[Regular Paper]

Effect of Aluminum Phosphate Species as New Matrix Component on Cracking Performance of FCC Catalyst with or without ZSM-5 Additive

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Higher propylene production inside fluid catalytic cracking (FCC) units is strongly desired to satisfy the increasing demand for petrochemical feedstock in recent years. Although propylene production can be increased *via* physical mixing of a suitable catalyst containing ZSM-5 (commonly referred to as additive) with FCC catalyst, this technique is usually associated with increased amount of distillate containing heavy fuel oil such as slurry oil (SLO). In this study, the effect of aluminum phosphate ([Al-P]) as a new matrix component was investigated. The use of an additive with FCC catalyst containing [Al-P] successfully formed liquefied petroleum gas containing propylene in higher yield compared with conventional FCC catalyst containing rare-earth, and suppressed the undesirable increase in SLO yield. This catalytic system has high potential for use in FCC units.

Keywords

FCC, Matrix, Monoaluminum phosphate, Additive, Propylene, ZSM-5

1. Introduction

Fluid catalytic cracking (FCC) is designed to upgrade heavy crude oil into lighter fractions with high added value such as gasoline. FCC units are generally operated to satisfy the following two demands. First, to increase production of the gasoline fraction with high octane number in order to reduce the impact on the environment. Second, to efficiently convert heavy fractions into gasoline and other light fractions, since heavy fuel oil such as SLO, the by-product of FCC process, tends to exceed the demand due to the reduced need for fuel oil C and other heavy oils.

Catalysts used in FCC units (FCC catalysts) generally contain rare-earths (REs). These catalysts have cracking activity, but usually decrease the octane number of the gasoline fraction, so the two demands for FCC are very difficult to satisfy. Modification of the FCC catalyst with monoaluminum phosphate (denoted [Al-P]) resulted in [Al-P]-containing catalyst with cracking activity as high as or greater than that of the catalyst modified with RE, and also greater effect to suppress the decrease in octane number of the gasoline fraction compared with the RE-modified catalyst^{1,2)}.

In addition to the above requirements, increased pro-

duction of light olefin such as propylene is also desirable. The demand for gasoline is decreasing yearly in Japan, whereas the demand for petrochemical feedstock, particularly propylene, is increasing due to the economic development of Asian countries. For these reasons, recent requirements for the FCC process include suppressing the formation of heavy oil and converting the gasoline fraction into propylene³⁾. Various modifications of the catalysts and the FCC process have been proposed to increase propylene production. For example, additives can increase propylene production. ZSM-5-containing additives (denoted as “additives” in this paper) enable more selective conversion of the FCC gasoline fraction to propylene compared with USY used without additives in the conventional FCC catalyst, mainly because of the high acid strength of ZSM-5. Additives are usually blended physically into the FCC catalyst at a concentration of a few percent.

RFCC and HS-FCC^{4)~7)} are known as improved FCC processes, which use catalysts consisting of a mixture of FCC catalyst and an additive. Typical reaction conditions include short contact time that could improve the range of reaction temperatures suppressing side reactions, so that production of propylene is increased and the yield of heavy oil is reduced.

Modification and expansion of the equipment of already-running processes is time-consuming and expensive. In contrast, using additives to increase propylene production would allow free control of propyl-

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ene production by increasing or decreasing the amount of additive (even down to zero). In addition, improvements could be made quickly and inexpensively. Consequently, use of additives is expected to be effective for increasing propylene production in FCC processes. However, the effect of the additive is likely to vary depending on the characteristics of the FCC catalyst with which the additive is combined.

Catalyst containing [Al-P] provides higher cracking activity and higher octane number of the gasoline fraction compared with conventional catalysts, and also has enhanced hydrothermal stability^{1),2)}. In addition, modification with RE metal is commonly used to enhance the performance of FCC catalysts. However, the effect of additives on these modified FCC catalysts is still unknown.

In this paper, we report the effect of additives on FCC catalyst modified with new matrix components, especially [Al-P].

