysts in hydrodeoxygenation process under mild conditions [66]. The coking (char) yield of Ni-Cu/AC catalyst (4.80%) was lower than Ni/AC catalyst (8.86%). The reason might be that the copper addition facilitated the reduction of nickel oxide and improved resistance to coke formation on Ni–Cu catalysts [67].

In Ni-Fe bimetallic catalysts, the addition of Fe can promote the C=O hydrogenation and inhibit the C-C breaking [68-69], which might result in the higher yield of phenols in Ni-Fe/AC treatment in comparison with Ni/AC treatment. The Ni-Fe/AC treatment also led to lower coking (char) yield (3.09%) than Ni/AC treatment (8.86%).

Bimetallic Ni-Mo catalyst was highly active and stable [70]. The Ni-Mo/AC catalysts can promote C-O activation and inhibit the C-C breaking [15], which might result in the higher DOD (degree of deoxygenation) of Ni-Mo treatment (66.02%) than Ni/AC treatment (63.60%).

Conclusions

The HDO upgrading of PCG raw bio-oil over different metal AC catalysts under mild conditions were carried out in the autoclave reactor. The effects of the different catalysts are evaluated in terms of organic liquid product yield and selectivity towards alkyl phenols and hydrocarbons. The results show that all catalysts had significant improvements on the physicochemical properties (water content, pH, oxygen content, higher heating value and chemical compositions) of the upgraded PCG bio-oil. All AC supported catalysts increased the hydrocarbon yield in upgraded bio-oil in comparison to raw bio-oil, while the Ni/AC catalysts produced the highest light hydrocarbons content at 32.63% in upgraded bio-oil. The addition of Fe, Cu and Mo to Ni/AC increased the yields of alkyl-phenols, and Ni-Mo/AC generated the upgraded bio-oil with the highest content of alkyl-phenols at 38.41%.

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References

- [1] Mohr SH, Wang J, Ellem G, Ward J, Giurco D. Projection of world fossil fuels by country. Fuel 2015;141:120-135.

- [2] Srokol Z, Bouche AG, van Estrik A, Strik RC, Maschmeyer T, Peters JA. Hydrothermal upgrading of biomass to biofuel; studies on some monosaccharide model compounds. *Carbohydr. Res.* 2004; 339:1717-1726.
- [3] Ranzi E, Cuoci A, Faravelli T, Frassoldati A, Migliavacca G, Pierucci S, Sommariva S. Chemical kinetics of biomass pyrolysis. *Energy Fuels* 2008; 22:4292-4300.
- [4] Cheng S, Wei L, Zhao X, Huang Y, Raynie D, Qiu C, Yu Y. Directly catalytic upgrading bio-oil vapor produced by prairie cordgrass pyrolysis over Ni/HZSM-5 using a two stage reactor. *AIMS Energy* 2015; 3:227-240.
- [5] Zhang Q, Chang J, Wang T, Xu Y. Review of biomass pyrolysis oil properties and upgrading research. *Energy Convers* 2007; 48: 87-92.
- [6] Shemfe MB, Gu S, Ranganathan P. Techno-economic performance analysis of biofuel production and miniature electric power generation from biomass fast pyrolysis and bio-oil upgrading. *Fuel* 2015;143: 361-372.
- [7] Zhang X, Wang T, Ma L, Zhang Q, Jiang T. Hydrotreatment of bio-oil over Ni-based catalyst. *Bioresour. Technol* 2013; 127:306-311.
- [8] Popov A, Kondratieva E, Mariey L, Goupil JM, El Fallah J, Gilson JP et al. Bio-oil hydrodeoxygenation: Adsorption of phenolic compounds on sulfided (Co) Mo catalysts. *J. Catal.* 2013; 297:176-186.
- [9] Xu X, Zhang C, Liu Y, Zhai Y, Zhang R. Two-step catalytic hydrodeoxygenation of fast pyrolysis oil to hydrocarbon liquid fuels. *Chemosphere* 2013; 93(4): 652-660.
- [10] He Z, Wang X. Hydrodeoxygenation of model compounds and catalytic systems for pyrolysis bio-oils upgrading. *Catal. Sustainable Energy* 2012; 1:28-52.
- [11] Zhao C, He J, Lemonidou AA, Li X, Lercher JA. Aqueous-phase hydrodeoxygenation of bio-derived phenols to cycloalkanes. *J. Catal.* 2011; 280:8-16.
- [12] Gutierrez A, Kaila RK, Honkela ML, Slioor R, Krause AOI. Hydrodeoxygenation of guaiacol on noble metal catalysts. *Catal. Today* 2009; 147: 239-246.

