

Development and Performance Evaluation of Catalyst for Productive Ethylene Cracking Feedstock in Selective Hydrocracking of Straight Run Diesel Oil

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Abstract

The upgrading of diesel oil to produce ethylene rich cracking feedstock is an important and promising technical route to reduce the ratio of diesel to gasoline. In the present work, a hydrocracking catalyst suitable for selective hydrocracking of straight run diesel oil to produce high-quality ethylene cracking feedstock at low cost was developed, by optimizing the composition of catalyst support materials, using amorphous silicon aluminum and aluminum oxide with high mesopore content as the main support, and modified Y zeolite with excellent aromatic ring opening selectivity as the acidic component. The catalyst has in-depth characterized by X-ray diffraction, transmission electron microscopy, scanning electron microscopy, N₂-low temperature adsorption-desorption, NH₃-temperature-programmed desorption, and IR techniques. And its catalytic cracking straight run diesel oil performance was evaluated. The results show that the prepared catalyst has high polycyclic aromatic hydrocarbon ring opening cracking selectivity. However, alkanes retained in diesel distillates can achieve the goal of producing more ethylene cracking feedstocks with low BMCI value under low and moderate pressure conditions. This work may shed significant technical insight for oil refining transformation.

Keywords

Straight Run Diesel, Mild Hydrocracking, Catalyst, Ethylene Cracking Feedstock, Process Research

1. Introduction

At present, China has excess refining capacity, unreasonable oil product structure, insufficient chemical capacity, and a large shortage of basic chemical raw materials such as aromatics and olefins. Refining transformation and upgrading is an inevitable choice to solve the contradiction between supply and demand and realize the sustainable development of China's refining industry.

With the decline in oil demand, China's diesel consumption has basically reached the peak, and the diesel consumption will decrease year by year. It is estimated that by 2025, the consumption ratio of diesel to gasoline will drop to 0.75. Therefore, reducing the ratio of diesel to gasoline, reducing oil consumption and increasing chemical consumption has become the development trend. Straight run diesel is the largest diesel component in the refinery, accounting for about 57wt% of the diesel pool composition. With the urgent demand of refinery production structure adjustment, transformation and upgrading, the reasonable and efficient processing and utilization of straight run diesel has become one of the focuses of refineries.

Ethylene is one of the important chemical raw materials in petrochemical industry. At present, China is the second largest ethylene producer in the world after the United States [1] [2] [3]. In 2019, China's total ethylene production capacity exceeded 30 Mt for the first time [4]. In 2021, ethylene production capacity exceeded 40 Mt, with an annual growth rate of 14.6%, and propylene production capacity of 50 million tons, with an annual growth rate of 13.7%. It is expected that the annual growth rate of 6% - 8% will still be maintained in the next few years, but there is still a large gap in consumption. With the long-term stable growth of market demand and production capacity, refining and chemical industry needs to broaden the source of ethylene cracking raw materials and increase ethylene production through multiple routes.

Hydrocracking technology is one of the important means of oil refining transformation and upgrading. It has the advantages of strong raw material adaptability, flexible processing scheme, high target product yield, and good product quality. In particular, hydrocracking technology based on chemical raw materials, with low BMCI value of hydrocracking tail oil and rich in paraffins, is a good raw material for steam cracking to ethylene unit, and has become a key technology for oil refining transformation and upgrading.

In order to increase the supply of ethylene raw materials, accelerate the pace of enterprise transformation and upgrading, and improve the market competitiveness, a petrochemical company of PetroChina plans to build a new ethylene plant, and at the same time use the existing diesel hydrofining unit for transformation, so as to realize the conversion of diesel into ethylene raw materials with low cost and high efficiency. In order to improve the economic benefit of refining and chemical enterprises, PetroChina Daqing Petrochemical Research Center has carried out the technology development of producing high quality ethylene cracking feedstock with low cost by selective hydrogenation ring opening

cracking of straight run diesel oil.

