EFFECTS OF MOLECULAR SIEVES ON THE CATALYTIC PYROLYSIS OF OILY SLUDGE

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To improve the pyrolysis efficiency of oily sludge, a molecular sieve catalyst (Al-MCM-41) was synthesized by the impregnation method. The effects of different temperatures and catalyst concentrations on the pyrolysis products were studied. The results showed that the oil recovery rate reached 83.48% after pyrolysis at 430°C for 3 h at a Si/Al ratio of 60 and a catalyst dosage of 1%. Thus, the catalytic pyrolysis improves the recovery of light oil components and promotes the pyrolysis of oily sludge.

Keywords: Oily sludge; Catalytic pyrolysis; Molecular sieve catalyst; Crude oil recovery

1. Introduction

A significant amount of oily sludge is produced in the process of crude oil exploration, production, transportation, storage and refinement. China produces a large amount of oil field and storage tank sludge every year [1]. Oily sludge is a complex mixture of water, oil, sediment and organic compounds, which contains a large number of organic chemical agents, heavy metal substances, bacteria, and other harmful substances [2]. If these substances are directly discharged without treatment, they can cause great harm to the environment. Meanwhile, they will also change the physical and chemical characteristics of soil and soil morphology, resulting in barren land and withered vegetation [3]. Oily sludge is classified as hazardous waste (waste category: HW08 mineral oil) because of its large yield, difficult treatment, and potential environmental harm [4].

At present, heat treatment technologies for oily sludge mainly include incineration and pyrolysis. The oily sludge is converted into coal fuel by incineration technology, and mixed with other fuels. In addition to the treatment of oily sludge, heat energy can be recovered. However, the cost of flue gas

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treatment is relatively high, and it is easy to form secondary pollutants [5]. However, the cost of flue gas treatment is relatively high, and it is easy to form secondary pollutants [5]. In contrast, pyrolysis technology is used for cracking and evaporation of the mineral oil and other organic components of oily sludge by high-temperature heating under oxygen-free conditions, and three products are generated: gaseous, liquid and solid products. The advantage of this technology is that after thorough treatment, some oil and gas resources and heat are recovered [6-8]. Some researchers have employed molecular sieve catalysts to reduce the activation energy of pyrolysis process, so as to improve its yield and quality [9-12]. In this study, an MCM-41 molecular sieve catalyst is prepared by impregnation method. It is used for the catalytic pyrolysis of oily sludge in a tubular pyrolysis furnace to study the effects of pyrolysis temperature and catalyst concentration on the low-temperature pyrolysis of oily sludge, i.e. on the pyrolysis products and medium oil recovery effect.

2. Experimental materials and methods

2.1 Experimental materials

In this experiment, black brown, a relatively thick oily sludge from an oil sludge treatment station of Changqing oilfield in the northern Shaanxi Province is taken as research. The oil and water contents were 19.41% and 15.75% respectively. Al-MCM-41 molecular sieve catalyst was prepared by impregnation method.

2.2 Catalytic pyrolysis experiment on oily sludge

A certain amount of catalyst and 40 g of oily sludge were evenly mixed and placed in a tubular pyrolysis furnace. Under a nitrogen flow of 100 mL/min and a heating rate of 10°C/min, pyrolysis was conducted for a certain time. The effects of temperature, catalyst addition and other factors on the oil recovery were investigated and the pyrolysis products were analyzed.

$$w = m_p / m_s * 100\%$$

Where, w is the oil recovery rate (%); m_p is the mass of the pyrolysis oil (g) and m_s is the mass of oil in the oily sludge (g).

2.3 Synthesis and characterization of the catalysts

Preparation: Aluminum isopropoxide ($C_9H_{21}AlO_3$) was dissolved in 50 mL of anhydrous ethanol. The Si/Al ratios of 20, 40, 60 and 80 were obtained by changing the amount of aluminum isopropoxide with the same amount of MCM-41. The mixture was then stirred for 20 min until the aluminum source was dissolved. Subsequently, calcined MCM-41 was added, stirring for 12 h, washing and filtering, and drying at 80°C. The dried samples were roasted at 550°C for 5 h to obtain samples with different aluminum contents.