- [13] Centeno A, Maggi R, Delmon B. Use of noble metals in hydrodeoxygenation reactions. *Stud. Surf. Sci. Catal.* 1999; 127: 77-84.
- [14] Chen L, Zhu Y, Zheng H, Zhang C, Zhang B, Li Y. Aqueous-phase hydrodeoxygenation of carboxylic acids to alcohols or alkanes over supported Ru catalysts. *J. Mol. Catal. A: Chem* 2011;351:217-227.
- [15] Yang YN, Zhang HK, En-jing L, Zhang CH, Ren J. Effect of Fe, Mo promoters on acetic acid hydrodeoxygenation performance of nickel-based catalyst. *J. Mol. Catal. (China)* 2011; 25:30-36.
- [16] Yakovlev VA, Khromova SA, Sherstyuk OV, Dundich VO, Ermakov DY, Novopashina V, et al. Development of new catalytic systems for upgraded bio-fuels production from bio-crude-oil and biodiesel. *Catal. Today* 2009; 144: 362-366.
- [17] Furimsky E. Catalytic hydrodeoxygenation. *Appl. Catal., A* 2000;199: 147-190.
- [18] Zhang X, Wang T, Ma L, Zhang Q, Yu Y, Liu, Q. Characterization and catalytic properties of Ni and NiCu catalysts supported on $\text{ZrO}_2\text{-SiO}_2$ for guaiacol hydrodeoxygenation. *Catal. Commun.* 2013; 33: 15-19.
- [19] Olcese RN, Bettahar M, Petitjean D, Malaman B, Giovanella F, Dufour A. Gas-phase over Fe/SiO₂ catalyst. *Appl. Catal., B* 2012; 115: 63-73.
- [20] 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. *Appl. Catal., B*, 2010; 98: 213-223.
- [21] Duchet JC, van Oers EM, de Beer VHJ, Prins R. Carbon-supported sulfide catalysts. *J. Catal.* 1983; 80:386-402.
- [22] Figueiredo JL, Pereira MFR., The role of surface chemistry in catalysis with carbons. *Catal. Today* 2010; 150: 2-7.
- [23] Stakheev AY, Kustov LM. Effects of the support on the morphology and electronic properties of supported metal clusters: modern concepts and progress in 1990s. *Appl. Catal., A*. 1999; 188: 3-35.

