Effect of Ni/Co vermiculite as catalysts for Catalytic pyrolysis of plastic wastes

Yiqian Wang1,a, Zhipeng Sun1,b*

1 Materials and Energy school, Guangdong University of Technology, Guangzhou, Guangdong, 511400, China

*aemail: 540541720@qq.com,

*bZhipeng Sun email: zpsunxj@gdut.edu.cn

Abstract. In this study, the modified vermiculite adjusted with Ni and Co for pyrolysis of plastic is characterized by X-ray diffraction (XRD) and Brunauer Emmett Teller (BET). These results indicate that the ratio of Ni and Co can affect the surface area and pore diameter of catalyst. In addition, the results of GC show that Ni and Co not only have a good selectivity of C3, the main gaseous hydrocarbons of pyrolysis products, but also play an important role in dealing with low quality of oil products of plastic pyrolysis by controlling the concentration of metal oxide particles in the vermiculite layer. The adjustment of the molar ratio of Co and Ni can optimize the hydrogenation/dehydrogenation of metal active sites. It means that the greatly catalytic activity of supported Ni and Co catalysts is caused by moderate total acidity, relatively high surface area, and uniformly dispersed oxide particles on vermiculite support. Therefore, it suggests that adopting the clay catalyst is an efficient and environmentally friendly way to produce valuable products in pyrolysis of plastic waste.

1. Introduction

Plastic products play a significant role in daily life and industrial production because of its excellent comprehensive properties, convenient processing, cheap and easily available material. Considering the serious environment pollution and energy waste caused by the plastic, it is necessary to apply efficient technological method to recycle the plastic and greatly increase the added value of waste plastics. The pyrolysis reaction product, hydrocarbons, is often used as an alternative fuel or as a raw material for producing high value-added chemical products. Besides, the distribution range of cracked products can be narrowed and the proportion of valuable hydrocarbons (such as aromatics) has been significantly increased by selecting suitable catalysts, which is of great significance for increasing the added value of waste plastics.

Thus, the choice of catalyst is the key to the catalytic cracking reaction. Research on effective and economical catalytic for plastic is receiving increasing attention in the last years. There are many homogeneous lewis catalytic materials, such as commercial fluid catalytic cracking (FCC) catalysts [1], metallic oxides [2], zeolites [3], silicon aluminum catalyst (SiO2-Al2O3), mesoporous molecular sieves AI-MCM-41, FSM-16, Al-SBA-15, which both rely on the acidic sites on the catalyst to provide catalytic activity. Moreover, such catalysts can increase the contact area between catalyst and waste plastic melt and selectively promote the dehydrogenation of aromatic owing to its own rich pore structure and specific surface area. However, these catalysts in the pyrolysis may generate coke which will be deposited into the catalyst aperture, greatly reduce the catalyst activity and even loss activity [4].
It is reported that a series of mono/bimetallic ions modified catalysts have been applied in catalytic pyrolysis and found that the catalytic activity of Fe/Cu-Al-MCM-41 is higher than Al-MCM-41. Additionally, the effect of ZSM-5 molecular sieve modified with Ca and K show that Ca not only effectively control the hydrogen transfer reaction and inhibit the generation of aromatic hydrocarbons, but also promote the occurrence of dehydrogenation decomposition. It inspired us that adjusting texture structure by introducing metal, can control pore size and the acidic acidity of the catalyst, which have important influence on the composition of the liquid fuel and can enhance the yield of fuel oil product and promote the production of H2 [5, 6].

In this study, we chose modified vermiculite as catalyst support, Co, Ni as active components to crack mixed waste plastics. The crystal structure and surface area of the catalyst which are the key characters were adjusted by the amount ratio of the cobalt nickel substance in the chemical carrier. The study included: (i) characterization of catalysts using BET, XRD, (ii) study on the effect of different catalysts on the composition and yield of pyrolysis products.