The focus of this study is to develop a hydrocracking catalyst suitable for producing high quality ethylene cracking feedstock at low cost through carrier modification technology, selection and optimization of active components. To provide technical support for the refining transformation of the enterprise, the performance of straight run diesel hydrocracking to produce more ethylene cracking feedstock was studied under the process conditions of the existing diesel hydrofining unit in a petrochemical company of PetroChina.

2. Test Part

2.1. Preparation of Catalyst

43 g modified mesoporous Y molecular sieve, 25 g mesoporous alumina, 44 g mesoporous amorphous silicon aluminum, and 4 g sesbania powder were added into the crucible, and mix well; 10 g concentrated nitric acid and 3 g citric acid were added into 68 g deionized water, stir and dissolve them, then added them to the crucible with mixed powder, knead them evenly, and the mixture was squeezed into 1.5 mm cylindrical shape, dried at 120°C and calcined at 540°C for 4 h to prepare the carrier. The metal co-leaching solution was prepared with ammonium metatungstate and nickel nitrate in a certain proportion, and the cylindrical support strip was co-leaching by saturated impregnation method. After impregnation, the cylindrical support strip was kept healthy for 2 h, dried at 120°C for 4 h, and calcined at 500°C for 4 h to prepare the catalyst. According to the specific requirements, broken or cut to the required particle size or length, after vulcanization can be carried out hydrogenation reaction.

2.2. Catalyst Characterization

Bruker D8 Advance X-ray diffractometer (XRD) was used to analyze the phase and crystallization status of the catalyst. The determination conditions were as follows: Cu target, $K\alpha$ ray, scanning Angle 2θ range of 5° - 50°, scanning speed of 1°/min, working voltage of 40 kV, working current of 400 mA, step size of 0.02°.

The pore structure of the catalyst was characterized by ASAP2020 physical adsorption analyzer (Micromeritics). The catalyst samples were firstly degassed at 250°C and vacuum of 1.33×10^{-3} Pa for 12 h, and then cooled to -196°C for N₂ adsorption and desorption test.

FEI Tecnai G2 F20 transmission electron microscope (TEM) was used to investigate the distribution of sulfide metals in the support. The samples were ground and pretreated and evenly dispersed in cyclohexane solution. The microgrid was placed on filter paper with tweezers, and the solution was dropped on the surface of the microgrid with an eyedropper. After the solvent evaporated, the TEM sample was observed.

The acid content and strength of the catalyst were measured by NH₃-TPD made in laboratory. The specific operation steps are as follows: 500 mg sample

(20 - 40 mesh) was activated under nitrogen atmosphere at 600°C for 30 min, then the temperature was lowered and kept at 110°C, and ammonia was injected into it for 30 min until adsorption saturation. The NH₃ was removed by nitrogen purging at 110°C for 60 min. Finally, the sample was heated to 600°C at a heating rate of 10°C/min, and the desorbed NH₃ was determined by a thermal conductivity detector. The desorbed ammonia was absorbed with 1 mol/L HCl standard solution and titrated with 1 mol/L NaOH standard solution to obtain the total acid content of the sample.

2.3. Performance Evaluation of Catalyst

2.3.1. Evaluation Device

The evaluation was carried out in “PetroChina hydrogenation catalyst and process engineering test base”. The evaluation device is 200 mL fixed bed hydrogenation test device, as shown in **Figure 1**. The catalytic performance of the developed catalyst was evaluated by using the process of raw material and hydrogen passing through at one time.

2.3.2. Analysis Method

The oil analysis items and methods used in the test are shown in **Table 1**.

2.3.3. Raw Materials of Evaluation

The diesel feedstock used in the test is intermediate-based straight run diesel from a refinery of a petrochemical company of PetroChina, and its properties are shown in **Table 2**.

