

STUDY ON CHARACTERIZATION OF Ni/BIOCHAR CATALYST DERIVED FROM MICROALGAL BIOMASS

Vuong Van Pham¹, Hong Khanh Dieu Nguyen^{2,*}

¹*Vietnam Oil and Gas Group, No. 18 Lang Ha street, Hanoi city*

²*Hanoi University of Science and Technology, No. 1 Dai Co Viet street, Hanoi city*

*Email: dieuhong_bk@yahoo.com

Received: 16 January 2016; Accepted for publication: 2 August 2016

ABSTRACT

Biochar supported nickel (Ni/biochar) catalyst was prepared by incipient wetness method and characterized by using a series of techniques such as XRD, SEM, TEM, FT-IR, H₂-TPR and BET. These characterizations indicated the catalyst structure and demonstrated its potential for applications in reduction – oxidation reactions in particular the HDO process.

Keywords: carbon supported nickel, HDO, microalgal biomass, biochar.

1. INTRODUCTION

Nowaday most of catalysts applied for hydrodeoxygenation (HDO) process belonged to those used for the hydrodesulfurization (HDS) process because of their correspondences in the reaction mechanisms. These catalysts contained various reduction metals such as Co, Mo or Ni supported on aluminium oxides, and the metals could be partially sulfurized for stabilizing their activity and avoiding the catalysts poisons [1]. The generation of catalysts still showed good activity for the HDO processes, but the expenses for preparations, stabilizations and activations considerably restricted their applications. On the other hand a series of different catalysts were also invented such as NiW, noble metal based catalysts and FeS, but the major disadvantages still be concerned to their complicate preparation processes and high cost [2 - 4].

Pyrolyzing of biomass could produce two kinds of main products including biochar and bio-oil; in which, the bio-oil as feedstock played an important role in the HDO processes, but the biochar has not been used effectively yet. In fact the biochar could be important for soil nutrition improvement at present days, but it could be also modified by different techniques for preparing catalysts or adsorbants in the chemical technology. The structure of biochar belonged to the intermediate between that of carbohydrates in the biomass and graphite with systems of condensed polycyclic aromatic rings [5]. This property provided the biochar the ability for easily modifying because of the high surface tension of the rings. This led to our idea to impregnating some active metals such as Ni, Co... on the biochar surface; then the as-synthesized materials could be applied in the HDO process of the mentioned bio-oil. The Ni portions generated after hydrogen reduction of the synthesized catalyst played a crucial role in the activity of the Ni/biochar catalyst because there were the high active metal sites located on the biochar support.

The idea approached a close loop process using the microalgal biomass as feedstock and producing the hydrocarbons as the main product.

In a previous paper [6], the biochar supporting Ni catalyst (Ni/biochar) was prepared through incipient wetness method. The catalysts activity was also tested in the HDO process with the feedstock bio-oil showing good performance when reducing a large amount of the beginning oxygen content from the feedstock to the products. In this paper, the catalysts characterizations were investigated for clarifying the correspondence between the catalysts structure and properties and its ability on oxygen removal in the HDO process.

2. EXPERIMENTALS

2.1. Chemicals and equipments

$\text{Ni}(\text{NO}_3)_2$ was purchased from Merck for directly using without any further purification. Biochar was obtained through thermal pyrolysis of microalgal biomass type *Botryococcus*. H_2/N_2 supplier was purchased from Shanghai Eternal Faith Industry Co., Ltd., China.

2.2. Preparation of Ni/biochar catalyst

The catalyst Ni/biochar was prepared in a previous paper [6] following the two-step procedure including pyrolysis of microalgal biomass, wetness impregnation of $\text{Ni}(\text{NO}_3)_2$ at mass percentage of 20 % onto biochar, calcination at 400 °C for 4 hours and reduction Ni^{2+} to Ni^0 using H_2/N_2 gas mixture at 400 °C for 3 hours. The impregnation was finished by vaporizing the rest of water for maintaining the Ni content in the final catalyst.

The Ni/biochar catalyst was applied in the HDO process using feedstock bio-oil obtained from the pyrolysis in other studies. In this paper the Ni/biochar catalysts were established by many techniques such as XRD, SEM, TEM, FT-IR, NH_3 -TPD and BET.

