Reusability of Ni_2Fe_3 Metal Catalyst for Upgrading Pyrolyzed Bio-Oil from Cellulose

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Abstract Recyclable catalysts are desperately needed for upgrading pyrolyzed bio-oil which is produced from biomass conversion in order to reduce cost and protect the environment. However, most catalysts used for producing bio-oil from the pyrolysis of biomass cannot be recycled, leading to costly catalyst regeneration or waste if disposed of. In this study, Ni_2Fe_3 has been chosen as the model catalyst to test the recyclable property of the metal cluster catalyst system. Cellulose is used as the biomass model reactant. The results from pyrolysis experiments and GC-MS show that the catalytic property of Ni_2Fe_3 remains constant even after repeated experiments. From the analysis of bio-oil by GC-MS, the catalyst even shows slightly better performance with repeated use due to the pyrolytic interaction with cellulose during the experiment.

1. Introduction

Recyclable catalysts are attracting greater attention today due to increasing needs for greater cost-effectiveness of chemical transformations and overall productivity. Furthermore, recyclable catalysts also minimize environmental impact, ultimately contributing considerably to sustainable chemistry. Indeed, catalyst recycling fits the “principles of green chemistry” (Clark 1999; Anastas and Kirchhoff 2002; Poliakoff *et al.*, 2002; Horvath and Anastas 2007). Furthermore, the demand for useful homogeneous catalysts continues to increase every day due to the better activity and stability (Cornils *et al.*, 2017). Until now, various techniques and methods were developed. For instance, putting the immobilized catalyst precursor onto a support material, then the catalyst can be quantitatively separated by filtration and recycled (Müller, *et al.*, 2005; Song *et al.*, 2006). However, to date, only a few percentages of products are produced by homogeneous catalysis, especially for producing bio-oil. Most researchers use supported-catalysts to produce bio-oil or upgraded bio-oil, where the catalyst catalyzes the bio-oil vapors. For example, Lee’s group used Ni-based catalysts (Ni, Ni-Mo, and Mg-Ni-Mo)/activated charcoal (AC) to understand their catalytic effect on the yield and the quality of upgraded liquid fuel in supercritical ethanol (Lee *et al.*, 2019); Meunier’s group put Pt, Pd and Rh on alumina and used this catalyst to reformed some model compounds in order to investigate how they influence the products (Rioche *et al.*, 2005); Basagiannis’s group found that a catalyst consisting of Ru (5%) dispersed on 15% $\text{MgO}/\text{Al}_2\text{O}_3$ carrier exhibits high activity and selectivity in producing hydrogen (Basagiannis and Verykios 2007). However, all of this supported-catalyst will lose activity after the experiment, they cannot be recycled. There is a clear need to design and produce easily recoverable and recyclable homogenous catalysts. Based on our

knowledge and research activity, the cluster catalyst is an ideal choice.

A cluster is an ensemble of bound atoms or molecules that are intermediate in size between a molecule and a bulk solid. The metal cluster can also be used as a catalyst (such as $\text{Ru}_3(\text{CO})_{12}$, Au cluster, etc.); they sometimes also bound to some other metal or cluster (Oguri *et al.*, 2013). The cluster catalyst has extraordinary property, the absence of large bulk phases leads to a high surface-to-volume ratio, which is advantageous in any catalyst application as this maximizes the reaction rate per unit amount of catalyst material, which also minimizes cost. Other types of Nickel-based catalysts have been extensively employed in the industrial process of steam reforming because of their high activity and low cost (Cheng *et al.*, 2017; Ji *et al.*, 2017). Besides, the metal cluster catalyst has better physical properties, like large specific heat capacity and high thermal conductivity coefficient.

Considering potential large-scale applications, catalysts made of cheap and earth-abundant elements are crucial for economically viable energy conversion processes. Instead of using rare earth or expensive metals, it is better to focus on making catalysts with nickel and iron in order to build a new type of re-useable catalytic-cluster.

In this study, cellulose was chosen as the feed for pyrolysis, because it is the major component of biomass and often used as a model compound. Then, the Ni_2Fe_3 cluster catalyst (based on our group previous result) will be used for testing the recyclable property based on our previous test. The final goal of this study is to investigate the recyclable property of metal cluster catalysts in order to test its economic feasibility.

2. Experimental Method

2.1 Catalyst preparation and separation

The biomass feed, 38 μm powdered cellulose was brought from Wako Pure Chemical Industries, and cellulose was directly used without any modification.

