Application of Co Ni intercalated vermiculite catalyst in pyrolysis of plastics

Zicai Chen¹,a, Yiqian Wang¹,b, Zhipeng Sun¹,c*
¹Materials and Energy school, Guangdong University of Technology, Panyu, Guangzhou, P.R China
email: 583998968@qq.com, bemail: 540541720@qq.com
*Zhipeng Sun: cemail: zpsunxj@gdut.edu.cn

Abstract: Currently, the amount of municipal solid wastes that are hardly degradable in nature keep increasing, of which the waste plastics account for a large proportion. There is no doubt that it will generate severer environmental issues. Therefore, we are expected to develop an efficient way to recycle the useful components in the mixed plastics to reduce the waste of energy and protect the environment. Thermal cracking, as a key technology for plastic recycling, can convert plastics into high value-added fuel products and broaden the sources of raw materials for ethylene, propylene and high value fuel production. For general catalysts, its catalytic activity is affected not only by the specific surface area and pore volume, but also by the acidity. In this paper, we try to construct an adjustable acidity catalyst by adopting vermiculite as the support, and sodium chloride, cetyltrimethylammonium bromide as modifier. That can provide exposed environment for the active sites in the bulk phase. At the same time, cobalt and nickel were used as intercalation to load on vermiculite. Ultimately, we obtained BET, XRD characterization data to determine the structure and properties of the catalyst, and analyzed the cracking products by GC quantitatively and qualitatively to build a reasonable structure-activity relationship.

1. Introduction
With the progress of the times, the role and status of energy can not negligible. However, due to the exhaustion of fossil energy and increasingly severe environmental problems, it is urgent to develop environmental and friendly solid waste recycling technology [1]. Plastics are widely used in all walks of life because of that easy for processing, carrying, transporting, and that low cost, durability and resistance to corrosion [2]. Nonetheless, the recycling of plastics is limited by the diversity of its sources and the complexity of its composition. The traditional plastic recycling methods are mainly incineration, landfill and thermal cracking [3]. The incineration process is prone to produce various toxic gases to pollute the environment. And the landfill method produces harmful substances which will pass through the soil and water cycle, polluting the soil and water quality, and even flow into human body through the biological chain [4]. Therefore, scholars have conducted a series of research and proposed feasible waste plastic recycling methods, one of which is thermal cracking. It can improve the recycling efficiency of waste plastics by controlling the thermal decomposition and reaction atmosphere [5]. This waste plastic recycling treatment method can not only reduce the reaction temperature and shorten the reaction time, but more importantly, the product fractions obtained from the plastic cracking are concentrated, high octane number, low wax content, so that the oil quality is greatly improved [6]. Of course, these methods also have some drawbacks. For example, the thermal cracking process is also prone to coking, which is easy to block the outlet ports and may cause the catalyst to fail [7]. Therefore,
the use of suitable catalysts can reduce the energy barrier of the cracking reaction, promoting the cracking reaction more completely, and convert the traditional form of thermal cracking into high-efficiency and high-yield catalytic thermal cracking [8]. The development of this technology not only alleviate the shortage of petrochemical energy supply, but also solve the problem of “white pollution” caused by plastics, realizing the dual benefits of energy and environment.

2. Experimental

2.1. Materials
The plastic mixture used for the experiments were composed of polyethylene (PP), polypropylene (PE), PP:PE=1:2.5. The reason with these two components were used is that most plastic products in China are mainly composed of that and most of these two components exist in a mass ratio of 1:2.5. Vermiculite (325 mesh), cetyltrimethylammonium bromide, tetraethyl silicate , titanium isopropoxide, toluene, 2,2-bipyridine, nickel nitrate hexahydrate, cobalt nitrate hexahydrate, polyethylene, Polyethylene and other chemicals were commercially available.

2.2. Catalyst preparation

2.2.1 Modification of vermiculite.
Acidity vermiculite: 3g of pure vermiculite was placed in a 200ml three-necked flask, adding 100ml of DI water, and then added 10ml of dilute hydrochloric acid (38wt%) into 80°C water bath, stirring at 400rpm for 12h. Acidity vermiculite was gotten after centrifuging and drying. Sodium vermiculite: the acidified vermiculite was put in a 200ml three-necked flask, adding 100ml of saturated sodium chloride solution and heating in a water bath at 80 degrees. Stir at 400rpm for 12h, then centrifuged and dried to get sodium vermiculite. Organic vermiculite: The sodium vermiculite was placed in 0.1M CTAB solution, stirring at 80℃ for 12h, then dissolved the dry sample in tetraethyl silicate.