- [24] Venderbosch RH, Ardiyanti AR, Wildschut J, Oasmaa A, Heeres HJ. Stabilization of biomass-derived pyrolysis oils. *J. Chem. Technol. Biotechnol.* 2010; 85: 674-686.
- [25] Laurent E, Delmon B. Influence of water in the deactivation of a sulfided NiMo/ γ -Al₂O₃ catalyst during hydrodeoxygenation, *J. Catal.* 1994; 146: 281-291.
- [26] Elliott DC. Historical Developments in Hydroprocessing Bio-oils. *Energy Fuels* 2007; 21: 1792-1815.
- [27] Furimsky E. Catalytic hydrodeoxygenation. *Appl. Catal., A.* 2000; 199: 147-190.
- [28] Echeandia S, Arias PL, Barrio VL, Pawelec B, Fierro, JLG. Synergy effect in the HDO of phenol over Ni–W catalysts supported on active carbon: Effect of tungsten precursors. *Appl. Catal., B* 2010; 101: 1-12.
- [29] De S, Saha B, Luque R. Hydrodeoxygenation processes: Advances on catalytic transformations of biomass-derived platform chemicals into hydrocarbon fuels. *Bioresour. Technol.* 2015; 178: 108-118.
- [30] Angın D, Köse TE, Selengil U. Production and characterization of activated carbon prepared from safflower seed cake biochar and its ability to absorb reactive dyestuff. *Appl. Surf. Sci* 2013; 280:705-710.
- [31] Mortensen PM, Grunwaldt JD, Jensen PA, Knudsen KG, Jensen AD. A review of catalytic upgrading of bio-oil to engine fuels. *Appl. Catal., A.* 2011; 407: 1-19.
- [32] Saidi M, Samimi F, Karimipourfard D, Nimmanwudipong T, Gates BC, Rahimpour M R. Upgrading of lignin-derived bio-oils by catalytic hydrodeoxygenation. *Energy Environ. Sci.* 2014; 7: 103-129.
- [33] Dutta S, Wu KCW, Saha B. Emerging strategies for breaking the 3D amorphous network of lignin. *Catal. Sci. Technol.* 2014; 4: 3785-3799.
- [34] Elkasabi Y, Mullen CA, Pighinelli AL, Boateng AA. Hydrodeoxygenation of fast-pyrolysis bio-oils from various feedstocks using carbon-supported catalysts. *Fuel Process. Technol* 2014; 123:11-18.
- [35] Wang X, Meng L, Wu F, Jiang Y, Wang L, Mu X. Efficient conversion of microcrystalline cellulose to 1, 2-alkanediols over supported Ni catalysts. *Green Chem.* 2012; 14: 758-765.

- [36] Ji N, Zhang T, Zheng M, Wang A, Wang H, Wang X, et al. Catalytic conversion of cellulose into ethylene glycol over supported carbide catalysts. *Catal. Today* 2009; 147: 77-85.
- [37] Gai XK, Arano H, Lu P, Mao JW, Yoneyama Y, Lu C X, et al. Catalytic bitumen cracking in sub-and supercritical water. *Fuel Process. Technol* 2016; 142: 315-318.
- [38] Zhao X, Wei L, Cheng S, Julson J. Optimization of catalytic cracking process for upgrading camelina oil to hydrocarbon biofuel. *Ind. Crops Prod* 2015; 77: 516-526.
- [39] Zhao X, Wei L, Cheng S, Cao Y, Julson J, Gu Z. Catalytic cracking of carinata oil for hydrocarbon biofuel over fresh and regenerated Zn/Na-ZSM-5. *Appl. Catal., A* 2015; 507: 44-55.
- [40] Cheng S, Wei L, Zhao X. Develop Bifunctional Ni/HZSM-5 Catalyst for Converting Prairie Cordgrass to Hydrocarbon Biofuel. *Energy Sources, Part A* <http://dx.doi.org/10.1080/15567036.2015.1065298>.
- [41] Zhao X, Wei L, Cheng S, Huang Y, Yu Y, Julson J. Catalytic cracking of camelina oil for hydrocarbon biofuel over ZSM-5-Zn catalyst. *Fuel Process. Technol* 2015;139: 117-126.
- [42] Cheng S, Wei L, Zhao X, Kadis E, Julson J. Converting prairie cordgrass to hydrocarbon biofuel over Co-Mo/HZSM-5 using a two-stage reactor system. *Energy Technol.* <http://dx.doi.org/10.1002/ente.201500452>.
- [43] Liakakou ET, Heracleous E, Triantafyllidis KS, Lemonidou AA. K-promoted NiMo catalysts supported on activated carbon for the hydrogenation reaction of CO to higher alcohols: Effect of support and active metal. *Appl. Catal., B.* 2015; 165: 296-305.
- [44] Sy FAL, Abella LC, Monroy TG. Hydrogen Production via Thermo Catalytic Decomposition of Methane over Bimetallic Ni-Cu/AC Catalysts: Effect of Copper Loading and Reaction Temperature. *Int. J. Chem. Eng. Appl.* 2012; 3: 92-97.
- [45] Wang GJ, Zhang JK, Liu Y. Catalytic oxidative desulfurization of benzothiophene with hydrogen peroxide over Fe/AC in a biphasic model diesel-acetonitrile system. *Korean J. Chem. Eng.* 2013; 30: 1559-1565.

