Preparation of composite catalyst and its catalytic cracking properties of coal tar

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Abstract. China is rich in coal resources. Coal tar produced by coal combustion is a large amount of surplus. Naphtha and diesel oil with similar properties to kerosene and diesel oil can be produced by catalytic cracking of coal tar oil. In this article, metal-loaded UiO-66 and Y-type zeolite were synthesized by solution thermal method and microwave assisted method. And a high temperature resistant active component catalyst UiO-66-Y was prepared by compounding the two. According to the GC-MS characterization of the original coal tar and the products after cracking with UiO-66-Y, the results show that part of the aromatic compounds in the coal tar added with catalyst will be decomposed and a large number of light component esters will be synthesized at the same time. It provides a possible way to solve the current energy dilemma.

1. Introduction

China's resources are short and single[1-2]. As the main energy in China, most of the coal is used by combustion, which leads to a large amount of coal tar surplus[3]. However, the dependence on oil imports is increasing in China year by year. It had been found that naphtha and diesel oil which was very similar to those of diesel oil and kerosene used in our daily life can be prepared from coal tar by adding catalyst at high temperature[4]. If we can use these fuel oils instead of kerosene or diesel, we can save our country from this energy dilemma to a great extent. Therefore, the ideal way to solve the current dilemma is to design high-efficiency catalysts, which can make the heavy component in coal tars into light component with high cost performance through catalytic cracking.

Metal organic frameworks (MOFs) are formed by chemical bonds between metal ions and organic ligands[5-6]. UiO-66 is a MOF material, which is mainly composed of C8H6O4 as organic ligand and Zr4+ as metal ion[7]. Compared with traditional porous materials, it has many advantages such as high porosity and high specific surface area. Microporous Y-type zeolite has large pore diameter and high temperature resistance, so it is not easy to decompose under heating[8]. The ratio of surface area to mass of the material is high, and the density is low, which provides a favourable way for the diffusion of macromolecular particles.

In this paper, composite materials were synthesized by using Y-type zeolite and UiO-66 by microwave-assisted method and solution thermal method. Taking nickel and cobalt as active metals with high cost performance, a kind of UiO-66-Y metal supported catalyst materials with high
temperature resistance and active component activity was obtained to improve the catalytic activity and stability of coal tar cracking. By means of various characterization methods, the interaction between MOFs and active components is revealed, the internal reasons for the better performance of metal organic frameworks materials than other catalysts are found, and the role of MOFs catalytic materials in the reaction.

2. Experimental

2.1. Preparation of UiO-66

2.1.1. Preparation of UiO-66 by solution thermal method. Weighed 4.66 g ZrCl$_4$ and 3.32 g terephthalic acid, dissolved them in 120 mL DMF, stirred them at 25 °C for 30 min, make them dissolved, transferred them to the lined PTFE reactor, reacted at 120 °C for 24 h, cooled after removal, washed them twice with DMF and CH$_3$OH, centrifuged them at 7000 r/min for 10 min, then dry the products at 90 °C for 8 h, grind them to obtain white solid powder samples, recorded as UiO-66-s. Add 3 mL hydrochloric acid to the above raw materials and repeat the remaining steps of the above operation. The sample is recorded as UiO-66-sa.

2.1.2. Preparation of UiO-66 by microwave assisted method. Weigh 4.66 g ZrCl$_4$ and 3.32 g white terephthalic acid powder, dissolve them in 120 mL DMF, stir them at 25 °C for 30 min, make them dissolved, transfer them to the microwave hydrothermal synthesis instrument, set the final temperature to 120 °C for 4 h, then take them out. Cooling, centrifugation, filtration and drying are the same as solution thermal method, grind the white powder sample and record it as UiO-66-m. Add 3 mL hydrochloric acid to the raw materials and repeat the remaining steps of the above operation to get the sample recorded as UiO-66-ma.

2.2. Preparation of metal loaded catalyst
Take 1.9729 g, 3.9458 g and 5.9186 g Ni(NO$_3$)$_2$·6H$_2$O respectively and dissolve them in three beakers, add 8g Y-type zeolite (UiO-66-ma) into the beaker, and add a proper amount of distilled water to dissolve them evenly, conduct ultrasound in the ultrasonic cleaner for 20 min, and stir at room temperature for 30 min. Take it out and put it in a sealed place for 24 h at room temperature. Dry the sample in a drying oven. Put in nitrogen, calcine it at 300 °C for 3 h to get a green powder, corresponding to the loading of 5%, 10% and 15% Ni/Y (Ni/UiO-66).