2.2.2 Metal intercalation.
(1) Cobalt intercalation of vermiculite: 1.25mmol cobalt nitrate dissolved in 150ml DI water, then mixed with solutions which was 11.25mmol bipyridine in 20ml absolute ethanol, finally adding titanium intercalation sample, and stirring at room temperature. After that, the sample was collected by centrifuging, drying at 80°C and baking at 600℃, which the heating rate was 10℃/min, and roasting for 3h. (2) Nickel intercalation of vermiculite: Added titanium intercalation sample to the solutions and mixed the same concentration nickel sulfate with bipyridine solution, stirring at room temperature, centrifuge, dry at 80°C ,and then fired at 600°C. (3) Cobalt-nickel intercalation of vermiculite: 0.625mmol cobalt nitrate with 0.625mmol nickel sulfate dissolved in 150ml DI water, mixing 11.25mmol bipyridine solution and adding titanium intercalation sample, ang then repeating the above steps.

2.3. Catalyst experiment
The reactor was a TL-1200 tube furnace (purchased by Nanjing Bo Yun Tong Instrument Co., Ltd.), and the catalyst and plastic samples were at a ratio of 10% (mass fraction) (plastic catalyst was constant throughout the experiment). The weight of each plastic sample was about 15g each time. First, the system heated to 300°C at a rate of 30°C/min and kept it warm for 10 minutes. Then, the temperature increased to 480°C at a rate of 10°C/min, and then kept it warm for 20 minutes.

3. Results

3.1. XRD analyse
In this study, X-ray diffractometer was used to detect and characterize the modified vermiculite samples. To study its characteristic peak, the 2θ angle range was from 1° to 60° as shown in Fig. 1. By comparing
the original XRD patterns of vermiculite, the modified vermiculite had an obvious (001) diffraction peak. It showed that the modified vermiculite had a larger interlayer spacing, which indicated that the pillaring process of pillared clay was successful and the film structure was stretched out.

Fig. 1 XRD pattern of the clay-based catalyst

3.2. BET analyse

Table 1 showed that the specific surface area of each modified vermiculite catalyst increased comparing with the original vermiculite. From the data of VTPV (total pore volume) and SBET (specific surface area), it was found that the total pore volume of samples with large specific surface area were relatively large. It is said that pore structure could influence the specific surface area of samples, and the two parameters were positively correlated. At the same time, it also suggested that the internal metal oxide pillared structure formed by the modification could expand the pores and increase the specific surface area of the sample.

| catalyst      | $S_{be}$/$m^2g^{-1}$ | $S_{EA}$/$m^2g^{-1}$ | $V_{MPV}$/$cm^3g^{-1}$ | $V_{TPV}$/$cm^3g^{-1}$ |
|---------------|-----------------------|-----------------------|-------------------------|-------------------------|
| Verm          | 7.2                   | 7.6                   | n.d                     | 0.003                   |
| Organic verm  | 144.1                 | 99.7                  | 0.02                    | 0.24                    |
| Co/verm       | 203.6                 | 191.1                 | 0.006                   | 0.54                    |
| Ni/verm       | 104.9                 | 90.6                  | 0.01                    | 0.24                    |
| Co-Ni/verm    | 212.1                 | 157.1                 | 0.03                    | 0.25                    |

a Nitrogen adsorption at 77 K
b Multi-point BET method.
c External surface area and micropore volume was calculated from t-plot analysis
d Total pore volume at P/Po equal to 0.99, “n.d.” indicates “not detected”.

3.3. ICP-OES results

Inductively coupled plasma atomic emission spectrometry (ICP-OES) was mainly used to detect metal components in samples. This experiment mainly dealt with the detection of aluminium, cobalt, iron, potassium, magnesium, sodium, nickel and other elements in the sample. As shown in Table 2, the loading content of cobalt in Co/Verm sample was about 0.06%, that of nickel in Ni/Verm sample was about 0.05%, and that of cobalt and nickel in Co-Ni/Verm was about 0.04%. The results were in line with the metal ratio in the intercalation solution, which showed that the concentration of intercalation solution could determine the content of metal to some extent.
Table 2 Chemical analysis of parent clays (inductively couple plasma spectrum) (wt%)

| sample   | Al | Co  | Fe  | K  | Mg | Na  | Ni  |
|----------|----|-----|-----|----|----|-----|-----|
| Co/verm  | 7.9| 0.06| 15.6| 5.0| 7.1| 0.40| 0.01|
| Ni/verm  | 9.6| 0.01| 18.5| 6.1| 9.0| 0.26| 0.05|
| Co-Ni/verm| 7.1| 0.04| 13.9| 5.4| 6.5| 0.36| 0.04|