2. Experimental

2.1. Catalyst Preparation

Pure water (184.7 g) was added to 144.8 g of water glass (loss of ignition (LOI): 71.0 mass%, JIS No. 3) and mixed well with vigorous stirring. This mixture was added to 98.7 g of 25 wt% sulfuric acid solution (LOI: 7.8 mass%) with stirring at 50 °C using a thermostatic chamber to obtain a binder slurry. Separately, 173.6 g of pure water was added to 86.8 g of Y zeolite and stirred well (zeolite slurry). The zeolite slurry was added to the binder slurry with stirring to obtain a mixed slurry. Then the matrix components, 76.3 g of kaolin clay (LOI: 86.5 mass%), 4.3 g of monoaluminum phosphate ([Al-P]; LOI: 46.2 mass%) and 34.5 g of Al₂O₃ (LOI: 75.3 mass%), were added to the mixed slurry. The amount of [Al-P] was adjusted to 1 mass% of the mixed slurry on a dry basis. After stirring the mixed slurry well, the catalyst product was dried using an FOC-20 spray dryer (Ohkawara Kakohki Co., Ltd.).

The spray-dried catalyst was added to a 5 % aqueous solution of ammonium sulfate to remove residual Na element from the catalyst. After stirring for 30 min at 60 °C, the mixture was filtered and the residue was washed well with 60 °C water, and dried for 12 h at 120 °C. Catalyst without [Al-P] was used as the reference catalyst, and catalyst blended with [Al-P] was used as the [Al-P]-containing catalyst. After removal of Na from the catalyst without [Al-P], ion exchange treatment was performed in a hot water bath at 60 °C using aqueous solutions of lanthanum nitrate hexahydrate (Kanto Chemical Co., Inc.) to achieve 1 mass% (indicated below as 1 % RE) and 5 mass% (indicated below as 5 % RE) in the catalyst.

2.2. Evaluation of Catalytic Activity

FCC catalyst is typically used under specific condi-

tions in which catalytic activity is degraded by the effect of steam and poisoning metals. To mimic the catalyst used in the commercial FCC unit, deactivation treatment was first performed for the catalysts in this study, and then the resulting materials were used for evaluation. The OCTUP-11S obtained from JGC Catalysts and Chemicals Ltd. was used as an additive.

2.2.1. Deactivation Treatment of FCC Catalyst

Naphthenic nickel and naphthenic vanadium (Nihon Kagaku Sangyo Co., Ltd.) were added to cyclohexane and stirred (metallic solution) so that the amounts of Ni and V on the catalysts were 1000 massppm and 2000 massppm, respectively. To this metallic solution, the prepared FCC catalysts after thermal drying for 2 h at 600 °C were added and stirred, followed by removal of cyclohexane *via* evaporation at 100 °C. The resulting solids were thermally treated at 600 °C for 2 h to give Ni- or V-impregnated catalysts¹³⁾. These catalysts impregnated with poisoning metals were treated under steam flow at 800 °C for 6 h to obtain the deactivated catalysts.

2.2.2. Deactivation Treatment of Additive

The additive was treated with only hydrothermal degradation treatment, without impregnation of poisoning metal, under steam flow at 800 °C for 6 h.

2.2.3. Catalyst Performance Evaluation

The FCC catalyst after deactivation treatment was physically mixed with the additive in various amounts, and then catalyst performance was evaluated using the ACE-MAT unit (Kayser Technology Inc.). The ACE-MAT unit is illustrated in **Fig. 1**. Cracking performance with various catalyst/oil (C/O) ratios was evaluated at a reaction temperature of 510 °C using vacuum gas oil (VGO) obtained from the refinery of Cosmo Oil Co., Ltd. The produced fractions were analyzed by gas chromatography using an Agilent 7890A gas chromatograph (Agilent Technologies). The cracking activity was defined and calculated as 100 – [light cycle oil (LCO) yield (190–350 °C) + slurry oil (SLO) yield (350 °C or higher)]. The gasoline fractions were identified using an Agilent 6890 gas chromatograph (Agilent Technologies). The LPG yield was defined as the fractions up to 28 °C with the exception of C1 and C2

Fig. 1 Schematic Diagram of ACE-MAT Unit

FCC raw material oil collected from the refinery of Cosmo Oil Co., Ltd. was evaluated at the catalyst/oil (C/O) ratio of 6 (mass%/mass%). FCC catalyst used in this study contains 1 % RE.

Fig. 2 Catalytic Performances of FCC Catalyst, Additive, and Their Mixture

Fig. 3 Drawings Showing Framework Structures and Approximate Pore Diameters of (a) USY (framework type code: FAU) and (b) ZSM-5 (framework type code: MFI)

compounds.