2.3. Techniques for characterizing the Ni/biochar catalyst

Many techniques including XRD, SEM, TEM, FT-IR, NH_3 -TPD, H_2 -TPR and BET were used in the study for characterizing the biochar and Ni/biochar catalyst. The XRD was recorded in D8 Advance – Bruker; the SEM and TEM images were collected using Field Emission Scanning Electron Microscope S – 4800 and JEOL 1100 respectively; the FT-IR spectroscopy was recorded using Nicolet 6700 FT-IR Spectrometer; the NH_3 -TPD and H_2 -TPR were measured in AutoChem II 2920 Micromeritics and Micromeritics AutoChem II 2920 V4.01 respectively and the BET method was established using Chem BET – 3000.

3. RESULTS AND DISCUSSION

3.1. XRD patterns

Figure 1 described the XRD patterns of the biochar and Ni/biochar catalyst. Observations exhibited that both biochar and catalyst existed in amorphous phases with high background intensity. The patterns also pointed out none of any crystalline phases although the $\text{Ni}(\text{NO}_3)_2$ content in the beginning mass ratio was up to 20%wt. There were two ways to explain this phenomenon: the first reason was that NiO and portions generated in the catalysts calcination

and reduction homogeneously distributed on the biochar surface with extreme thin layers not being detected by XRD detector; the second reason was that the NiO and Ni portions possessed the amorphous phases, or in the other hand, that could be said that the Ni portions on the surface existed in a metallic glass state [7].

The latter was more reasonable because BET surface area of the biochar was not high enough for extremely homogeneous distributions (referred to the results obtained from BET technique in 3.6), especially with very high content of the provided Ni precursor. Otherwise, there was a considerable difference in the background shape of the XRD pattern between the biochar and the catalyst caused by the different nature of amorphous phase of the Ni portions and the biochar. Incase of the mentioned homogeneous distribution, they should be the same.

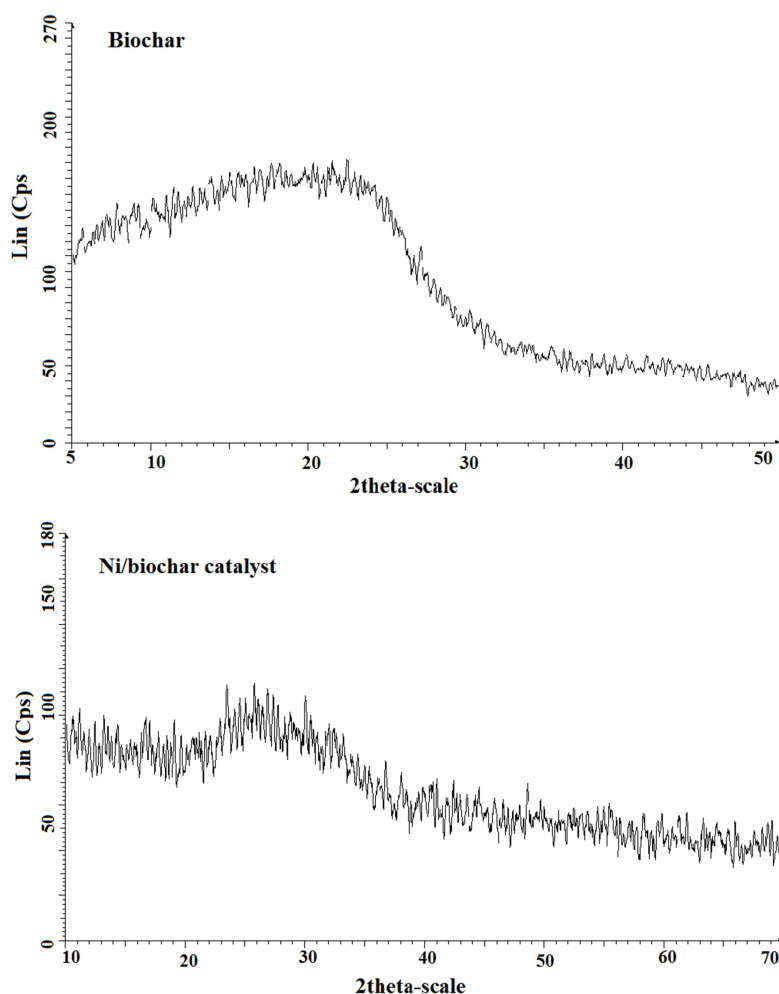
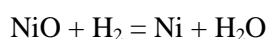


Figure 1. XRD patterns of biochar and catalyst Ni/biochar derived from microalgal biomass.