3. Results and Discussions

3.1. Catalyst Characterization Results

The XRD characterization results of hydrocracking catalyst are shown in **Figure 2**. As can be seen from **Figure 2**, the catalyst has a wide and low double characteristic peak at 46.1° and 66.7°, which represents the characteristic diffraction peak of γ -Al₂O₃ in all oxidation state catalysts, and the content is not high [5]. The characteristic peaks of Y molecular sieve appear in the hydrocracking

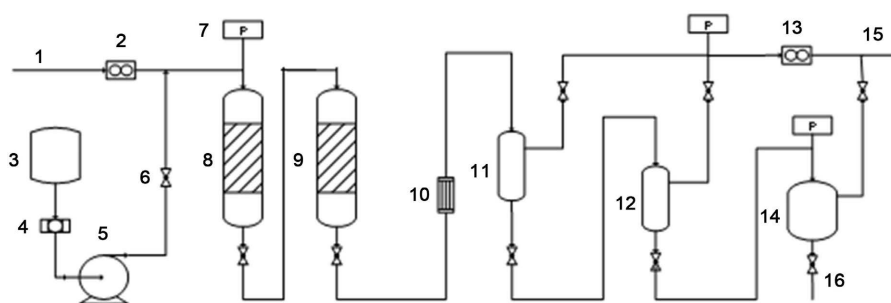


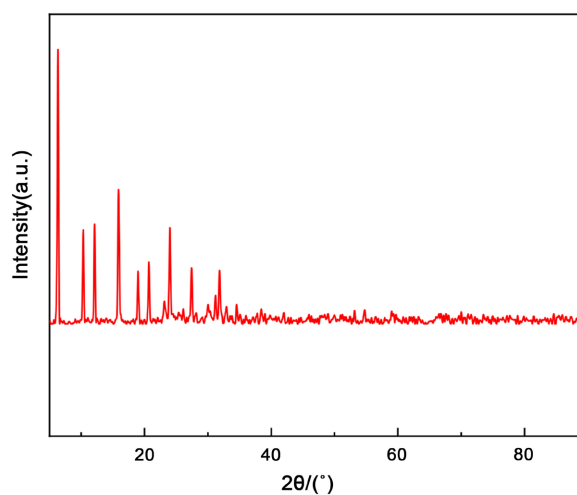
Figure 1. Flow diagram of 200 mL hydrogenation evaluation unit. 1. Hydrogen; 2. Hydrogen flowmeter; 3. Stock tank; 4. Filter; 5. Feed pump; 6. Ball check; 7. Pressure gauge; 8. First reactor; 9. Second reactor; 10. Cooler; 11. High pressure separator; 12. Low pressure separator; 13. Tail gas flowmeter; 14. Product tank; 15. Tail gas; 16. Sampling port.

Table 1. Analysis items and analysis methods.

Items	analysis method
density	GB/T 1884
Sulfur content of raw material	GB/T 17040
Nitrogen content of raw materials	ASTM D4629
Sulfur content of product	SH/T 0689
Nitrogen content of product	ASTM D4629
Distillation range	ASTM D86
True boiling point distillation	ASTM D2892
BMCI value	GB/T 6536
Hydrocarbon composition	SH/T 0606

Table 2. Properties of diesel feedstock.

Items	Intermediate based straight run diesel	
Density (20 °C), g/cm ³	0.8392	
sulphur content, µg/g	2673	
nitrogen content, µg/g	57	
Distillation range, °C	HK	171
	50%	273
	KK	367
BMCI value	27.1	
Hydrocarbon composition, wt%	Alkanes	45.4
	Cycloparaffins	33.6
	Aromatics	21.0
	Monocyclic	14.7
	Bicyclic	5.7
	Tricyclic	0.6

**Figure 2.** XRD spectra of the catalyst.

catalyst at 12°, 16°, 19°, 20° and 24°, respectively. From the XRD characteristic peaks of Y molecular sieve in the hydrocracking catalyst, it can be seen that the Y molecular content of the hydrocracking catalyst is relatively high. The characteristic diffraction peaks of metal oxides (NiO and WO₃) were not found in the spectrogram, which indicated that the metal oxides dispersed evenly on the molecular sieve support and the metal oxide particles formed were smaller (lower than the detection limit of the instrument). According to the above analysis, the hydrocracking catalyst is a catalyst supported by γ -Al₂O₃ and Y molecular sieve mixed with Ni and W.

The specific surface area, pore structure parameters and lateral compressive strength of the support and catalyst are listed in **Table 3**.