2. Experimental

2.1. Materials
10.7g PE (polyethylene) mixed with 4.3g PP (Polypropylene) used for the experiments because of the proportion was similar with the composition of plastic waste in daily life. The materials were used for the pyrolysis experiments in pellet size. Bipyridine, Cobalt nitrate hexahydrate, Nickel Nitrate were purchased as analytical grade chemicals and all experimental solutions were prepared by distilled water.

2.2 Catalyst preparation
Vermiculite is a clay mineral with special layered and stable interlayer cations [7]. According to previous study, the modified vermiculite can expose most of acidic sites, it is beneficial to introduce active metal sites for the modified vermiculite because vermiculite surface is easy to adsorb metal cations to balance the negative charge increased by the lost interlayer cations [8]. So modified vermiculite was chosen as the support. The introduction of Ni and Co were prepared by heating synthesis with aqueous solutions of CoSO\textsubscript{4}ꞏ7H\textsubscript{2}O and NiSO\textsubscript{4}ꞏ6H\textsubscript{2}O as precursors. Modified vermiculite was loaded with different concentration metallic compounds including the concentration of nickel once, twice and triple times higher than that of cobalt (designated as Ni/Co(I)-Verm, Ni/Co(II)-Verm, and Ni/Co(III)-Verm). Finally, the catalyst was obtained by centrifuging, drying at 80°C and calcining at 650°C for 2h.

2.3. Catalysts characterization
In this study, we used ASAP 2010 (Micromeritics) automated gas adsorption system to determine textural parameters of the samples. The surface area was determined using the BET models, when the distribution of mesopores was determined using the BJH model. Additionally, the crystal structure of materials was determined form XRD patterns equipped a Bruker D8 Advance diffractometer. Pyrolysis liquids and gas were also analysed by gas chromatography (GC), which was based on comparison of the retention times with those of calibration samples to identify the constituents.

3. Results

3.1. BET and XRD results
The textural parameters of Ni and Co based on the catalyst material was showed in Table 1. According to Table 1, with the increasing of the ratio of Ni and Co, the surface area and the pore size decreased. Ni/Co(I)-Verm has the maximum surface area among these samples, its surface area could be up to 52 m\textsuperscript{2}/g while the pore diameter was 5.9 nm. Comparing with that, Ni/Co(II)-Verm has 35.1 m\textsuperscript{2}/g surface area and 2.9nm pore size, and Ni/Co(III)-Verm has 31.3 m\textsuperscript{2}/g surface area and 2.7nm pore size,
respectively. It meant that water bath heating of the modified vermiculite loading with Ni and Co had a moderate effect on the porosity characteristics of material. There was slight loss of the surface area and meso/macropore volume in the case of the increasing of ratio of Ni and Co, which might be mainly attributed to the micropores blockage caused by metal phases embedded in crystalline vermiculite. As shown in Figure 1, X-ray diffractograms (XRD) of metal-modified vermiculite catalysts and the corresponding metal oxide phases were measured to study their crystallinity. After loading with Ni and Co simultaneously, catalysts presented diffraction peaks which were consistent with the characteristic peaks of Ni-Verm. The crystallization degree of diffraction peaks at 9.1°decreased with the extended molar ratio of Ni and Co. And the corresponding peaks attributed to Ni species in the catalyst were identifiable while the we could see that there were no obvious peak corresponding to Co-Verm. It might be due to the content of Ni was larger than Co. Therefore, the dispersion of Ni seems to depend more on loading degree as compared to Co, because the peaks due to Co in the Ni/Co(II)-Verm and Ni/Co(III)-Verm catalyst could be hardly identified. Furthermore, according to previous study, the crystallites of metallic Ni after the pyrolysis reaction exhibited much smaller size compared to the size of Co in the catalyst, which may result in the broad of the peak at 9.1°.