Characterization: The X-ray diffraction (XRD) analysis and the energy-

dispersive X-ray spectroscopy (EDS) element analysis were conducted according to a PANalytical X'Pert powder X-ray diffractometer (Parker Hannifin Co., Netherlands). Scanning electron microscopy (SEM) images were collected by a JSM-6360LV microscope (JEOL; HV mode, resolution: 3.0, 8.0, and 15 nm; LV mode, resolution: 4.0 nm; magnification: ×5–×3000 000). Infrared (IR) spectra were recorded on a PE-680 spectrometer (PerkinElmer; range: 7800–350 cm^{-1}; KBr). The microporous structure of catalyst was analyzed using a physical adsorption instrument (ASAP2020 HD88).

2.4 Analysis of the pyrolysis products

The water content of oily sludge was analyzed according to the determination of water content in petroleum products (GB 260-77). The oil content was determined with the Soxhlet extraction method. The composition of pyrolysis oil was analyzed using an Agilent 7890a-5975c GC-MS. A four-component analysis was carried out on the pyrolysis oil according to the standard of SH/T 0509-92.

3. Results and discussion

3.1 Catalyst characterization

3.1.1 X-ray diffraction

In Fig. 1, XRD patterns of the molecular sieves loaded with aluminum show four diffraction peaks, namely the characteristic peaks of (100), (110), (200) and (210) planes. With the increase of aluminum metal concentration, the intensity of the diffraction peak at 2.3° decreases and disappears gradually between 3° and 7°. These changes are due to the substitution of aluminum for part of silicon in the molecular sieve, resulting in the decrease of particle size and structural order of the sample [13]. It indicates that aluminum metal is successfully loaded onto the molecular sieve.

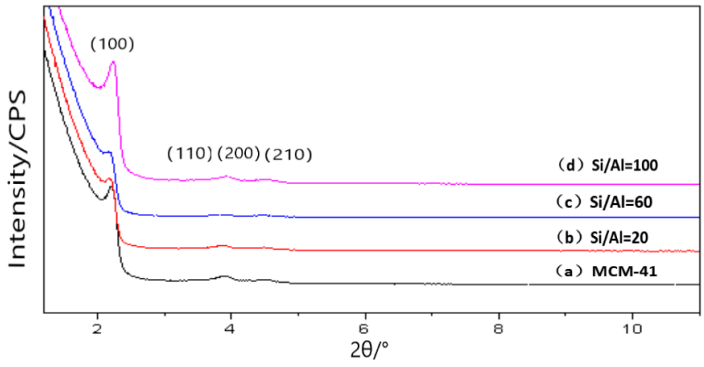

Fig. 1. XRD patterns of MCM-41 and Al-MCM-41 samples prepared by the impregnation method

3.1.2 Scanning electron microscopy

SEM images of Al-MCM-41 samples prepared by impregnation method (Fig. 2 (b)–(d)) show that the morphology of Al-MCM-41 materials with different Si/Al ratios is similar to that of the carrier (Fig. 2 (a)).