The decomposition reaction of the $\text{Ni}(\text{NO}_3)_2$ and the reduction of the NiO portions were illustrated as followed reaction equations:



3.2. SEM images

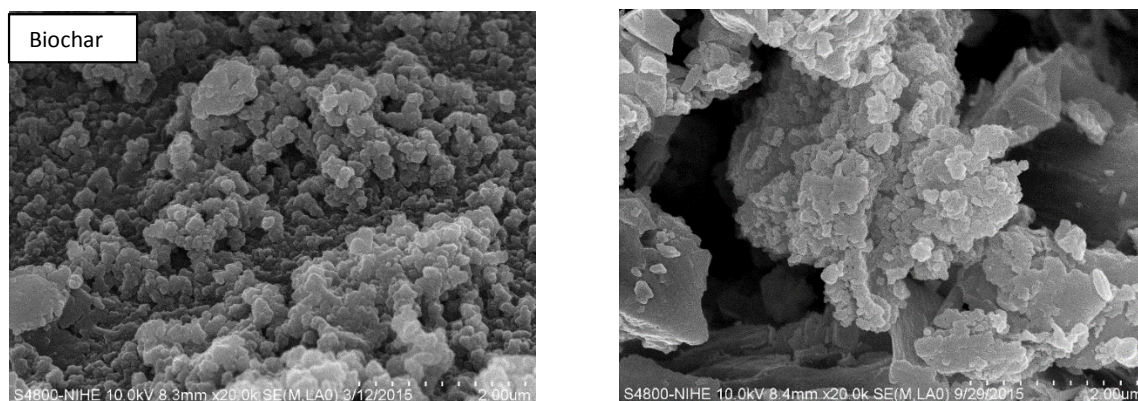


Figure 2. SEM images of the biochar and the Ni/biochar catalyst.

Figure 2 showed the SEM images of the biochar and the Ni/biochar catalyst. In the same implications, the SEM images clearly indicated difference in morphology of the two materials: the biochar mainly contained uniform 20 nm sized particles agglomerated together producing a large clusters while the Ni/biochar catalyst consisted of small thin size particles arranged in the layer structure beside the same clusters as the biochars morphology. The observations were well adaptive to the different background shapes of their XRD patterns confirming that the NiO and Ni portions on the catalyst surface existed in the amorphous states. The Ni distribution was well looked in the TEM images.

3.3. TEM images of the Ni/biochar catalyst

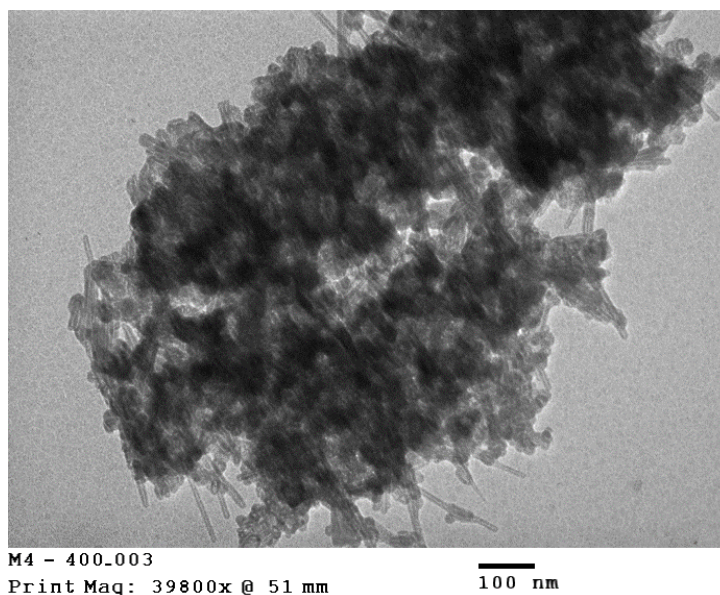


Figure 3. TEM image of the Ni/biochar catalyst.