- [46] Li B, Sun K, Guo Y, Tian J, Xue Y, Sun D. Adsorption kinetics of phenol from water on Fe/AC. *Fuel* 2013;110: 99-106.
- [47] Arbeláez O, Reina TR, Ivanova S, Bustamante F, Villa AL, Centeno MA, Odriozola JA. Mono and bimetallic Cu-Ni structured catalysts for the water gas shift reaction. *Appl. Catal., A* 2015; 497:1-9.
- [48] Simakova I, Simakova O, Mäki-Arvela P, Simakov A, Estrada M, Murzin DY. Deoxygenation of palmitic and stearic acid over supported Pd catalysts: effect of metal dispersion. *Appl. Catal., A* 2009; 355: 100-108.
- [49] Borodzinski A, Bonarowska M. Relation between crystallite size and dispersion on supported metal catalysts. *Langmuir* 1997; 13: 5613-5620.
- [50] Blomsma E, Martens JA, Jacobs PA. Isomerization and hydrocracking of heptane over bimetallic bifunctional PtPd/H-beta and PtPd/USY zeolite catalysts. *J. Catal.* 1997; 165: 241-248.
- [51] Anderson JR. *Structure of Metallic Catalysts*. New York: Academic Press; 1975.
- [52] AbdelDayem, HM. Platinum-copper on carbon catalyst synthesised by reduction with hydride anion. *Platinum Met. Rev.* 2007; 51:138-144.
- [53] Cesar DV, Pérez CA, Salim, VMM, Schmal M. Stability and selectivity of bimetallic Cu-Co/SiO₂ catalysts for cyclohexanol dehydrogenation. *Appl. Catal., A* 1999; 176: 205-212.
- [54] Duvenhage DJ, Coville NJ. Fe: Co/TiO₂ bimetallic catalysts for the Fischer-Tropsch reaction: part 3: the effect of Fe: Co ratio, mixing and loading on FT product selectivity. *Appl. Catal., A* 2005; 289:231-239.
- [55] Das PC, Pradhan NC, Dalai AK, Bakshi, NN. Carbon monoxide hydrogenation over zirconia supported Ni and Co-Ni bimetallic catalysts. *Catal. Lett.* 2004; 98: 153-160.
- [56] Zhao M, Church TL, Harris AT. SBA-15 supported Ni-Co bimetallic catalysts for enhanced hydrogen production during cellulose decomposition. *Appl. Catal., B* 2011; 101: 522-530.

- [57] Saw ET, Oemar U, Tan XR, Du Y, Borgna A, Hidajat K, et al. Bimetallic Ni–Cu catalyst supported on CeO₂ for high-temperature water–gas shift reaction: Methane suppression via enhanced CO adsorption. *J. Catal.* 2014; 314: 32-46.
- [58] Biniwale RB, Kariya N, Ichikawa M. Dehydrogenation of cyclohexane over Ni based catalysts supported on activated carbon using spray-pulsed reactor and enhancement in activity by addition of a small amount of Pt. *Catal. Lett.* 2005;105:83-87.
- [59] Furimsky E, Massoth FE. Deactivation of hydroprocessing catalysts. *Catal. Today* 1999; 52: 381-495.
- [60] Oh S, Hwang H, Choi HS, Choi JW. The effects of noble metal catalysts on the bio-oil quality during the hydrodeoxygenative upgrading process. *Fuel* 2015; 153: 535-543.
- [61] Zhou R, Lei H, Julson J. The effects of pyrolytic conditions on microwave pyrolysis of prairie cordgrass and kinetics. *J. Anal. Appl. Pyrolysis.* 2013; 101:172-176.
- [62] Mortensen PM, Grunwaldt JD, Jensen PA, Jensen AD. Screening of Catalysts for Hydrodeoxygenation of Phenol as a Model Compound for Bio-oil. *ACS Catal* 2013; 3: 1774-1785.
- [63] French RJ, Stunkel J, Baldwin RM. Mild hydrotreating of bio-oil: effect of reaction severity and fate of oxygenated species. *Energy Fuels* 2011; 25:3266-3274.
- [64] Savva PG, Goundani K, Vakros J, Bourikas K, Fountzoula C, Vattis D, et al. Benzene hydrogenation over Ni/Al₂O₃ catalysts prepared by conventional and sol–gel techniques, *Appl. Catal., B* 2008; 79: 199-207.
- [65] He Z, Wang X. Highly selective catalytic hydrodeoxygenation of guaiacol to cyclohexane over Pt/TiO₂ and NiMo/Al₂O₃ catalysts. *Front. Chem. Sci. Eng.* 2014; 8:369-377.
- [66] Park Y, Kang T, Cho YS, Kim P, Park JC, Yi J. Finely-dispersed Ni/Cu catalysts supported on mesoporous silica for the hydrodechlorination of chlorinated hydrocarbons. *Stud. Surf. Sci. Catal.* 2003; 146: 637-640.