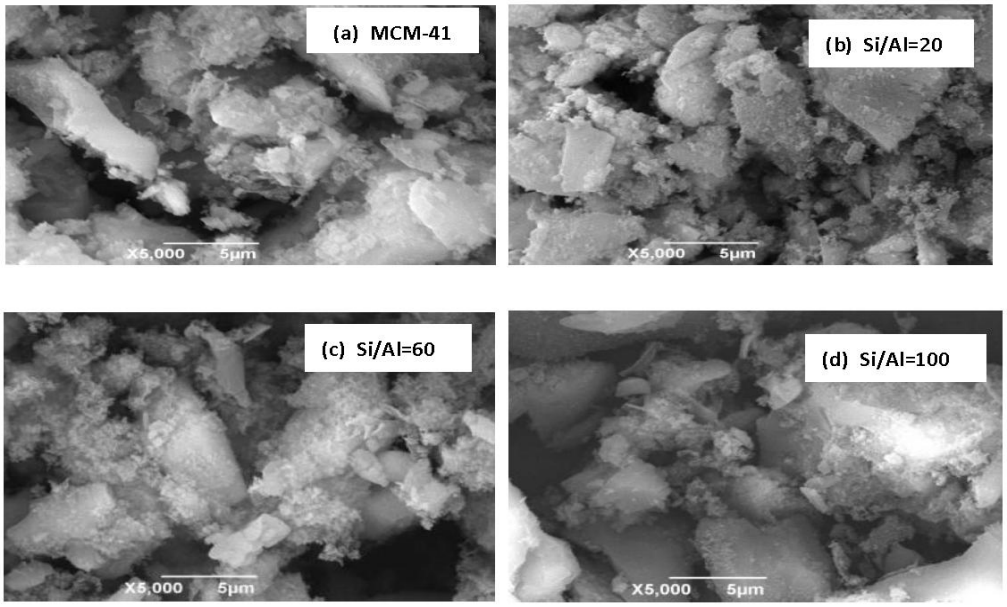

Fig. 2. SEM images of MCM-41 and Al-MCM-41 samples prepared by impregnation method

The observed flake-like morphologies indicate that these materials have relatively large specific surface areas and are suitable for subsequent catalytic reactions. The energy-dispersive X-ray spectroscopy (EDS) element analysis of Al-MCM-41 catalysts prepared by impregnation method (Fig. 3 (b)–(d)) shows that the upper surfaces of these materials contain aluminum metal, while that of MCM-41 carrier (Fig. 3 (a)) does not. In addition, the peak intensity of aluminum decreases significantly with the decrease of aluminum load. The results indicate that aluminum metal is successfully loaded onto the surface of MCM-41 by impregnation method.

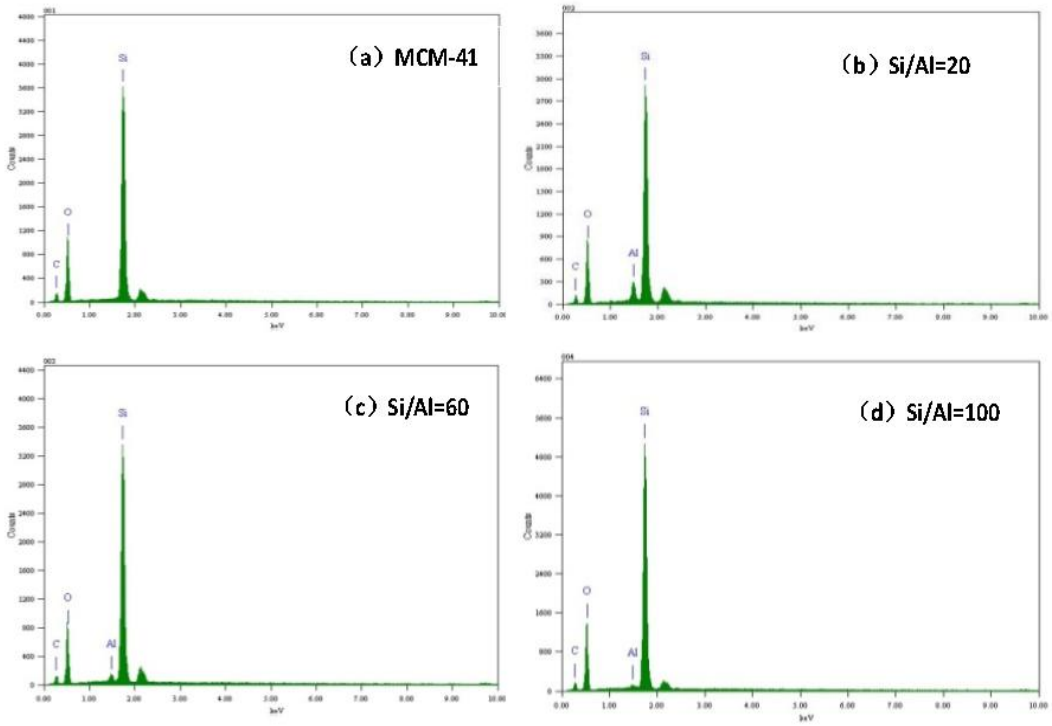

Fig. 3. EDS spectra of MCM-41 and Al-MCM-41 samples prepared by impregnation method