Figure 3 is a representative transmission electron microscope photograph of the vulcanized hydrocracking catalyst. The lamellar structure of the active phase of WS₂ or NiS can be clearly seen. The hydrocracking catalyst accumulates in a large number of layers, because the metal of the hydrocracking catalyst and the carrier interact with each other to form the NiWS-II active phase [6], which has stronger hydrogenation activity. A suitable accumulation layer number will provide more edge sites of the active phase for reactant and product molecules to adsorb.

Figure 4 is the NH₃-TPD curve of the catalyst, and **Table 4** is the acid amount and acid intensity distribution obtained by integrating the image of the corresponding catalyst [6]. As shown in the figure, the hydrocracking catalyst has a high weak acid desorption peak around 200°C. The peak strength of the hydrocracking catalyst is strong, and the peak area is large, indicating that there are more acidic centers on the surface of the catalyst, and the total acid content is large, so the hydrocracking catalyst should have high cracking activity.

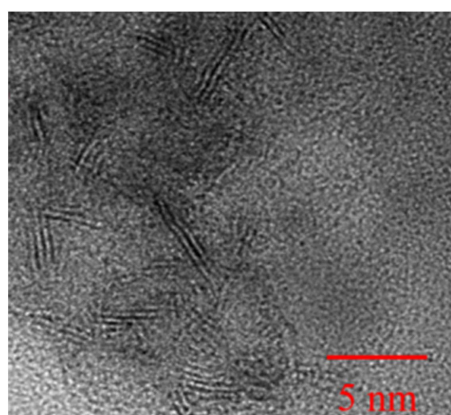
3.2. Properties and Characteristics of Middle Base Straight Run Diesel Oil

Alkanes in ethylene cracking feedstock can be directly cracked to produce ethylene and other low-carbon olefin products, while cycloalkanes and aromatics are more prone to condense to produce heavy aromatics or even coking. Therefore, the yield of ethylene and other low-carbon olefins in the products is determined by the content of alkanes, while the content of cycloalkanes and aromatics will affect the operation cycle of cracking unit [7] [8]. Generally, correlation index (BMCI) is used to characterize the aromaticity of hydrocarbons. The higher the value is, the higher the aromaticity is and the worse the cracking performance is.

From **Table 2**, it can be seen that the intermediate base straight run diesel has the characteristics of low density, low nitrogen content and high naphthenic hydrocarbon and aromatics content; from the analysis data of hydrocarbon composition, it can be seen that the chain alkane content of the intermediate base direct run diesel is 45.4 wt%, the cycloalkanes content is 33.6 wt%, the aromatics content is 21 wt%, and the polycyclic aromatic hydrocarbons content is 6.3 wt%, the BMCI value is 27.1. Compared with high quality ethylene cracking feedstock,

Table 3. Physical properties of the support and catalyst.

	Items	Value
carrier	specific surface area, m ² /g	426
	pore volume, mL/g	0.46
	Strength, N/cm	205
catalyst	specific surface area, m ² /g	278
	pore volume, mL/g	0.35
	Strength, N/cm	236

**Figure 3.** TEM of the catalyst.**Table 4.** Acid content of catalyst.

Items	Amount of acid, mL/g
weak acid	3.79
moderately strong acid	4.04
strong acid	1.11
total acid	8.94

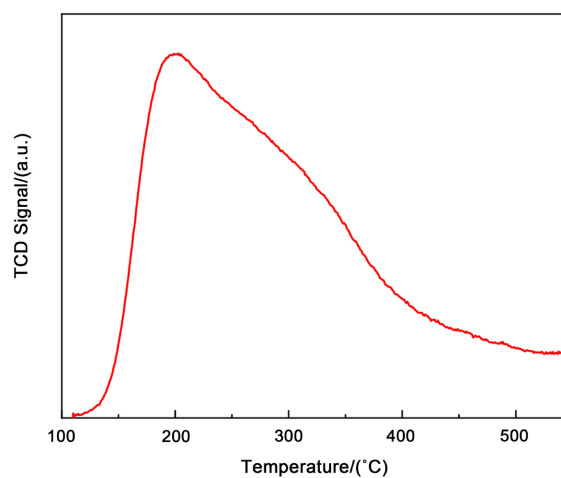
**Figure 4.** NH₃-TPD profile of catalyst.