Figure 3 showed the TEM image of the Ni/biochar catalyst. There was many dark regions distributed along with light background corresponded to the Ni clusters on the biochar surface respectively. The dark regions with size about 30 - 50 nm could be assigned for the agglomeration of the Ni metals during the calcination and the reduction of the Ni/biochar catalyst. An interesting observation was obtained when occurring some long bar morphologies indicating the formation of carbon nanotubes [7, 8]. This structure could be generated during the pyrolysis of the microalgal biomass. The carbon nanotubes possessed mesoporous structure, so they could be useful for increasing diffusion ability of the Ni clusters on the catalysts surface and avoiding the overagglomeration of the active sites during the calcination.

3.4. FT-IR spectroscopies

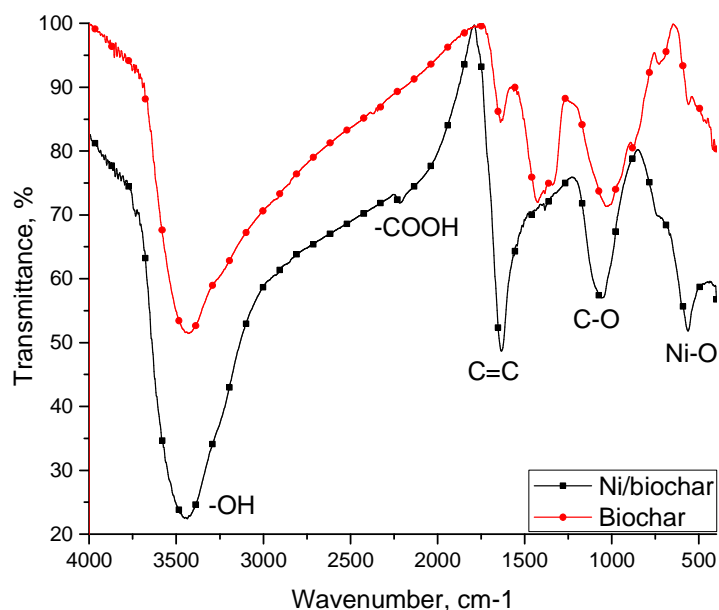
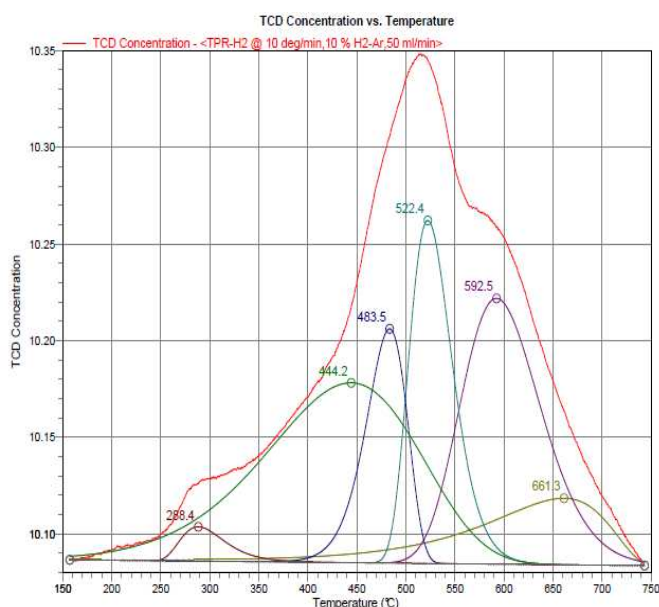


Figure 4. FT-IR spectroscopies of the biochar and Ni/biochar catalyst.

