Study on Preparation of Fuel Oil from Three Kinds of Molecular Sieve Catalytic Cracking Waste Lubricating Oil

Jing Gong
School of Materials and Chemical Engineering, Minjian University, Fuzhou 350108, China
Email: 1445855606@qq.com.

Abstract. Three different molecular sieves hy, Rey and self-made Ti-MCM-41 were used as catalysts to produce fuel oil from catalytic cracking waste lubricating oil, the effects of reaction temperature and catalyst dosage on the yield of liquid product were investigated, and the distribution of carbon atoms and the distribution of alkanes, olefins, cycloalkanes and aromatics in liquid products obtained by cracking reaction with different catalysts were analyzed. The results show that, under the condition of adding 0.35g catalyst to 100g waste lubricating oil at 400℃, the catalytic effect of Ti-MCM-41 is the best. The yield of liquid product is 69.6%, which is more suitable for cracking waste lubricating oil than hy and Rey. Different catalysts have different selectivity for the liquid products of cracking reaction, the carbon number in the liquid products obtained from Ti-MCM-41 catalytic cracking is the most widely distributed in the range of light components, in which the contents of alkanes, cycloalkanes and aromatics are relatively high, which is consistent with the main chemical components of gasoline, and does not contain olefins, compared with the liquid products obtained from hy and Rey catalytic cracking, it is more suitable to be used as the blending component of commercial gasoline.

Keywords. Waste lubricating oil; catalytic cracking; Molecular sieve catalyst; fuel oil.

1. Introduction
With the development of economy, from the traditional agriculture to the rapid development of electronic industry, as well as People’s Daily life and other aspects can not do without lubricating oil. From 2013 to 2018, the global lubricating oil consumption increased from 39.6 million tons to nearly 46.6 million tons, with an average annual growth rate of 3.53% [1], however, the pollution of waste mineral oil to the environment is also worrying. So far, the treatment and disposal of waste lubricating oil has adopted two methods: direct incineration and waste lubricating oil regeneration. Direct incineration produces a lot of toxic substances and causes serious air pollution. In theory, it is an appropriate choice to treat the waste lubricating oil properly to become recycled oil, but a considerable part of the waste lubricating oil is impossible to regenerate, because the freezing point of the recycled oil can not meet the standard. Through catalytic cracking of waste lubricating oil and blending of additives, vehicle fuel oil of good quality can be obtained, which not only solves the problem of environmental pollution, but also brings economic benefits [2]. Waste lubricating oil was used as raw material in this study, the reaction of HY and REY zeolites used in crude oil cracking and TI-MCM-41 zeolites made by ourselves to liquid fuel from catalytic cracking waste oil was investigated. It provides a theoretical basis for the recovery and disposal of waste lubricating oil.
2. Materials and Methods

2.1. Test Material
Waste lubricating oil (Fujian Century Toyota Automobile Service Co., Ltd.); HY Molecular Sieve (Dalian Haixin Chemical Co., Ltd.); REY molecular sieve (Yueyang Huijing New Material Technology Co., Ltd.); Sodium hydroxide, cetyltrimethylammonium bromide, petroleum ether and other reagents are analytical pure.

2.2. Main Instruments
TD-3500 X-ray diffractometer (Beijing Aode Instrument Equipment Co., Ltd.); 722S infrared spectrometer (Shanghai Linguang Technology Co., Ltd.); Trace1300 / ISQ gas phase mass spectrometer (Thermo Fisher technology, USA), etc.

2.3. Preparation and Characterization of Ti-MCM-41 Molecular Sieve
Adding metal elements to MCM-41 molecular sieve, it can avoid the disadvantages of less lattice defects in MCM-41 framework, the modified MCM-41 molecular sieve has unlimited possibilities and application prospects [3]. Titanium is abundant in nature, Ti-MCM-41 was prepared by hydrothermal synthesis. Tetraisopropyltitanate was used as titanium source, tetraethyl orthosilicate as silicon source and cetyltrimethylammonium bromide as main template, at 75°C, Ti-MCM-41 molecular sieve was synthesized by molar ratio n(Si(OC2H5)4):n(C12H28O4Ti) = 1:0.02. The obtained product was roasted in a muffle furnace at a heating rate of 4°C/min to 550°C for 5h, get a white powder sample.