3.1.3 Infrared spectroscopy

The IR spectra (Fig. 4) of Al-MCM-41 materials prepared by impregnation method show that the characteristic peaks appear near 460, 806 and 1080 cm-1, which are attributable to the bending vibrations, symmetric stretching and asymmetric shrinkage vibrations of Si–O–Si bonds in the Al-MCM-41 structure. The characteristic peak near 3400 cm-1 corresponds to the stretching vibration of Si–OH on the surface of Al-MCM-41 molecular sieves. With the increase of aluminum loading, the peak width at 1080cm-1 increases significantly. This change is due to the existence of long Al–O bonds after silicon in the molecular sieves after the substitution of silicon by aluminum, which indicates that the aluminum metal is successfully supported on the molecular sieve.

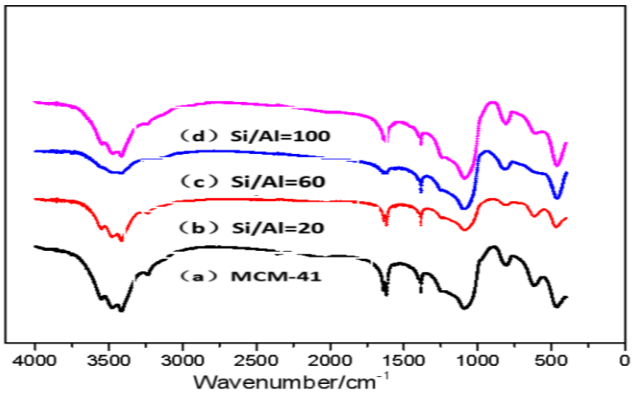

Fig. 4. IR spectra of MCM-41 and Al-MCM-41 samples prepared by impregnation method

3.1.4 N_2 adsorption–desorption analysis

As shown in Fig. 5, N_2 adsorption–desorption isotherms for MCM-41 and Al-MCM-41 (Si/Al=20) molecular sieves are typical of mesoporous materials. Based on the capillary condensation effect, a significant transition is observed at the relative pressure (P/P_0) of ~0.4.The long platform shows that N_2 adsorption process is in mesoporous adsorption equilibrium state, indicating that MCM-41 and Al-MCM-41 molecular sieves have narrow/w and uniform pore structures [13]. Based on the Barrett-Joyner-Halenda (BJH) model, the mean pore diameters of MCM-41 and Al-MCM-41 sieves were calculated as 2.92 and 3.43 nm respectively (Fig. 6). The specific surface areas were determined to be 857.27 and 1055.16 cm^2/g respectively.

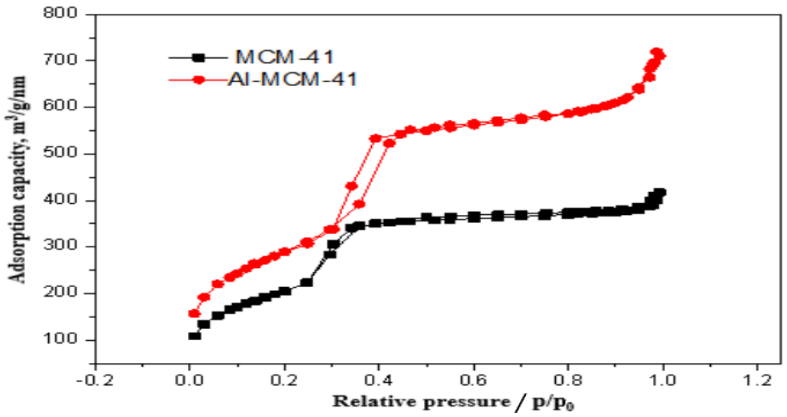

Fig. 5. N_2 adsorption–desorption isotherms of MCM-41 and an Al-MCM-41 sample prepared by impregnation method