The Ni_2Fe_3 catalyst was prepared by the sol-gel method, which produced a cluster structure (De and Tapfer, 1996; Jayaprakash *et al.*, 2015). The chemicals were ethylene glycol, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and citric acid, which also purchased from Wako Company (Osaka, Japan). The mol ratio between metal ion (Fe, Ni) and citric acid was 1:1.2. The preparation of catalysts was performed at room temperatures following: 14.5 g $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 6.97 g $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 40 ml distilled water and stirred for 4.5 hours. Then 6 ml of ethylene glycol and 13.4 g citric acid were added to the beaker. The transparent solution was stirred for 20 hours in order to prepare a uniform chemical solution. The transparent sol was dried at 110°C in an oven for 26 hours. Next, using a furnace, it was calcined at 700°C for 6 h to burn off hydrocarbons in flowing 95% N_2 , 5% H_2 gas. Finally, the catalysts were crushed into powder using a mortar and pestle.

After each experiment, the catalyst would be separated with char by physical method, using a magnetic and aluminum plate. Then using this catalyst in the next experiment.

2.2 Pyrolysis method

Cellulose (5 g) was loaded in a 50 mm diameter quartz tube reactor mixed with the catalyst (5 g). The entire system was purged with flowing nitrogen gas for 4 min in order to expel all air. Afterward, the reactor was heated to the set temperature (450°C) with a heating rate of $45^\circ\text{C}/\text{min}$ in flowing N_2 gas. Nitrogen gas carried the pyrolyzed vapors from the reactor to the condenser.

Figure 1. Experimental set-up for pyrolysis reaction

The vapors were condensed using cold water in the condenser. The bio-oil was collected and analyzed by GC-MS. The char and catalysts were separate, finally using this catalyst to repeat the above experiment, multiple

times. The amount of bio-oil and char & coke were weighed, and then the amount of gas was calculated by subtracting the amount of bio-oil and char & coke from the initial feed (Figure 1).

2.3 XRD, BET and SEM test

XRD analysis of catalysts was conducted by X-ray Diffractometer (Mini Flex 600, Tokyo, Japan). 45 kV and 15 mA were used for the X-ray tube operation. The scan range (2 theta) of the XRD pattern was collected from 5° to 90° using filtered Cu radiation.

Specific surface areas were measured using the Brunauer-Emmett-Teller method with N_2 (BEL SORP mini; Bel Japan Inc., Tokyo, Japan).

Images of catalysts were obtained by a scanning electron microscope (VE-9800, Tokyo, Japan) operated at 10 kV. The glass slide washed by ethanol to get clear images. Then the samples were loaded and dried on a copper grid (carbon-coated) before the test.

2.4 GC-MS analysis method

In order to identify compounds and analyze the composition of the bio-oil samples, GC-MS equipment was used to analyze bio-oil samples. The analysis was performed on a GC-2010 Plus equipped with a GC-MS-QP2010 SE mass-detector made by Shimadzu Corporation (Tokyo, Japan). The column type was Stabilwax-DA 30 m x 0.25 mm, 0.25 μm diameter (Bellefonte, U.S). The analysis was run with a 10 : 1 split entry. The oven temperature was held at 40°C for 5 min and then ramped to 50°C at $1^\circ\text{C}/\text{min}$. Next, it was ramped to 130°C at $2^\circ\text{C}/\text{min}$. Finally, the temperature was ramped to 260°C at $4^\circ\text{C}/\text{min}$ and held for 10 min. The compounds were identified by comparing the mass spectra to NIST 11 MS library of compounds using the GC-MS software. A similarity threshold of over 80 was used to identify the compounds. All GC-MS experiments were conducted in duplicates, and the standard deviations were calculated.

3. Results and Discussion

3.1 XRD and SEM analysis

X-ray diffraction patterns of all catalysts powder samples are shown in Figure 2. The first time represented the catalyst after the first experiment; the second time represented the catalyst after the second experiment (the same condition as the first experiment, the catalyst was used again after separation.) Figure 2 indicated that the XRD pattern agreed well with each other, and after comparing the used catalyst and unused catalyst showed the catalyst XRD pattern was unchanged during pyrolysis experiments and the catalyst can be recycled. Meanwhile, there were not any spurious diffraction

Figure 2. XRD patterns of unused and used catalysts.

peaks observed in the patterns, indicating no other impurity component and the sol-gel method was reliable for producing cluster structures. It should be noted that previous literature on the synthesis of bimetallic catalysts (Ni, Fe) only exhibited a single peak indicating the formation of a Ni-Fe solid solution (Nie, de Souza et al. 2014). The intensity of XRD peaks of the sample in Figure 2 reflected that the formed particles were crystalline and broad diffraction peaks indicated very small size crystallites.

The SEM images are shown in Figure 3, were of a typical particle with an uneven surface. A powder-like structure usually exhibited better catalytic properties as indicated previously (Yao *et al.*, 2014). From the images, it is easy to see that the pure

Figure 3. SEM images of a) unused and b) used (after 5 experiments) catalyst particles

Figure 4. Bio-oil, gas and char&coke yields from pyrolysis of cellulose without and with recycled catalyst

metal clusters did not have a large surface area due to consisting of many small clusters. BET results confirmed that the surface area was relatively small, only $\sim 2 \text{ m}^2/\text{g}$. Additionally, the particle size was the same after the experiment, which means the catalyst particles did not change, corresponding to XRD results.