Figure 1 shows the XRD pattern of Ti-MCM-41 molecular sieve. According to figure 1, the obvious diffraction peaks of mesoporous molecular sieve Ti-MCM-41 appeared at about 2°, 3.95° and 4.25°, corresponding to (100), (110) and (200) crystal planes of hexagonal mesoporous cells respectively, the peak shape is consistent with the characteristic peak of mesoporous materials reported in literature [4], it shows that the synthesized molecular sieve is mesoporous structure, there is a regular pore structure. After calcination at 550°C for 5h, the three diffraction peaks are still obvious, indicating that the prepared Ti-MCM-41 molecular sieve has high thermal stability.

![Figure 1. XRD pattern of Ti-MCM-41 molecular sieve.](image)

Figure 2 is the FTIR spectrum of Ti-MCM-41 molecular sieve. As can be seen from figure 2, an absorption peak appears at 1042cm⁻¹, which is caused by the asymmetric stretching vibration of silicon oxygen tetrahedron in the skeleton, there is an absorption peak at 959 cm⁻¹, which is the vibration characteristic peak of Ti-O-Si bond, it is composed of the vibration peak 935cm⁻¹ of Ti-O-Si and the stretching vibration peak 980cm⁻¹ of Si-OH, it is proved that Ti component is branched or diffused into the mesoporous structure of silicon. The absorption peak near 797 cm⁻¹ is caused by the symmetrical stretching vibration of silicon oxygen tetrahedron in the skeleton, the absorption peak at 435cm⁻¹ is the bending vibration of Si-O bond. These absorption peaks indicate that the sample presents the characteristics of Ti-MCM-41 molecular sieve.
2.4. Experimental Method
Weigh 100g of waste lubricating oil into the reactor (self-made), and add a certain amount of molecular sieve catalyst, shake for 30s to fully mix the two, place the flask on the electric heating jacket and fill it with nitrogen, slowly raise the temperature to a certain temperature. The gas obtained from cracking is condensed through the condensing pipe, and the liquid product is collected in the conical flask, when no liquid flows into the conical flask, the catalytic cracking reaction can be regarded as reaching the end point. The liquid product was weighed and the yield of the liquid product was calculated. The liquid product was analyzed by gas chromatography-mass spectrometry using TG-5MS capillary column (30m × 0.25mm × 0.25μm) Separate, The initial temperature of the column is 40℃, and the constant temperature is maintained for 2min, the temperature rises to 270℃ at the heating rate of 20℃ / min, and the constant temperature is maintained for 5min; The inlet temperature is 300℃, the flow rate is 1.5mL/min, He is the carrier gas, and the split ratio is 30:1. The peak area normalization method was used for qualitative and quantitative analysis.

The yield of liquid product is calculated as follows:

\[ Y = \frac{M_1}{100} \times 100\% \]

where Y—Liquid product yield; 100—Weight of raw waste lubricating oil, g; M_1—Weight of liquid product, g.

3. Results and Analysis
3.1. Effect of Reaction Temperature on the Yield of Liquid Products
Table 1 shows the reaction results of catalytic cracking with 0.3g three different molecular sieves added to waste lubricating oil at different temperatures. It can be seen from the results in table 1 that the yield of liquid product obtained by using Ti-MCM-41 as catalyst is higher than that of HY and REY. This is because the pore sizes of hy and Rey molecular sieves are small, and the macromolecules in the waste lubricating oil cannot diffuse in the pores, The reaction is mainly carried out on and near the outer surface of the catalyst. Ti-MCM-41 molecular sieve has large pore size distribution and medium acidity, which can make macromolecules enter the pore for cracking reaction [5]. Therefore, Ti-MCM-41 is more suitable as cracking catalyst than HY and REY when fuel oil is the main target product. With the increase of reaction temperature, the yield of liquid product increases gradually, when the temperature reaches 400℃, the liquid product yield decreases when the temperature continues to rise. This is because part of the fuel oil is further cracked into small molecules, the temperature is too high, the energy consumption increases, and the carbon deposition is accelerated [6]. Therefore, the suitable temperature of Ti-MCM-41 catalytic cracking waste lubricating oil is about 400℃.
Table 1. Effect of reaction temperature on liquid product yield.