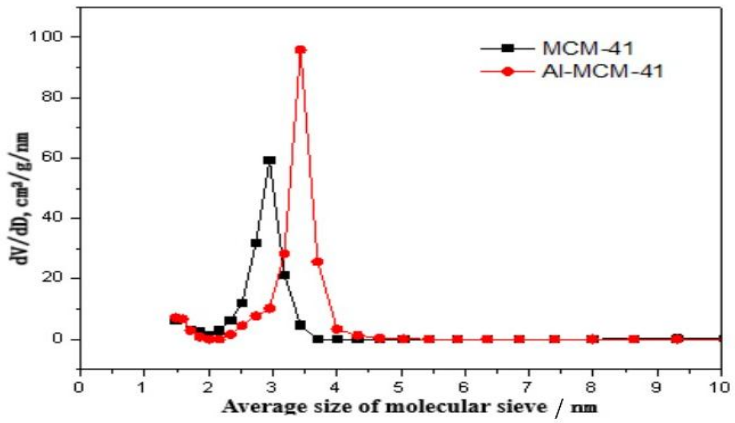

Fig. 6. Pore size distributions of MCM-41 and an Al-MCM-41 sample prepared by impregnation method

3.2 Factors influencing the pyrolysis process

3.2.1 Effect of the metal concentration on the pyrolysis process

Pyrolysis was conducted for 4 h at a pyrolysis temperature of 450°C and a catalyst dosage of 1%. The recovery rate of pyrolysis oil was analyzed and the influence of the metal concentration of catalyst on the pyrolysis of oily sludge was investigated.

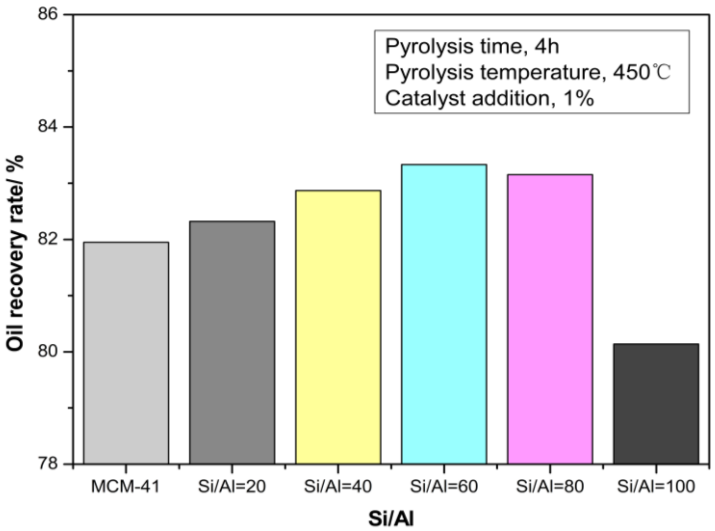

Fig. 7. Effect of metal loading on recovery of pyrolysis oil

Fig. 7 shows that the recovery rate of pyrolysis oil gradually increases with the decrease of metal concentration loaded on the molecular sieve. At a Si/Al ratio of 60, the oil recovery reaches a maximum of 82.46% and then decreases.

which is conducive to the catalytic pyrolysis of oil-containing sludge and improves the recovery rate of pyrolysis oil [14,15]. The loading of aluminum metal improves the acidity and catalytic performance of the catalyst, which is conducive to the catalytic pyrolysis of oily sludge and improves the recovery of pyrolysis oil [14,15]. Therefore, the optimum catalyst ratio is Si/Al = 60.

3.2.2 Effect of the reaction temperature on the pyrolysis process

Pyrolysis was conducted for 4 h at a catalyst dosage of 1%. The recovery rate of pyrolysis oil was used as an index to analyze the effect of the pyrolysis temperature on the pyrolysis of oil-containing sludge. The relationship between the pyrolysis temperature and oil recovery at pyrolysis temperatures of 410–460°C is shown in Fig. 8.