3.4. Analysis of pyrolysis experiment results

Table 3 showed the yields of solid residues, gases and petroleum products. The percentages (wt%) was obtained by catalytic pyrolysis of mixed plastics at high temperatures. For different catalysts, solid residues were negligible in all the pyrolysis processes, which indicated that the conversion of plastic materials was high, and the gas yield did not increase significantly during the catalytic pyrolysis process. It also revealed that large number of secondary pyrolysis did not occur during the catalytic pyrolysis process.

Table 3 The influence of different catalyst on the yield of pyrolytic products (wt.%)

| catalyst | Oil product | Gas product | Residue |
|----------|-------------|-------------|---------|
| No catalyst | 74.7 | 23.3 | 2.0 |
| Organic verm | 80.6 | 19.4 | 0.1 |
| Co/verm | 73.2 | 26.7 | 0.1 |
| Ni/verm | 70.7 | 28.0 | 1.3 |
| Co-Ni/verm | 73.9 | 26.0 | 0.1 |

3.5. Composition analysis of gas products

Table 4 showed the composition of gas products (detected by GC) in no catalytic and catalytic operation. The pyrolysis gas was mainly composed of mixed gaseous hydrocarbons, such as H2 and C1-C5. When the catalyst was introduced into pyrolysis, the H2 content increased significantly. It indicated that the modified catalyst had high selectivity for hydrogen production.

Table 4 Composition of the pyrolysis gas (vol%)

| catalyst | CH4 | C2 gas | C3 gas | C4 gas | C5 gas | H2 |
|----------|-----|--------|--------|--------|--------|----|
| No catalyst | 12.6 | 23.2 | 35.6 | 15.4 | 13.3 | n.d. |
| Organic verm | 11.3 | 20.9 | 33.0 | 15.8 | 10.9 | 8.1 |
| Co/verm | 10.0 | 18.8 | 28.0 | 14.4 | 9.3 | 19.5 |
| Ni/verm | 9.7 | 17.4 | 37.6 | 13.0 | 14.5 | 7.8 |
| Co-Ni/verm | 10.5 | 19.1 | 28.8 | 12.5 | 9.5 | 19.7 |

3.6. Composition analysis of oil products

The main components of oil products and their respective percentages were shown in Table 5. It is mainly composed of C9-C12 and C13-C20. Co/Verm and Ni/Verm catalysts had higher selectivity for fractions with carbon number greater than C13. Organic Verm and Co Ni/Verm catalysts had higher selectivity for fractions with carbon number less than C13.

Table 5 Main components of the oil product determined by GC (% area)

| catalyst | Light hydrocarbons (≤C13) | Heavy hydrocarbons (>C13) |
|----------|--------------------------|--------------------------|
|         | C9          | C10         | C11         | C12         | C13         | C14         | C15         | C16         | C17         | C18<         |
| No catalyst | 22.9 | 6.6 | 6.4 | 6.9 | 6.7 | 13.9 | 10.7 | 7.9 | 5.4 | 12.6 |
| Organic verm | 34.8 | 5.3 | 4.7 | 5.5 | 4.3 | 13.7 | 9.2 | 7.2 | 4.3 | 10.6 |
| Co/verm | 21.7 | 7.5 | 6.6 | 7.8 | 6.4 | 11.2 | 9.8 | 7.7 | 5.4 | 15.7 |
| Ni/verm | 17.7 | 6.4 | 5.8 | 7.1 | 6.1 | 12.0 | 11.0 | 8.5 | 6.6 | 18.7 |
| Co-Ni/verm | 55.5 | 5.1 | 8.4 | 2.8 | 2.4 | 2.4 | 3.0 | 1.7 | 1.7 | 16.9 |
4. Conclusion
After a series of modifications (acidification, sodium, organism, titanium insertion, cobalt nickel insertion, etc.), the specific surface area of the vermiculite catalyst broadened by 20-30 times. And the expansion of the interlayer spacing have increased the supporting metal content, which greatly raised the hydrogen content in the catalytic cracking product. Due to the interaction between acidity and texture properties, the modified catalyst could produce a large amount of diesel oil, distillate from petroleum products and H2 in natural gas products. According to our research results, we proposed an efficient way for the catalytic pyrolysis of plastics, and provided the possibility for further exploration of the industrial application of modified catalysts.

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