

Application of TiO₂/Bentonite on the Catalytic Pyrolysis of Oil Sludge

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Abstract: Oil sludge is one of the hazardous wastes produced in the processes of petroleum exploitation, refining, transportation and storage. Implementing the harmless and resource treatment of oily sludge is an urgent problem to be solved. In this paper, TiO₂/bentonite was prepared by sol-gel method, and then was characterized by scanning electron microscope, X-ray diffraction, Infrared Spectroscopy. The effect of TiO₂/bentonite on improving the yields of oil product was studied. As a result, the oil recovery yield increased from 86.63%w/w to 95.69%w/w. The oil quality is improved compared with no catalyst after the TiO₂/bentonite was added in the oil sludge.

1 INTRODUCTION

Oily sludge is an oily solid waste which generated from the oil exploration, transportation, refining, and oily sewage treatment plants. At present, China produces about 30 million tons of oil sludge per year, and hundreds of millions of tons of sludge are dumped, causing extremely serious pollution to the soil and groundwater. The main ones are the sludge and oil sand produced during the petrochemical industry, which have the characteristics of large production volume, high oil content, high heavy oil component, less comprehensive utilization methods, and difficult processing (Yue and Li, 2010). Oily sludge generally contains a large amount of benzene, phenol, hydrazine and other substances, which are also accompanied by toxic substances and radioactive elements. If improper treatment of oily sludge, it will not only pollute the environment, endanger humans, animals and plants, but also cause the waste of recyclable resources of the oil sludge (Liu et al., 2013). Therefore, it is urgent to realize the resource and harmless treatment of oily sludge.

The common treatment methods for oily sludge include incineration, conditioning, separation, solvent extraction, electrochemical treatment, and pyrolysis. The pyrolysis of the sludge (Wang and Zou, 2004) as an emerging process technology, bases on the thermal instability of the organic matter in the sludge and decomposes the organic matter to

gas, liquid fuel, and carbon under the condition of the atmosphere without oxygen. Pyrolysis has the advantages of thorough treatment, better effect of reducing volume, low secondary pollution, and energy recovery. It is a treatment method that can effectively make the sludge resource, reduce, and harmless (Wang and Zou, 2004). In terms of the role of mesoporous molecular sieve catalysts in catalytic cracking of heavy oils, it is proposed that bentonite-loaded titanium catalysts should be used in the pyrolysis of oil sludge to explore new ideas for the influence of pyrolysis temperature, oil recovery rate and carbon residue during pyrolysis. Yan Li and other authors have reported: Influencing factors for catalytic pyrolysis of oily sludge and analysis of pyrolysis products.

2 EXPERIMENTAL SECTION

2.1 Experimental Reagents

Butyl phthalate. Anhydrous ethanol. Distilled water, acetic acid. Bentonite. Petroleum ether. The reagents used were all analytically pure reagents. The experimental water used was deionized water.

2.2 Preparation of Bentonite Loaded TiO₂ Catalyst

25 mL of anhydrous ethanol and 1 mL of butyl titanate were mixed at room temperature, and stirred for 1 hour to obtain solution A. 2 mL of glacial acetic acid was added to 10 mL of absolute ethanol and mixed thoroughly to form solution B; solution B was slowly added dropwise to solution A under magnetic stirring, and solution C was obtained after homogeneous mixing. 2 g of bentonite was weighed into solution C and stirred, then 8 mL of distilled water was added dropwise, and stirred until the gel. The gel was washed with deionized water, suction filtered, dried in an incubator at 80°C, and calcined at a temperature of 500°C for 3 hours. The resulting white powder is denoted as TiO₂/bentonite (1) (Dong et al., 2013). The amount of butyl titanate is increased by one time and the other conditions are unchanged. The resulting white powder is denoted as TiO₂/bentonite (2).

2.3 Characterization of Catalyst TiO₂ / Bentonite

Scanning electron microscopy (SEM) with EDAX; Fourier transform infrared spectroscopy (FTIR) analysis. The catalyst was subjected to XRD analysis.