- [67] Bykova MV, Ermakov DY, Kaichev VV, Bulavchenko OA, Saraev AA, Lebedev MY, et al. Ni-based sol–gel catalysts as promising systems for crude bio-oil upgrading: Guaiacol hydrodeoxygenation study. *Appl. Catal., B* 2012; 113:296-307.
- [68] Sitthisa S, An W, Resasco DE. Selective conversion of furfural to methylfuran over silica-supported Ni Fe bimetallic catalysts. *J. Catal.* 2011; 284: 90-101.
- [69] Wang XF, Wang F, Chen MY, Ren J. Studies on nickel based bimetallic catalysts for hydrodeoxygenation. *J. Fuel Chem. Technol.* 2005; 33: 612-616.
- [70] Zhang W, Zhang Y, Zhao L, Wei W. Catalytic activities of NiMo carbide supported on SiO₂ for the hydrodeoxygenation of ethyl benzoate, acetone, and acetaldehyde. *Energy Fuels* 2010; 24:2052-2059.

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TABLE 1

Properties of the PCG bio-oil at 20°C	
Properties	Data
Water content (wt.%)	48.91 ± 1.41
pH	2.41 ± 0.01
Carbon content (wt.%)	20.01 ± 1.87
Hydrogen content (wt.%)	10.31 ± 0.57
Nitrogen content wt.%)	0.87 ± 0.05
Oxygen content^a (wt.%)	68.81 ± 2.49
Higher heating value(MJ/kg)	11.33 ± 0.08

^a Calculated by difference.

TABLE 2

BET parameters of different Catalysts

Catalyst	Surface area (m ² /g)	Pore Size (nm)	Pore volume (cm ³ /g)		
	BET	Average	Total ^b	Micropores	Mesopores
AC	730.61	5.14	0.92	0.53	0.39
Ni/AC	723.14	4.92	0.87	0.51	0.36
Ni-Fe/AC	687.96	4.84	0.83	0.42	0.41
Ni-Cu/AC	682.83	4.74	0.81	0.48	0.33
Ni-Mo/AC	626.66	4.78	0.81	0.47	0.34

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TABLE 3

Average metal particle size and dispersion of the four prepared catalysts

Catalyst	Average metal particle size (nm)	Total metal dispersion (%)
6%Ni/AC	9.45	10.68
6%Ni-6%Cu/AC	10.40	9.86
6%Ni-6%Fe/AC	13.11	8.25
6%Ni-6%Mo/AC	18.90	6.39

TABLE 4

Mass balance of upgrading products from different catalytic treatments

Treatments	Bio-oil		Char	Gas
	Oil phase (wt.%)	Aqueous phase (wt.%)	Char (wt.%)	Gas (wt.%)
Ni/AC	20.17	51.35	8.86	19.63
Ni-Fe/AC	17.35	51.34	3.09	28.24
Ni-Cu/AC	21.57	51.62	4.80	22.02
Ni-Mo/AC	21.91	49.37	8.78	19.96