| Temperature/℃ | Y(HY)% | Y(REY)% | Y(Ti-MCM-41)% |
|---------------|--------|---------|---------------|
| 300           | 30.3   | 33.1    | 53.4          |
| 350           | 36.4   | 39.8    | 61.9          |
| 400           | 37.8   | 40.5    | 69.2          |
| 450           | 37.9   | 39.2    | 68.8          |

3.2. Effect of Catalyst Dosage on Liquid Product Yield

Table 2 shows the reaction results of catalytic cracking of waste lubricating oil by adding different amounts of three molecular sieves at 400℃. It can be seen from the results in Table 2 that with the increase of catalyst dosage, the yield of liquid products increases at the beginning. This is because increasing the amount of catalyst can increase the contact probability between reactants and catalyst and improve the catalytic cracking efficiency. Compared with HY and REY, the yield of Ti-MCM-41 liquid product always maintained the highest, but it increased first and then decreased, the reason for this result may be that the excess catalyst increases the side reactions in the reaction process, for example, the secondary catalytic cracking reaction is enhanced, resulting in the increase of gaseous small molecular products. It can be seen that the catalytic effect is the best when the dosage of Ti-MCM-41 is about 0.35g.

Table 2. Effect of catalyst dosage on liquid product yield.

| Consumption/g | Y(HY)% | Y(REY)% | Y(Ti-MCM-41)% |
|---------------|--------|---------|---------------|
| 0.2           | 23.4   | 30.1    | 52.3          |
| 0.35          | 38.0   | 40.9    | 69.6          |
| 0.5           | 38.1   | 40.3    | 67.2          |

Table 3. Carbon atom number content in liquid products of cracking reaction with different catalysts.

| Carbon content | W(HY)% | W(REY)% | W(Ti-MCM-41)% |
|----------------|--------|---------|---------------|
| C6             | 37.86  | 0.00    | 22.80         |
| C7             | 0.00   | 9.89    | 19.69         |
| C8             | 8.64   | 33.25   | 10.87         |
| C9             | 14.23  | 32.12   | 9.38          |
| C10            | 5.96   | 16.13   | 12.83         |
| C11            | 7.45   | 0.00    | 8.21          |
| C12            | 12.66  | 0.00    | 7.92          |
| C13- C17       | 13.20  | 8.61    | 8.30          |

3.3. Distribution of Carbon Atoms in Liquid Products of Cracking Reaction with Different Catalysts

In order to further study the composition and content of liquid products, the waste lubricating oil was cracked at 400℃ and the amount of catalyst was 0.35g. The liquid product obtained from the reaction was quantitatively analyzed by gas chromatography-mass spectrometry. The mass distribution of carbon atom number of liquid products in cracking reaction of different catalysts was listed in Table 3. It can be seen from the results in Table 3 that all three molecular sieves promote the cracking of waste lubricating oil, due to the influence of molecular diffusion, the pore structure of molecular sieve affects the carbon atom distribution of the product, but the liquid products are mainly light components. The main products of HY Molecular sieve cracking reaction are concentrated in C6, C9 and C12, the main products of the cracking reaction of REY molecular sieve are concentrated between C8 and C10. The main products of cracking reaction of Ti-MCM-41 molecular sieve are concentrated between C6 and C10. It shows that different molecular sieves have different selectivity for liquid products of cracking reaction. The carbon number obtained from catalytic cracking of Ti-MCM-41 molecular sieve is most widely distributed in the range of light components, Because of its large
 pore size distribution, many large and small molecules in the waste lubricating oil can enter and interact with the Bronsted acid site in the pore, thus, C-C bond fracture occurs and light components with different carbon numbers are generated [7].