2.4 Catalytic Pyrolysis Experiment of Oily Sludge

The catalyst and oily sludge were mixed and placed in a pyrolysis furnace, treated at a certain temperature for a period of time, the oil recovery rate was investigated, and the influence of the catalyst on the pyrolysis was examined. The experimental conditions were as follows: nitrogen flow rate 100 mL·min⁻¹, temperature 450 °C, pyrolysis time 4 h, heating rate 10°C·min⁻¹, catalyst TiO₂ /bentonite addition 1%.

The oil recovery rate X is calculated according to the following formula:

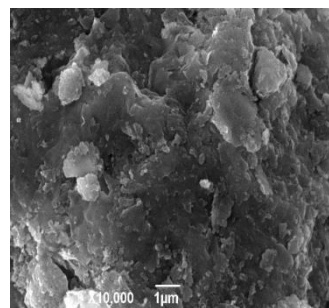
$$X = W_1 / W \times 100\% \quad (1)$$

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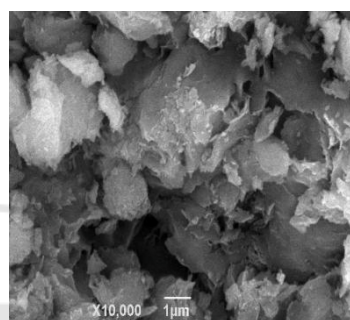
In the formula: W₁ is the recovered oil quality, g; W is the oil quality in the sludge, g.

3 RESULTS AND DISCUSSION

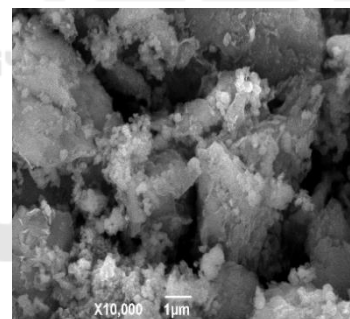
3.1 Features of the Catalyst



a. Bentonite



b. TiO₂ / bentonite (1)



c. TiO₂ / bentonite (2)

Figure 1: SEM image of Bentonite and TiO₂ /bentonite.

3.1.1 Morphological Features

Figure 1 is a SEM image of the support bentonite, the catalyst TiO₂ /bentonite (1) and the TiO₂ /bentonite (2). It is shown that TiO₂/bentonite and carrier Bentonite have little change in morphology. But TiO₂/bentonite is flaky, this feature can effectively increase the catalytic specific surface area. Increase the area of contact with oily sludge to improve the catalytic effect.

Figure 2 is spectrum elemental analysis diagram of bentonite, TiO₂/bentonite (1), and TiO₂/bentonite (2). We can see that the samples contain Ti, which indicates that TiO₂ was successfully supported on bentonite. In addition, the relative peak value of Si decreases with the increase of titanium oxide load.

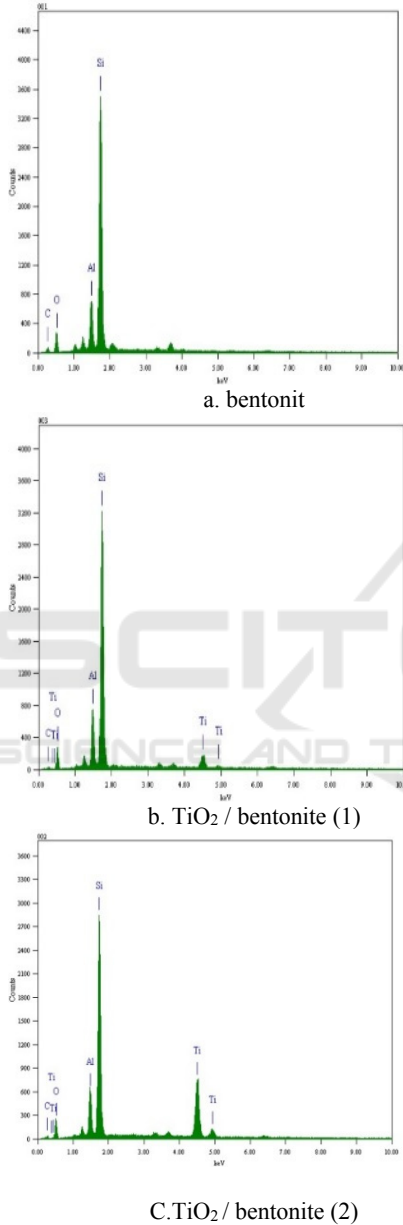


Figure 2: EDAX of Bentonite and TiO₂ /bentonit.