Replace the raw materials with 1.9729 g, 3.9458 g and 5.9186 g Co(NO$_3$)$_2$·6H$_2$O and repeat the remaining steps of the above operation to obtain dark red powder, corresponding to the loading of 5%, 10% and 15% Co/Y (Co/UiO-66).

2.3. Preparation of composite materials
Weigh 3 g of non-calcined UiO-66 (5% Ni/UiO-66) and Y-type zeolite (10% Ni/Y). Mixed by mechanical stirring evenly, placed in a muffle furnace, and heated at 300 °C for 3 h under a nitrogen atmosphere to obtain a sample of UiO-66-Y.

3. Results and discussion

3.1. Characterization of UiO-66
Figure 1. Thermogravimetric curve of UiO-66. (UiO-66-s; UiO-66-sa; UiO-66-m; UiO-66-ma)

It can be seen from the Figure 1 that the reason for the weight loss of the four catalysts at about 100 ℃ is the loss of water molecules on the surface of UiO-66 due to the high temperature. The reason of weight loss in the temperature range from 100 ℃ to 600 ℃ is due to the collapse and decomposition of the internal skeleton structure of UiO-66 materials.

Figure 2. Scanning electron micrograph of four catalysts. (a: UiO-66-s; b: UiO-66-sa; c: UiO-66-m; d: UiO-66-ma)

Figure 2 is the SEM of four catalysts. It can be seen from the figure that the crystal particles of UiO-66-ma (d) are more uniform, have more pore structure and appearance structure, and the proportion of crystal area in the polymer is higher.

Figure 3. XRD patterns of UiO-66-s, UiO-66-sa, UiO-66-m and UiO-66-ma.

The XRD figures of the four catalysts are shown in Figure 3. The samples prepared under different conditions show the same curve as the reported UiO-66, which shows that the purity of the materials we synthesized is higher, and the crystal morphology of the sample UiO-66-ma is better, and the characteristic peak is more consistent with the original literature.
Figure 4. The adsorption-desorption isotherms of UiO-66-ma.

Figure 5. The pore size distribution of UiO-66-ma.

We have tested the nitrogen adsorption curve of UiO-66-ma in Figure 4 and Figure 5, the best crystal type sample, and obtained that its N\(_2\) isotherm is type I, indicating that it is mainly microporous structure, while the adsorption desorption curve is not completely overlapped, and the part that is not overlapped forms a ring, indicating that the material contains pore structure.

3.2. Characterization of metal supported UiO-66 and Y-type zeolite

As shown in Figure 6 and Figure 7, the XRD patterns of Y-type zeolite and UiO-66 loaded with different amounts of Ni and Co are shown. It can be seen that the characteristic peaks of 5% Ni/UiO-66, 15% Co/UiO-66, 10% Ni/Y and 5% Co/Y are the most obvious, the diffraction peaks are the same as those in the original literature, and the crystal forms are better.

Figure 6. The XRD images of metal loaded of Co/UiO-66 (a) and Ni/UiO-66 (b).

Figure 7. The XRD images of metal loaded of Co/Y (a) and Ni/Y (b).
3.3. Performance evaluation of composite catalyst

10 g coal samples were respectively put into a low-temperature distillation by aluminium retort. The pyrolysis products were collected during the experiment. The collected gas was analyzed by gas chromatograph.

It can be seen from Figure 8 that, most substances are detected at about 5-25 min, and less substances are detected after 40 min. A total of 158 substances have been detected, including 59 kinds of fat, 57 kinds of aromatic compounds, 13 kinds of alcohol compounds and 15 kinds of phenolic compounds containing benzene ring.

![Figure 8. The GC-MS total ion flow chromatogram of coal tar](image)

As can be seen from Figure 9, most substances are detected within 5-40min. According to the identification results of all substances detected by GC-MS, 237 substances were found in coal tar and catalyst after pyrolysis, including 12 aromatics, 218 fats and 12 acids. Compared with the detection types of coal tar without catalyst, the number of aromatic compounds decreased significantly, and the types of ester compounds increased significantly.

![Figure 9. The GC-MS ion flow chromatogram of UiO-66-Y and coal tar](image)

4. Conclusion

UiO-66-Y metal-loaded catalytic materials were prepared by combining UiO-66 and Y-type zeolite by microwave assisted method and solution thermal method. The composite materials not only have the advantages of MOFs materials: high area per unit mass and low density, but also has the advantages of molecular sieve materials: high temperature resistance and high maximum load per unit area. Through GC-MS analysis of raw coal tar and its products after cracking on UiO-66-Y catalyst, it is found that UiO-66-Y can promote the decomposition of some aromatic compounds in coal tar and synthesize a large number of ester compounds at the same time.

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