Figure 4 revealed the FT-IR spectroscopy of the biochar and Ni/biochar catalyst. The analysis results pointed out appearances of many the same organic groups in the polycyclic aromatic system of the biochar and catalyst including -OH phenolic groups at $\sim 3400\text{ cm}^{-1}$, -OH carboxylic acid at $\sim 2200\text{ cm}^{-1}$ and C=C aromatic rings at $\sim 1650\text{ cm}^{-1}$. These results reflected the same framework of the biochar and the catalyst. Especially with the Ni/biochar catalyst, there were additions of Ni-O vibration at $\sim 510\text{ cm}^{-1}$ assigning for a redshift from that of the bulk NiO at $\sim 460\text{ cm}^{-1}$ [9] demonstrating the appearance of Ni-O-C bonds formed by NiO and the support through oxygen bridges. The partial transference of electron density from Ni-O to the polycyclic aromatic system could be corresponded for this phenomenon. There was also an absence of Ni-C connections illustrating none of the carbon bridges occurring like Ni-C_{support} connections. In addition, the redshift could not be observed when considering the Ni-C_{support} because the Ni²⁺ portions always attracted the electron from the aromatic system through the conjugation effect reducing the electron density of this system.

3.5. H₂-TPR analysis



Reduction peaks °C	H ₂ consumptions, mmol/g
288.4	0.06943
444.2	1.28235
483.5	0.45003
522.4	0.68493
592.5	0.97467
661.3	0.40975

Figure 5. Diagram and results from H₂-TPR of the Ni/biochar.

NiO as a product of the decomposition of Ni(NO₃)₂ could be existed on the biochar surface either bulk or connected with support. Normally, the bulk NiO tended to agglomerate during the calcination because of their weak connection to the support producing the very large size clusters on the surface and lowering the activity of the catalyst in the oxidation-reduction reactions, particularly the HDO reaction. Contrarily, if the connections between the biochar and the NiO portions became too strong, the reduction of the NiO could be hard to establish and required high temperature for a long time – a critical factor for increasing the agglomeration of the active sites. Therefore, a suitable connection with intermediate bond energy between the biochar and the NiO was highly recommended; in which the reduction temperature ranged from 400 to ~500 °C. The H₂-TPR technique was applied to estimate this reduction ability of the catalyst, and this was also related to the activity of the generated Ni portions in the HDO process. The H₂-TPR diagram and results were described in Figure 5.

The results showed 6 reduction peaks corresponding to 6 states of the connections between the NiO and the biochar at different temperatures. In which, the peak at 288.4 °C could be assigned to the reduction of the bulk NiO portions weakly attaching to the support; the peak at 444.2 °C, 483.5 °C and 522.4 °C corresponded to the NiO portions connected with the biochar at medium strength through Ni-O-C_{support} (referred to the FT-IR spectroscopy analysis in 3.4); the peak at 592.5 °C and 661.3 °C characterized for the NiO portions with strong bonds with the support. As given mention above, the connections with medium strength between the NiO with biochar were the most suitable for the Ni/biochar catalysts activity. Assuming that all the NiO portions were reduced from Ni²⁺ to Ni⁰, then the generated Ni site density was equal to the moles of the consumed hydrogen during the reduction. Therefore, the amount of the suitable connected NiO portions with medium strength took an account for $(1.28235 + 0.45003 + 0.68493)/(0.06943 + 1.28235 + 0.45003 + 0.68493 + 0.97467 + 0.40975) = 62.44\%$ of the total amount of the NiO located on the biochar surface. The high percentage of the active NiO portions on the biochars surface considerably enhanced the catalysts activity in the oxidation-reduction processes.

3.6. BET measurements

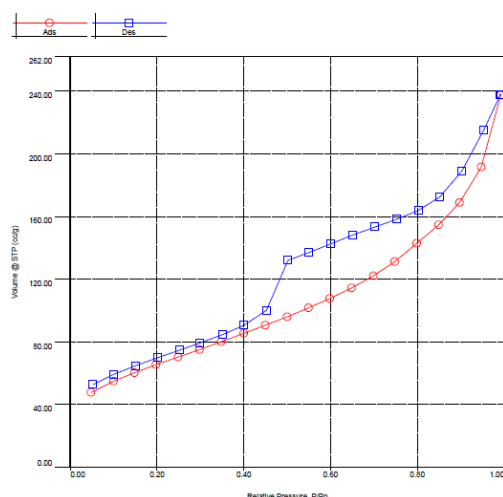
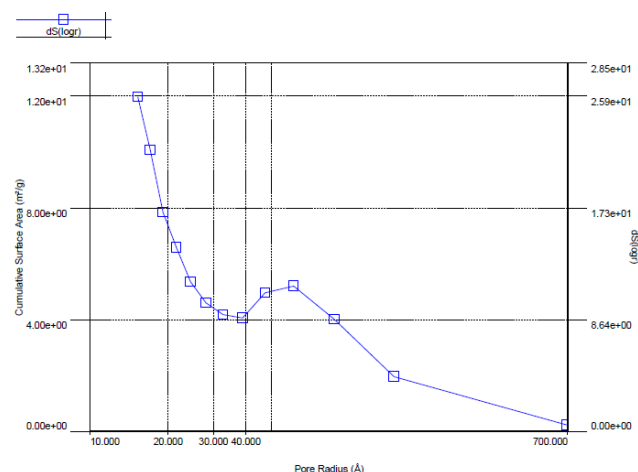