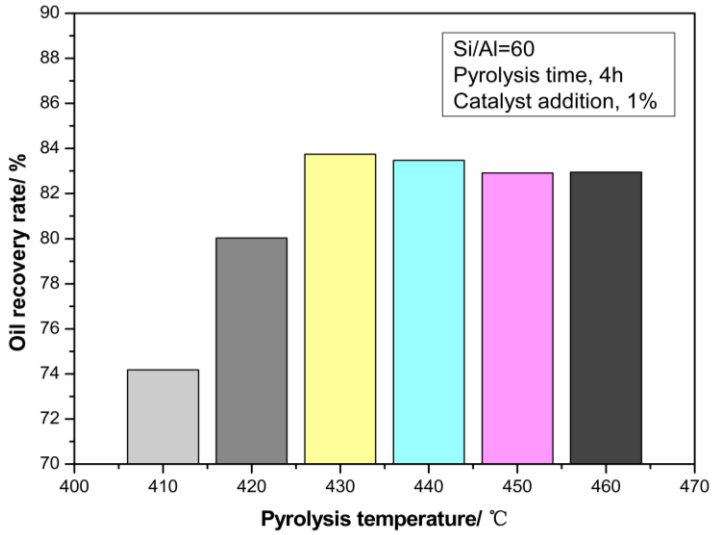

Fig. 8. Effect of pyrolysis temperature on recovery of pyrolysis oil

Fig. 8 shows that the recovery rate of pyrolysis oil increases with the increase of pyrolysis temperature. When the temperature reaches 430°C, the recovery rate of pyrolysis oil is 83.75%. Subsequently, the recovery rate of pyrolysis oil changes insignificantly with the increase of temperature and shows a downward trend. The degree of sludge pyrolysis is low at low temperature. However, with the increase of temperature, the macromolecular organic matter in the sludge is transformed into medium and small molecules, and the pyrolysis efficiency is gradually improved. With the continuous increase of temperature, the concentration of non-condensable gas increases in the process of pyrolysis, resulting in the decrease of the recovery rate of pyrolysis oil [16, 17]. Therefore, the optimal pyrolysis temperature is 430°C.

3.2.3 Effect of the pyrolysis time on the pyrolysis process

The recovery rate of the pyrolysis oil was used as an index to analyze the effect of pyrolysis time on the pyrolysis of oily sludge at a pyrolysis temperature of 430°C and a catalyst dosage of 1%. The relationship between the pyrolysis time and oil recovery for pyrolysis times in 1–5 h is shown in Fig. 9.

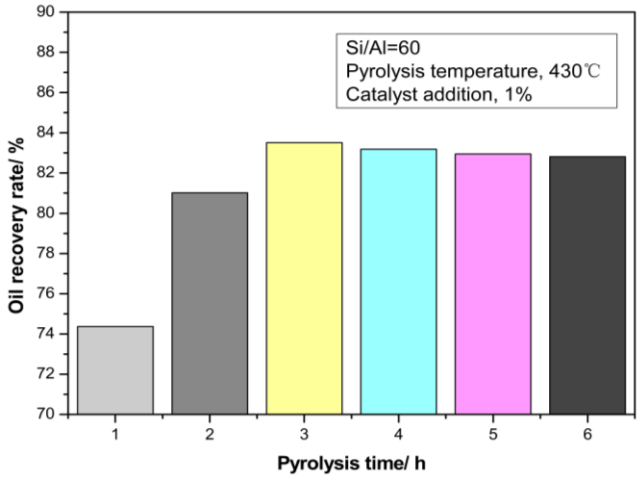

Fig. 9. Effect of the pyrolysis time on the recovery of pyrolysis oil

As shown in Fig. 9, with the increase of pyrolysis time, the recovery rate of pyrolysis oil first increases and then decreases. At a pyrolysis time of 3 h, the recovery rate of pyrolysis oil reaches the maximum value of 83.48% after 3 h pyrolysis, and then the recovery rate of the pyrolysis oil is relatively stable and shows a downward trend. This phenomenon occurs because, the pyrolysis of oil sludge is incomplete at a relatively short time and hydrocarbons remain in the sludge, and thus the oil recovery rate is low. However, in the long-term pyrolysis process, full exhalation of the hydrocarbons in the oil sludge results in an obvious increase in the liquid product. The secondary cracking of pyrolysis oil will form lighter gas-phase products, thus reducing the recovery rate of pyrolytic oil [18]. As a result, the optimal pyrolysis time is 3 h.