Table 5. Evaluation results of the intermediate based direct diesel in a Petrochemical Company.

Items	intermediate based straight run diesel		Product		
Process conditions					
Pressure, MPa			6.7		
Hydrogen-oil ratio, (V/V)			500:1		
Temperature (Refining/cracking), °C	-		350/365		
LHSV of cracking, h ⁻¹			1.84		
Liquid yield/wt%	-		97.6		
Fractions at different temperatures, °C	-	Whole fraction	<155	155 - 235	>235
Yield of different fractions, wt%	-	-	53.92	23.18	22.90
Density, (g/cm ³) (20 °C)	0.8392	0.7330	0.6970	0.7904	0.7966
sulfur content, (µg/g)	2673	3.8	0.5	3.4	6.1
nitrogen content, (µg/g)	57	<1	<1	<1	<1
Distillation range, °C					
HK	171	29.2	29.7	167.8	244.1
10%	202	79.7	45.2	179	257.4
30%	237	118.2	68.9	185.7	262.8
50%	273	163.7	90.9	194.3	271.1
70%	308	232.5	109.4	204.9	284.4
90%	345	271.2	131.1	217.7	311.2
KK	367	321.1	167.4	226.4	337.6
BMCI value	27.1	-	9.6	22.8	10.5
Hydrocarbon composition, wt%					
Alkanes	54.4	-	-	45.2	71.4
Cycloparaffins	33.6	-	-	45.7	25.7
Aromatics	21.0	-	-	9.1	2.9
Monocyclic	14.7	-	-	8.9	2.9
Bicyclic	5.7	-	-	0.1	-
Tricyclic	0.6	-	-	0.1	-
Naphtha + diesel yield, wt%	-		76.82		

straight run diesel has lower alkane content, higher aromatics content and higher BMCI, so it is not suitable to be used as ethylene cracking feedstock directly.

If intermediate based straight run diesel is used to produce ethylene cracking feedstock, it is necessary to enrich naphthenic and aromatic hydrocarbons into

naphtha fraction through selective ring opening cracking and other reactions, and retain alkanes in diesel products, so as to improve the content of alkanes in diesel products, reduce the content of aromatic hydrocarbons and obtain high-quality ethylene cracking feedstock.

3.3. Performance Evaluation of Selective Hydrocracking of Straight Run Diesel

In this study, using the intermediate based straight run diesel as raw material, the performance of selective hydrotreating cracking of straight run diesel oil was evaluated by using mature hydrotreating catalyst and developed diesel hydrocracking catalyst under the condition of unit production plan.

Table 5 shows the evaluation results of the intermediate based straight run diesel.

The results showed that the yield of ethylene cracking feedstock (naphtha + diesel) could reach 76.82 wt% under the conditions of pressure of 6.7 MPa, refining/cracking reaction temperature of (350/365) °C, hydrogen/oil ratio of 500:1 and cracking space velocity of 1.84 h⁻¹, and the BMCI values of naphtha and diesel were 9.6 and 10.5 respectively, which could be used as ethylene cracking feedstock. However, the BMCI value of kerosene is 22.8, the aromatics content of kerosene is still very high, which is not suitable for ethylene cracking and can be used as blending component of low pour point diesel.

4. Conclusions

1) A diesel oil hydrocracking catalyst was successfully prepared by using amorphous silica alumina and alumina with high mesoporous content as main carriers, modified Y molecular sieve with excellent aromatics ring opening selectivity as acidic component and W-Ni as active metal component.

2) Under the conditions of low pressure, high space velocity and low hydrogen to oil ratio (pressure 6.7 MPa, cracking space velocity 1.84 h⁻¹, hydrogen/oil ratio 5000:1), the yield of ethylene cracking feedstock can reach 76.82 wt%, and the BMCI values of naphtha and diesel are 9.6 and 10.5 respectively, which can be used as high-quality ethylene cracking feedstock with low BMCI value.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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