Figure 6. Adsorption – desorption isotherms of the Ni/biochar catalyst.



Hình 7. Pores distribution of the Ni/biochar catalyst.

The adsorption – desorption isotherm of the Ni/biochar catalyst indicated a large hysteresis between the adsorption and desorption isotherms including the characterization of the appeared mesoporous structure. The BET surface area reached $65.712 \text{ m}^2/\text{g}$ proved that the amount of the mesopores were not as high as some typical mesoporous materials such as MCM-41 or SBA-15. The pore distribution also confirmed these conclusions because it showed a range of pore diameters focusing at 40 \AA . The mesopores could be assigned for the generation of the carbon nanotubes observed in the TEM image of the catalyst. Otherwise, the pore distribution haven't concentrated on the narrow diameters demonstrating the amount of the carbon nanotubes was low.

4. CONCLUSION

The Ni/biochar catalyst possessed amorphous phases generated through combination of biochar, NiO and Ni clusters. The catalyst also contained a dominative amount of medium-strength interactions between the NiO clusters and the biochar through Ni-O-C connections. The texture and morphology properties of the catalyst showed the existence of mesoporous structure and a small suppressed amount of coexisted carbon nanotubes. The high content of the connected NiO portions located on the biochar surface could play an important role in strengthening the activity of the catalyst in the HDO process.

REFERENCES

1. Bulusheva D. A., Rossa J. R. H. - Catalysis for conversion of biomass to fuels via pyrolysis and gasification: A review, *Catalysis Today* **171** (2011) 1– 13.
2. Elliott D. C. - Historical Developments in Hydroprocessing Bio-oils, *Energy Fuels* **21** (2007) 1792-1815.

3. Wildschut J., Mahfud F. H., Venderbosch R. H., Heeres H. J. - Hydrotreatment of Fast Pyrolysis Oil Using Heterogeneous Noble-Metal Catalysts, *Ind. Eng. Chem. Res.* **48** (2009) 10324-10334.
4. Rocha J. D., Luengo C. A., Snape C. E. - The scope for generating bio-oils with relatively low oxygen contents via hydrolysis, *Org. Geochem.* **30** (1999) 1527-1534.
5. Rosalind E. Franklin - Crystallite Growth in Graphitizing and Non-Graphitizing Carbons, *Proc. R. Soc. Lond. A* **209** (1951) 196-218.
6. Vuong Van Pham, Hong Khanh Dieu Nguyen - Preparation of Ni/Biochar obtained from microalgal biomass for hydrodeoxygenation of pyrolysis oil, *Proceedings the 2nd International conference on Chemical engineering, Food and Biotechnology - ICCFB2015* (2015) 123-130.
7. Xian-fa Lia, Xue-gang Luo - Preparation of Mesoporous Activated Carbon Supported Ni Catalyst for Deoxygenation of Stearic Acid into Hydrocarbons, *Environmental Progress & Sustainable Energy* **34** (2) (2015) 607-612.
8. Göksel Özkan, Serdar Gök, Gülay Özkan - Active carbon-supported Ni, Ni/Cu and Ni/Cu/Pd catalyzed steam reforming of ethanol for the production of hydrogen, *Chemical Engineering Journal* **171** (2011) 1270– 1275.
9. Assem Barakat, Mousa Al-Noaimi, Mohammed Suleiman, Abdullah S. Aldwayyan, Belkheir Hammouti, Taibi Ben Hadda, Salim F. Haddad, Ahmed Boshala, Ismail Warad - One Step Synthesis of NiO Nanoparticles via Solid-State Thermal Decomposition at Low-Temperature