3.2.4 Effect of the catalyst concentration on the pyrolysis process

The recovery rate of pyrolysis oil was analyzed at the temperature of 430°C and a pyrolysis time of 3 h to study the effect of catalyst concentration on the pyrolysis of oily sludge.

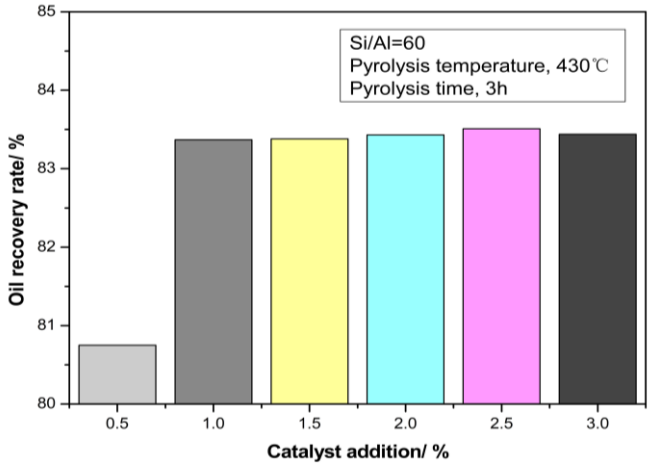

Fig. 10. Effect of catalyst concentration on the recovery of pyrolysis oil

Fig. 10 shows the addition of catalyst in the pyrolysis process of oily sludge. When the catalyst concentration increases from 0.5% to 1%, the pyrolysis oil recovery notably increases. At a catalyst concentration of 1%, the pyrolysis oil recovery rate reaches 83.48%. In other words, the maximum catalytic effect is achieved at a catalyst concentration of 1%. Thereafter, the recovery rate of pyrolysis oil insignificantly changes with the increase of catalyst concentration. The main factor affecting this process is the oil content of oily sludge. Considering the preparation cost of catalyst, the ideal catalyst concentration is 1%.

3.2.5 Effect of the pyrolysis temperature on the pyrolysis products

The effect of temperature on pyrolysis products of oily sludge was investigated at a catalyst concentration of 1%. The relationship between the pyrolysis temperature and the products at 410–460°C is shown in Fig. 11.

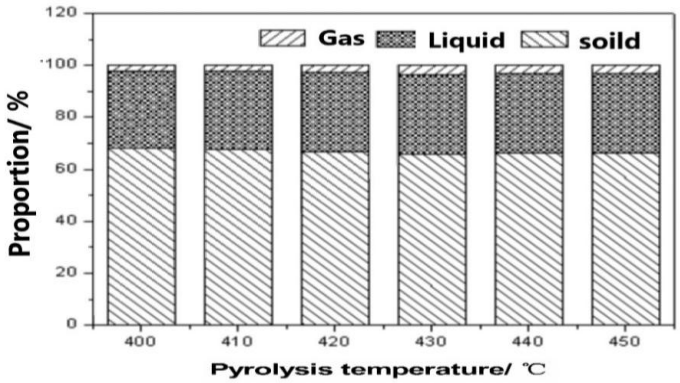

Fig. 11. Effect of temperature on pyrolysis products

Fig. 11 shows that the amount of gaseous pyrolysis products significantly increases with the increase of temperature. The number of liquid products first increases and then decreases, and the amount of solid products decreases with the increase of temperature. These phenomena are mainly due to the increase of temperature. With the increase of temperature, the macromolecular substances in the sludge are decomposed into small molecules and the pyrolysis of liquid components increases. However, when the temperature continues to rise, intermediate pyrolysis, that is, secondary cracking occurs, and the liquid products are partially cracked into gaseous products. Therefore, the amount of liquid pyrolysis products decreases after first increasing, while the number of gaseous products increases [19].

3.2.6 Effect of the catalyst concentration on the pyrolysis products

The effect of catalyst concentration on pyrolysis products of oily sludge was investigated at the pyrolysis temperature of 430°C, as shown in Fig. 12.