3.1.2 Infrared Spectral Analysis

The infrared spectrum of supported and unsupported bentonite is shown in Figure 3. It can be seen the OH stretching vibration of Si-OH-Al in montmorillonite structure nearby 3630 cm⁻¹. It also

can be seen the O-H stretching vibration of adsorbed water in the interlayer of montmorillonite structure nearby 3439 cm⁻¹. It had stretching vibration band of O-H near 1642 cm⁻¹, and the peak near 1035 cm⁻¹ is attributed to the asymmetry bending stretching of Si-O-Si. The bending vibration absorption peak of Si-O-Al near 519 cm⁻¹, the peak near 1407 cm⁻¹ is attributable to the bending stretching of Si-O-Si. After supported in IR, the peak near 500-700 cm⁻¹ is attributable to the bending stretching of Ti-O. The results revealed that TiO₂ were inserted into bentonite's layers (Wang et al., 2015).

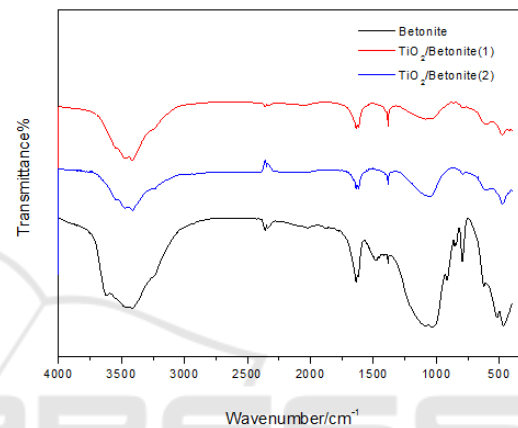


Figure 3: IR spectrums of bentonite and TiO₂ /bentonite.

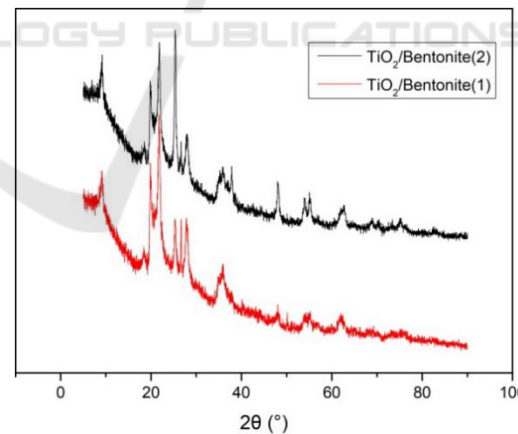


Figure 4: XRD of TiO₂/bentonite.

3.1.3 X-ray diffraction Pattern Characteristics

A wide-angle XRD spectra of TiO₂/bentonite (1) and TiO₂/bentonite (2) is shown in Figure 4. The anatase phase of the corresponding diffraction peaks (101), (004), (200), (105), (211) appeared at 2θ = 25.2°, 37.8°, 48.1°, 54.0° and 55.2° in both samples.

Rutile phase diffraction peak does not appear. Shown that the sample has only an anatase phase, without rutile phase (Zhang et al., 2014). TiO₂/bentonite (1) and TiO₂/bentonite (2) were characterized by XRD and the interlayer distance of them obviously increased. It can be seen from the figure that the interlayer spacing of TiO₂/bentonite (2) is larger than that of TiO₂/bentonite (1), and the number of diffraction peaks is increasing. The results revealed that TiO₂ were inserted into bentonite's layers.

3.2 Study on Factors Affecting Pyrolysis of Oily Sludge

3.2.1 Effect of Catalyst Types on the Effect of Pyrolysis Treatment

The pyrolysis experiments were performed on the two catalysts at an addition of 1%. The results are shown in Table 1.

Table 1: Effect of catalyst type^a.