3.2 Pyrolysis Results

3.2.1 Yield results of pyrolysis

The catalysts were mixed with the cellulose directly. The bio-oil and char & coke were weighed, and yields were calculated after each pyrolysis experiment. Figure 4 shows the bio-oil mass yields of the different experiment time. The gas yield was calculated by subtracting the mass of bio-oil and char & coke from the initial mass of cellulose. Each experiment was conducted more than one time to measure the repeatability.

The bio-oil yield from uncatalyzed cellulose pyrolysis was 39.2% and had a standard deviation of 0.8%. The yield with the catalyst for the first experiment was 47.2%, and 46.8% for the second experiment, 46.9% for the third experiment, 47.3% for the fourth experiment and 47.1% for the fifth experiment. From the results, it was obvious that the used catalysts can still improve the yield of bio-oil, which is an important property, because other catalysts have show decreased bio-oil yields, like ZSM-5, ZrO_2 & TiO_2 , and silica (Stefanidis *et al.*, 2014; Xia *et al.*, 2015; Behrens *et al.*, 2017).

The reason for the bio-oil yield increase was due to the difference in specific heat capacity and thermal conductivity coefficient. Specific heat capacity was the amount of heat energy required to raise the temperature of a substance per unit and the thermal conductivity coefficient indicates the rate of heat transfer. The specific heat capacity was 0.38 kcal/kg.k for cellulose, 0.11 kcal/kg.k for Ni, 0.11 kcal/kg.k for Fe (ToolBox, website), respectively, which means no matter composition of nickel and iron both can increase its temperature quickly, the heated metal can help transfer heat uniformly to the cellulose. The thermal conductivity coefficients are (Madelung and White 1991) (see Table 1), 0.23 W/m.K for cellulose, 73.3 W/m.K for Ni, 61.6 W/m.K for Fe and were used estimate

Table 1. Specific heat capacity and thermal conductivity coefficients for cellulose, Ni metal, Fe metal and cellulose with NiFe catalyst (SHC represents specific heat capacity, (kJ/kg.k); HCC represents thermal conductivity coefficient(W/m. °C))
 $\bar{X} = \frac{x_1fr_1 + x_2fr_2}{2}$, $\bar{X}$ used to define the mix thermal conductivity coefficient compound of cellulose and Ni₂Fe₃, x represents the thermal conductivity coefficient of compounds, fr represents the ratio of compounds

	SHC (kcal/kg.k)	HCC (200°C) (W/m. K)	HCC (300°C) (W/m. K)	HCC (400°C) (W/m. K)
Cellulose	0.38	0.23		
Ni	0.11	73.3	64.0	59.3
Fe	0.11	61.6	54.7	48.9
Cellulose+Ni ₂ Fe ₃		12.48

Figure 5. The relationship between bio-oil yield without catalyst and with catalyst for repeated use up to 5 times

for calculation of 22.2 W/m.K for the Ni₂Fe₃ catalyst mixed with cellulose. Ni and Fe coefficients are nearly 120 times higher than that of cellulose, which means for cellulose without a metallic catalyst being present, heat transfer from the reactor furnace to the cellulose is relatively poor. Some hot spots may develop in the cellulose during experiments, which tends to produce gas. However, after adding a NiFe catalyst, the thermal conductivity coefficient is enhanced 50 times, which can help transfer heat well and cause a uniform temperature profile which increases the bio-oil yield (see Table 1). There maybe some additional reactions that occur during the experiment that also enhance the yield, which will be investigated in future work

From Figure 5, it appears that the yield of bio-oil did not change, which means the NiFe metal cluster catalyst did not lose activity after experiments. It was a very important property for the catalyst if the catalyst can be recycled and costs can be minimized while improving reaction efficiency can be achieved due to reduced need to replace the catalyst.

3.2.2 GC-MS results of cellulose results

In order to know the composition of the bio-oils, the GC-MS equipment was used for analyzing all the bio-oil samples. The results of the identified peaks are presented below in Table 2. On average, 3% of the peaks were unidentified. Because the pyrolysis of cellulose resulted in hundreds of compounds, it was hard to list all of them. The compounds were classified into different groups based on their functional group. These groups were classified as acids, alcohols, furans, esters, hydrocarbons

(HC), ketones, phenols, sugars, and others. Table 2 shows the major product of uncatalyzed cellulose were sugars (47.7%), ketone (17.5%), furans (20.7%), and acids (4.9%). In this study, phenolic compounds were also found in uncatalyzed cellulose pyrolysis bio-oil, which is the same as other researcher's results (Behrens *et al.*, 2017). Other main components of the bio-oils derived from noncatalytic and catalytic pyrolysis of cellulose were in good agreement with the literature results (Fabbri *et al.*, 2007; Lu *et al.*, 2011; Xia *et al.*, 2015).