TABLE 5

Physicochemical properties of different upgrading bio-oils

Treatments	Ni/AC	Ni-Fe/AC	Ni-Cu/AC	Ni-Mo/AC
Water content (wt.%)	8.10 ± 0.77	11.98 ± 1.10	6.12 ± 0.33	6.52 ± 1.30
pH	3.63 ± 0.06	3.48 ± 0.03	3.13 ± 0.01	3.50 ± 0.01
Carbon (wt.%)	65.13 ± 0.23	67.64 ± 0.98	64.29 ± 1.19	66.55 ± 1.94
Hydrogen (wt.%)	8.28 ± 0.36	9.30 ± 0.84	8.54 ± 1.14	8.72 ± 0.88
Nitrogen (wt.%)	1.55 ± 0.20	1.36 ± 0.02	1.29 ± 0.06	1.35 ± 0.04
Oxygen^b (wt.%)	25.04 ± 0.79	21.70 ± 0.15	25.88 ± 0.01	23.38 ± 1.09
HHV(MJ/kg)	29.65 ± 0.32	31.61 ± 1.17	31.50 ± 1.37	31.58 ± 1.08
DOD	63.60 ± 1.15	68.46 ± 0.23	62.39 ± 0.02	66.02 ± 1.59

^b Calculated by difference.

TABLE 6

Chemical composition analysis of upgraded bio-oils (OP) by GC-MS

Compounds	Raw	Ni/AC	Ni-Fe/AC	Ni-Cu/AC	Ni-Mo/AC
Relative content (%)	bio-oil				
Phenols	55.88	54.65	71.28	65.98	69.99
Alkyl-phenols ^c	0	0.86	33.84	31.46	38.41
Ethers	2.83	0	0.29	0	2.00
Ketones	8.55	0.68	0.63	0.36	1.87
Esters	3.98	0	0.36	0	2.61
Alcohols	7.49	3.2	1.67	5.72	3.40
Acids	3.05	0.43	0	0	0.46
Hydrocarbons ^d	8.78	39.42	24.98	26.60	16.37
Light hydrocarbons (C6-C12)	6.32	32.63	23.01	24.62	13.80
Heavy Hydrocarbons (C13-C35)	2.46	6.79	1.97	1.98	2.57

^c Alkyl-phenols are included in phenols

^d Sum of light hydrocarbons and heavy hydrocarbons

TABLE 7

NCG distributions of different treatments				
Gas (Vol.%)	Ni/AC	Ni-Fe/AC	Ni-Cu/AC	Ni-Mo/AC
H ₂	75.29	61.16	70.58	68.08
CO ₂	9.86	20.01	11.70	12.73
CH ₄	1.97	3.46	3.78	4.27
C ₂ H ₆	0.72	1.45	1.66	1.55
C ₂ H ₄	7.12	0.08	0.09	0.09
C ₃ H ₈	1.59	5.84	5.40	5.80
C ₃ H ₆	2.81	7.63	6.39	7.05
C ₄ H ₁₀	0.54	0.22	0.30	0.25
C ₄ H ₈	0.01	0.11	0.07	0.13
C ₅ H ₁₂	0.09	0.04	0.03	0.05

Figure captions

FIGURE 1

XRD patterns of different AC catalysts (a-AC, b-6% Ni/AC, c-6%Ni-6%Cu/AC, d-6%Ni-6%Fe/AC and e-6%Ni-6%Mo/AC)

FIGURE 2

TEM images of all metal AC catalysts (a-AC, b-6%Ni/AC, c-6%Ni-6%Cu/AC, d-6%Ni-6%Fe/AC and e-6%Ni-6%Mo/AC)

FIGURE 3

The histograms of particle size distribution for the four prepared catalysts: a-6%Ni/AC, b-6%Ni-6%Cu/AC, c-6%Ni-6%Fe/AC and d-6%Ni-6%Mo/AC.

FIGURE 1

XRD patterns of different AC catalysts (a-AC, b-6% Ni/AC, c-6%Ni-6%Cu/AC, d-6%Ni-6%Fe/AC and e-6%Ni-6%Mo/AC)

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TEM images of all metal AC catalysts (a-AC, b-6%Ni/AC, c-6%Ni-6%Cu/AC, d-6%Ni-6%Fe/AC and e-6%Ni-6%Mo/AC)

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