Catalyst type	No catalyst	TiO ₂ / bentonite (1)	TiO ₂ / bentonite (2)
Nitrogen flow rate / (mL·min ⁻¹)	100	100	100
Temperature/°C	450	450	450
Pyrolysis time/h	4	4	4
Heating rate / (°C·min ⁻¹)	10	10	10
Oily sludge quality/g	20.07	20.03	20.05
Recovered oil/g	2.85	3.08	3.15
Oil recovery yield/%	86.63	93.90	95.74

Effect of catalyst types on pyrolysis treatment

It is shown from table 1 that the recovery rate of pyrolysis sludge without catalyst is lower than that of TiO₂/bentonite (1) and TiO₂/bentonite (2). And the catalytic effect of TiO₂/bentonite (2) is more excellent, this is because not only is the titanium content in TiO₂/bentonite (2) higher than TiO₂/bentonite (1), but also TiO₂/bentonite (2) is larger than the surface of TiO₂/bentonite (1), increased the contact area of the reaction. This is consistent with the results of the previous analysis.

3.2.2 Effect of Catalyst Addition on Thermal Treatment Effect

From Figure 5, we can see that the oil recovery rate increases with the increase of catalyst addition amount when the catalyst addition is between 0.5%-1.0%, and it increases from 86.05% to 90.49%;

When the amounts of catalyzer are more than 1%, the increase of catalyst has little effect on oil recovery. This is mainly because the oil content of oily sludge is low, when the amounts of catalyzer 1%, oil recovery rate has reached over 90%, the activity of the catalyst has been fully played. Considering the cost of the catalyst, when the optimum amounts of catalyzer 1%, the oil recovery rate is the highest.

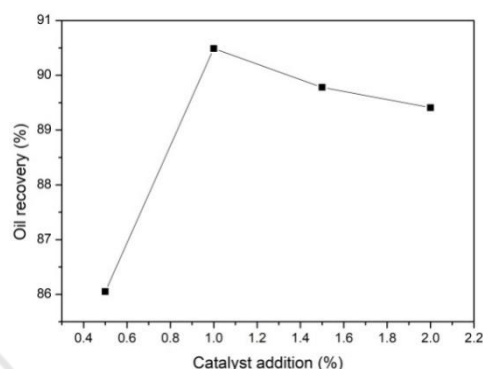


Figure 5: Effect of catalyst dosage on oil recovery yield.

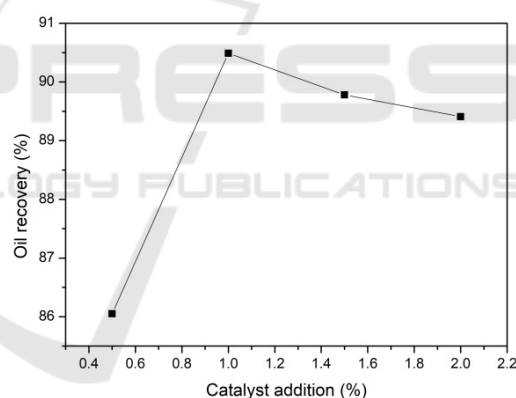


Figure 6: Effect of pyrolysis temperature on oil recovery yield.

3.2.3 Influence of Pyrolysis Temperature on Pyrolysis Treatment

The pyrolysis time was 4 h, the nitrogen flow was 100 mL/min, and the amount of catalyst added was 1%. The effect of temperature on pyrolysis of oil-containing sludge was investigated. Figure 6 shows the results.

From Figure 6, we can see that the oil recovery rate increases obviously with the increase of reaction temperature when the temperature between 400-420 °C, and it increases from 80.40% to 94.14%, but the recovery rate of sludge pyrolysis oil decreased when

the temperature over 420°C, Because the oily sludge does not occur pyrolysis reaction at lower temperatures, when the temperature gradually increased, macromolecular organic compounds began to pyrolysis into some small molecules, oil recovery rate gradually increased, as the temperature continues to rise, macromolecular pyrolysis reaction process with many intermediate products will occur secondary pyrolysis (Li et al., 2006), this results in a positive proportion of gas production and a gradual decrease in oil recovery rates. When the temperature is 420 °C, and the recovery rate is 10% higher than that without catalyst. It is indicated that the catalyst has a strong catalytic effect on the pyrolysis process.