3.4. Distribution of Alkanes, Olefins, Cycloalkanes and Aromatics in Liquid Products of Cracking Reaction with Different Catalysts

Fuel oil is a complex mixture composed of a variety of hydrocarbons, mainly including alkanes, olefins, cycloalkanes and aromatic hydrocarbons. It can be seen from the results of three molecular sieve catalytic cracking waste lubricating oils that the liquid products are mainly alkanes, olefins, cycloalkanes and aromatic hydrocarbons, the content of alcohols, ketones and other compounds is very low, and the product composition is basically between C6 - C12, which is similar to that of gasoline [8]. The mass distribution of alkanes, olefins, cycloalkanes and aromatic hydrocarbons obtained by cracking waste lubricating oil with three molecular sieves at 400°C and 0.35g is shown in table 4. It can be seen from the results in table 4 that the liquid products of catalytic cracking of three molecular sieves contain alkanes, cycloalkanes and aromatic hydrocarbons, and the liquid products of hy cracking contain the most cycloalkanes, up to 67.03%, the content in the liquid product of Ti-MCM-41 cracking is the second, up to 41.44%, and the liquid product does not contain olefins, this may be because hy and Ti-MCM-41 have good aromatization and hydrogen transfer properties [7]. Olefins produced by catalytic cracking immediately undergo aromatization reaction, followed by hydrogen transfer reaction to generate cycloalkanes. The liquid product of Ti-MCM-41 cracking contains the most alkanes, up to 35.40%, followed by the liquid product of HY cracking, up to 20.81%, this may be due to the larger pore size of Ti-MCM-41. The liquid products of Rey cracking contain olefins and aromatic hydrocarbons, which is due to the weak hydrogen transfer performance of REY. Moreover, due to the unsaturated characteristics of olefins, it has active chemical properties and poor oxidation stability, which is easy to cause gasoline discoloration, gumming and carbon deposition, and can not exist for a long time [8].The contents of alkanes, cycloalkanes and aromatic hydrocarbons in the liquid products of Ti-MCM-41 cracking are relatively high, which is consistent with the main chemical components of gasoline, compared with the liquid products of hy and Rey cracking, it is more suitable to be used as the blending component of commercial gasoline.

| Hydrocarbons | HY    | REY   | Ti-MCM-41 |
|--------------|-------|-------|-----------|
| W(Alkanes)/% | 20.81 | 11.24 | 35.40     |
| W(Olefins)/% | 0.00  | 8.92  | 0.00      |
| W(Cycloalkanes)/% | 67.03 | 9.37  | 41.44     |
| W(Aromatics)/% | 5.56  | 62.85 | 18.08     |

4. Conclusion

(1) HY, REY and self-made Ti-MCM-41 molecular sieves were used to produce liquid fuel by catalytic cracking of waste lubricating oil, the three molecular sieves have certain effects, among them, Ti-MCM-41 has the best catalytic effect. Under the condition of 400°C and 0.35g catalyst in 100g waste lubricating oil, the yield of liquid product is the highest, up to 69.6%, it is more suitable for cracking waste lubricating oil than hy and Rey.

(2) The catalytic liquid products of the three molecular sieves are mainly light components, and all contain alkanes, cycloalkanes and aromatic hydrocarbons. The liquid products of HY cracking are concentrated in C6, C8 and C12, the liquid products of REY cracking are concentrated between C8 and C16, the liquid products of Ti-MCM-41 cracking are concentrated between C8 and C18, it shows that different molecular sieves have different selectivity for liquid products of cracking reaction. The liquid product of Ti-MCM-41 cracking has the widest carbon number distribution in the range of light components, with high contents of alkanes, cycloalkanes and aromatic hydrocarbons, and does not contain olefins, it is consistent with the main chemical components of gasoline, and is more suitable for blending components of commercial gasoline than the liquid products of hy and Rey cracking.
Acknowledgments
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