Table 1. Textural properties of different catalysts.

| Catalyst       | S_{bet} (m^2.g^{-1}) | V (cm^3.g^{-1}) | Pore diameter (nm) |
|----------------|----------------------|-----------------|-------------------|
| Ni/Co(I)-Verm  | 52                   | 0.13            | 5.29              |
| Ni/Co(II)-Verm | 35.1                 | 0.07            | 2.9               |
| Ni/Co(III)-Verm| 31.3                 | 0.06            | 2.7               |

Figure 1. XRD spectrum of modified vermiculite after different metal concentration

3.2. Pyrolysis yields

Table 2 showed the gas composition (detected by GC) before and after catalyst. Comparing with no catalysts, the composition of oil products cracked by catalyst mainly concentrated on Light hydrocarbons. The pyrolysis gas was mainly composed of C{sub}1-C{sub}5 mixed gaseous hydrocarbons. It could be seen that C{sub}3 was the main fraction of pyrolysis gases in catalytic pyrolysis. The fraction of C{sub}3 increased from 47.2 wt% produced by no catalyst to 59.0 wt% produced by Ni/Co(II)-Verm. The result showed that among the current tested catalysts, Ni/Co-Verm had higher C{sub}3 yields whatever the ratio of Ni and Co. This might be due to the acidity of these catalysts, which was influenced by the
content of the Ni. In addition, Ni and Co presented a particularly high selectivity for the heavy hydrocarbons fraction as shown in Table 3. It is also worth mentioning that when the ratio of Ni and Co increased, the content of heavy hydrocarbons increased from 49.8% to 61.3%, which is higher than pure Co-Verm, but lower than Ni-Verm. The results further indicated the controlling effect of metal ion. Since it is well-known that the hydrocarbons in the range of \(>\text{C}_{13}\) are representative of diesel products, the modified Ni/Co catalysts have the good potential to be applied in producing valuable diesel fuel from plastic waste.

| Table 2. Composition of the pyrolysis gas (vol%) |
|------------------------------------------------|
|       | CH\(_4\) | C\(_2\) | C\(_3\) | C\(_4\) | C\(_5\) |
| No catalyst | 6.6 | 12.8 | 47.2 | 10.6 | 22 |
| Co-Verm | 3.1 | 17.0 | 38.6 | 5.6 | 35.6 |
| Ni-Verm | 7.8 | 14.4 | 51.3 | 10.9 | 14.7 |
| Ni/Co(I)-Verm | 7.4 | 13.3 | 49.2 | 12.4 | 17.2 |
| Ni/Co(II)-Verm | 8.6 | 17.7 | 59.0 | 5.8 | 16.6 |
| Ni/Co(III)-Verm | 8.6 | 15.6 | 57.4 | 4.8 | 16.9 |

| Table 3. Main components of the oil product determined by GC (% area) |
|------------------------------------------------|
| Light hydrocarbons (\(\leq\text{C}_{13}\)) | heavy hydrocarbons (\(>\text{C}_{13}\)) |
| No catalyst | 84.7 | 15.3 |
| Co-Verm | 53.2 | 46.8 |
| Ni-Verm | 35.6 | 64.4 |
| Ni/Co(I)-Verm | 50.2 | 49.8 |
| Ni/Co(II)-Verm | 38.7 | 61.3 |
| Ni/Co(III)-Verm | 44.5 | 55.5 |

4. Conclusions
In summary, we reported that the pyrolysis reaction was conducted by modified vermiculite supported Ni and Co catalysts prepared by water bath heating. These Ni/Co based catalysts exhibited excellent catalytic activity and selectivity, evidenced by the increased generation of C\(_3\) and a large amount of diesel fraction in the oil product. The BET and XRD characterized their respective characteristic textural properties, which illustrated the correlation between the structure textural properties with the pyrolysis product. Furthermore, it revealed that the vermiculite was desirable catalyst support due to high thermal stability and existence of various hydrated interlayer cations by pathway in pyrolysis. It inspired us that the application of metal modified clay catalyst played an important role in recycling of a variety of municipal solid waste.

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