3.2.4 Effect of Time on Catalytic Pyrolysis of Oily Sludge

From figure 7, we can see in the process of sludge pyrolysis, the oil recovery rate increases gradually with the prolongation of residence time when the reaction time is between 1-3h, and the recovery rate increased from 61.9% to 95.69%. When the reaction time is between 4-5h, the oil recovery rate is decreasing. The reason is that the pyrolysis reaction is a parallel reaction, the different depth of the pyrolysis reaction has a great effect on the distribution of product yield, which will increase the residence time of the first reaction product in the pyrolysis reactor, accelerate the secondary reaction rates, and increase the gaseous phase products produced by pyrolysis and the solid products produced by condensation, it weakens the effect of reaction time on liquid yield and reaction conversion. It can also be seen that during the reaction, when the reaction stays for a short time, some of the sludge has not reached the current temperature of the full state of pyrolysis, and when the reaction time is too long, the oil occurred the secondary pyrolysis (Li et al., 2006), the formation of gas to discharge, the collection of oil production reduced and the recovery rate of the reduction. Therefore, in order to obtain the higher efficiency and the shorter processing time, the best reaction residence time is 3h, The pyrolysis time of catalyst is 1h shorter than that without catalyst. The experimental results show that the reaction time is greatly reduced by adding the catalyst, which reduces the load of equipment and the energy required for the experiment.

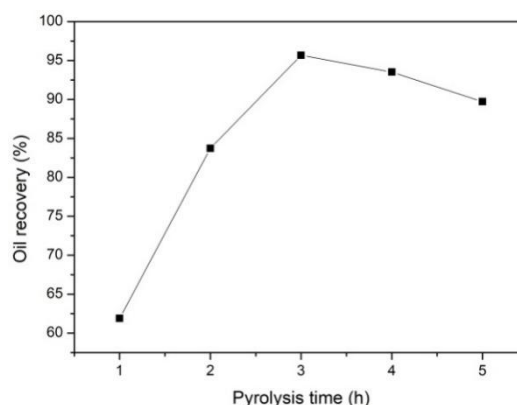


Figure 7: Effect of pyrolysis time on oil recovery yield.

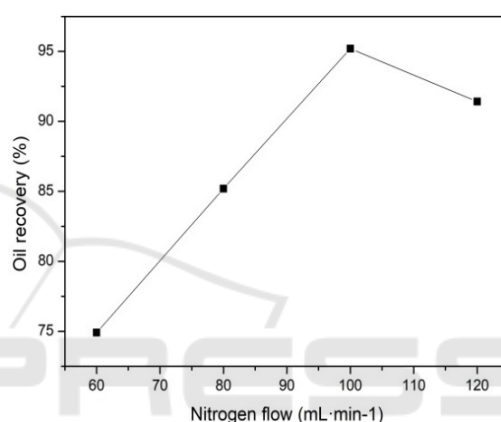


Figure 8: Effect of nitrogen flow rate on oil recovery yield.

3.2.5 Effect of Nitrogen Flow Rate on the Results of Pyrolysis Treatment

At the pyrolysis temperature of 420°C and the pyrolysis time of 3 h, the effect of nitrogen flow rate on the pyrolysis of oily sludge was investigated. Figure 8 shows the results.

It can be concluded that the oil recovery rate increases with the increase of nitrogen flow rate. Also, it can reach the maximum value when the nitrogen flow reaches up to 100 mL/min, but it would decrease when nitrogen flow increased. Because the oil and gas products in the pyrolysis furnace can not be purge out in time when the nitrogen flow rate is too small, causing the secondary pyrolysis in the furnace and the oil recovery rate is lower; there is little no-condensing products that were purge out in the excessive Nitrogen flow, resulting in decreasing of oil recovery yield (Zhao, 1985; Li et al., 2018).

4 CONCLUSIONS

The TiO₂/bentonite supported catalysts were successfully prepared, and the catalytic effect was better with the increase of TiO₂ content. When the pyrolysis temperature is 420 °C, the pyrolysis time is 3 h, and the nitrogen flow rate is 100 mL/min, the oil recovery rate can reach 95.69% by adding the catalyst, and the addition of the catalyst can improve the oil quality.

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