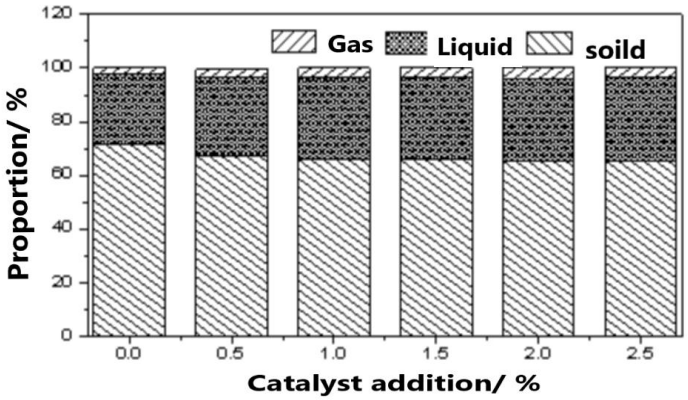

Fig. 12. Effect of catalyst concentration on the pyrolysis products

Fig. 12 shows that the gas- and liquid-phase concentrations in the pyrolysis products significantly increase after the addition of catalysts to the pyrolysis of oil-containing sludge. However, the decrease of solid-phase content indicates that the catalyst addition affects the pyrolysis of oil-containing sludge. With the increase of catalyst concentration, both the liquid- and gas-phase components of the pyrolysis products increase. When the concentration of catalyst is 1%, the gas- and liquid-phase concentrations in the pyrolysis products are stable because of the constant oil content in the sludge is and the maximum activity of the catalyst When more catalyst is added, a pyrolysis effect cannot be observed [14,16].

3.3 Effect of catalyst addition on the pyrolysis products

The concentrations of pyrolysis oil components were analyzed at the pyrolysis temperature of 430°C and catalyst dosage of 1%, as shown in Fig. 13.

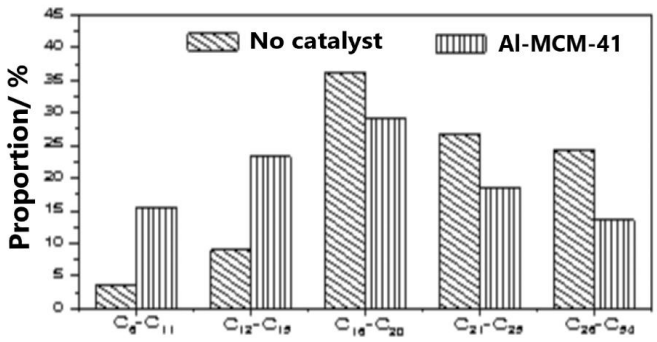

Fig. 13. Analysis of the contents of pyrolysis oil components

Fig. 13 show that the pyrolysis oil products mainly consisted of C16–C20 hydrocarbons. Compared with the pyrolysis oil produced without addition of catalysts, the pyrolysis oil produced by adding catalysts has fewer heavy-oil but more light-oil components. It indicates that catalyst addition improves the quality of pyrolysis oil. The analysis of four components of pyrolysis oil (Table 1) shows that the content of saturated hydrocarbons in pyrolysis oil increases significantly with catalyst addition, and the asphaltene, gum, and aromatic hydrocarbon contents decrease. This indicates that catalyst addition makes the heavy oil in sludge lighter and promotes the pyrolysis of sludge [20,21].

Table 1

Analysis of the four components of the pyrolysis oil

	Components (%)			
	Saturated hydrocarbons	Aromatic hydrocarbons	Gelatinous hydrocarbons	Asphaltene
No catalyst	20.21	33.79	1.82	7.26
Added catalyst	28.79	17.03	1.08	1.92

4. Conclusion

(1) After the addition of Al-MCM-41 molecular sieve catalyst with a Si/Al ratio of 60, the recovery rate of pyrolysis oil reaches 83.48% and the pyrolysis efficiency significantly improves at 430°C, a catalyst dosage of 1% and a pyrolysis time of 3 h.

(2) The pyrolysis oil is mainly composed of C16–C20 hydrocarbons. Compared with the pyrolysis process without a catalyst, the yield of C6–C15

fraction significantly increases due to catalytic pyrolysis. The addition of catalysts makes the pyrolysis oil lighter and the saturated hydrocarbon content increases significantly.

Acknowledgments

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