In order to investigate if the property of catalyst would change or not after experiments, each group would be discussed in detail below. The data showed the relationship between the bio-oil component and the number of experiments in Figure 6 (based on averaged data).

First of all, in Table 2, the data indicated that hydrocarbon (HC) was formed, which is an excellent component to improve the quality of bio-oil although the ratio is only 1%.

Secondly, all catalysts reduced acid and sugar composition which is a favorable property. Acids reduced the pH value of bio-oil, corroding common metals such as aluminum, mild steel, brass and so on. So it had an adverse effect on the quality of bio-oil. Reducing sugar can improve the quality of bio-oil due to their large oxygen content, the results agreed well with other studies that sugar was possible to be removed by catalysts (Wang *et al.*, 2016; Behrens *et al.*, 2017). Figure 6 showed the relationship between several experiments and the composition of bio-oil. It is clear that the NiFe metal cluster catalyst still works well after repeated experiments. Reduced sugar percentage from 47.7% to 30.5%, acid from 5% to 2.5%. Furthermore, the property of the catalyst showed a slight improvement after the first time experiment, similar to other group's results (Liu *et al.*, 2019). After mixing used catalysts and bio-char, they obtained better results.

Third, Figure 6 showed that catalysts lead to an increase in furan and ketone percentage. The reason why we focused on ketone content was that many methods can change the ketone to hydrocarbon compounds to improve the quality of bio-oil as the chemical reaction advance (King *et al.*, 2015; Mehta *et al.*, 2015; Ly *et al.*, 2017). So it is a favorable result for the bio-oil composition to have increased ketone concentration. Increased furan concentration is also good for bio-oil, since it can improve the combustion value.

Table 2 Composition of cellulose pyrolysis products without catalyst versus number of repeated catalyst experiments (peak area % of identified peaks, hydrocarbon (HC) compounds, unidentifiable compounds were classified as others)

sample	Acid%	Alcohol%	Esters%	Furans%	Ketone%	Phenols%	Sugar%	HC%	Others%
None	4.9±0.2	2.3±0.1	2.0±0.1	20.7±0.7	17.5±2.6	1.7±0.4	47.7±0.2	0	2.1±1.2
1st time	3.0±0.3	2.3±0.1	2.4±0.2	25.9±0.7	29.7±0.8	2.2±0.2	31.5±0.6	0.5±0.4	2.4±0.4
2nd time	2.1±0.2	2.5±0.3	3.4±0.9	25.4±1.1	29.9±1.1	2.1±0.6	30.0±0.3	1.1±0.8	3.5±0.4
3rd time	2.0±0.1	2.3±0.4	3.8±0.2	25.6±1.1	29.4±1.1	2.5±1.0	30.3±0.7	1.4±0.1	2.7±0.5
4th time	1.9±0.1	2.4±0.2	3.2±0.4	26.0±0.3	29.6±0.4	2.9±0.2	30.7±0.3	0.7±0.5	2.6±0.3
5th time	1.8±0.5	2.4±0.7	3.2±0.4	25.7±1.2	30.0±3.5	2.6±0.4	30.2±2.4	1.1±0.8	2.9±0.2

Figure 6. Chemical relative compositions of the organic phase of bio-oil without catalyst and after repeated catalyst use up to 5 times

Finally, the catalyst did not affect the phenol, alcohol, and ester amounts. The phenol compounds are usually formed from secondary reactions of the cellulose vapors (Stefanidis, Kalogiannis et al. 2014; Wang, Ma et al. 2016), which is why it did not change a lot in this study. Based on the above analysis, the following reaction pathway is proposed. The cellulose decomposed into sugar first, and then the sugar decomposed further into acid, furan, and ketone compounds. The same mechanism has been proposed in our previous study (Li, Cheng et al. 2020). We believe this reaction sequence can help explain the composition of the pyrolyzed bio-oil and catalyst interaction.

4. Conclusion

The Ni_2Fe_3 cluster catalysts were prepared by the sol-gel method successfully and the recyclable property was tested. The results indicated a new potential type of stable recyclable catalyst can be used for pyrolysis and the yield of bio-oil and composition was also stable after

repeated experiments. This Ni_2Fe_3 cluster catalyst also showed a different reaction pathway when compared to other supported catalysts in the literature, directly transferring heat to the biomass while catalyzing the vapors. Furthermore, this cluster catalyst can reduce catalyst costs due to its recyclability since it is easy to separate from char.

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