3. Results and Discussion

3.1. Performances of FCC Catalyst, Additive, and Mixtures

Figure 2 compares the catalytic performances of the FCC catalyst, additive, and mixtures. Catalysis using only additive mainly provided SLO, whereas only FCC catalyst mainly formed light fractions such as LPG or gasoline. The ZSM-5 zeolite used in the additive has pores which are too small to crack the heavy fraction (Fig. 3). Mixtures of FCC catalyst with additive resulted in decreased gasoline yield and increased LPG yield. These results indicate that mixtures of FCC catalyst and additive can increase propylene production.

3.2. Effect of Additive

The effects of various amounts of additives were examined on the catalytic performance of FCC catalyst blended with 1 % RE. As shown in Fig. 4, gasoline yield decreased and LPG yield increased with higher amount of additive. The addition of additive may have resulted in excess cracking of the gasoline fraction into the LPG fraction, which is consistent with the findings

Fig. 4 Effect of Amount of Additive on the Yields of (a) LPG, (b) Gasoline, and (c) SLO over FCC Catalyst Containing 1 % RE

FCC catalyst used in this study contains 1 % RE.

Fig. 5 Carbon Number Distributions in the Fractions of LPG and Gasoline with Various Amount of Additive

in section 3.1. and previous reports^{8),9)}. In addition, the SLO yield increased with higher amount of additive. Based on the results in section 3.1., the content of FCC catalyst in the total catalytic mixture introduced into the FCC unit decreased with higher amount of additive, resulting in almost no cracking of the heavy fraction.

Figure 5 shows the changes in the carbon number distribution of the LPG and gasoline fractions caused by additive in the FCC catalyst. The results indicate that blending with additive caused excessive cracking of C6-C9 hydrocarbons and conversion into LPG. Figure 6 shows the distribution of each hydrocarbon type within C8 during the reaction. The fractions of isoparaffin and olefin, especially olefin, significantly decreased. The additive presumably caused excessive cracking of the olefin component in C6-C9, with conversion to LPG.

3.3. Effect of the Combination of FCC Catalyst with Additive on Product Yield

Figure 7 compares the catalytic performances of FCC catalysts with different contents of RE and FCC catalyst containing [Al-P]. LPG yield increased with higher content of RE from 1 to 5 %, whereas the yield

Fig. 6 Effect of Additive on the Composition of C8 Fraction Obtained over FCC Catalyst Containing 1 % RE

Fig. 7 Effects of [Al-P] and RE on the Yields of (a) LPG and (b) SLO

of LPG was lower with the catalyst containing [Al-P] (Fig. 7(a)). In addition, SLO yields were in the order: 1 % RE > 5 % RE > [Al-P]-containing catalyst (Fig. 7(b)). These results are considered to reflect the improved stability and acid property of zeolite optimally modified with RE or [Al-P]^{1),2)}.

Figure 8 shows the catalytic performances of modified FCC catalysts with additives. In the presence of additive, yields of both LPG containing propylene and SLO increased, which is the common tendency among all catalysts in this study. In the case of 1 % RE blended with additive, the unwanted SLO yield increased while maintaining the LPG and propylene yields as high as that over the catalyst containing [Al-P]. In the case of 5 % RE blended with additive, the yield of demanded LPG decreased although SLO yield remained at the same level as that over the catalyst containing [Al-P]. Conversely, LPG and propylene yields were high and the SLO yield was well suppressed, which could not be achieved by the effect of only RE. Therefore, catalyst containing [Al-P] is preferable for enhancing the yield of LPG, which contains propylene, and reducing the yield of undesired SLO.

Amount of additive is constant.

Fig. 8 Effect of Mixing Additive with [Al-P]- or RE-containing Catalyst on the Yields of (a) LPG (left axis), Propylene (right axis), and (b) SLO

Table 1 Olefin Content of Gasoline Fraction Formed over Each Catalyst [vol%]

[Al-P]-containing catalyst	Catalyst containing 1 % RE	Catalyst containing 5 % RE
Base	+ 0.1	- 13.2

Possible reasons for the excellent performance of the catalyst containing [Al-P] include (1) the ability of [Al-P]-containing catalyst to suppress the hydrogen-transfer reaction, (2) high olefin content within the gasoline fraction as shown in Table 1, and (3) sufficient stabilization of zeolite by [Al-P]. Accordingly, the catalyst containing [Al-P] has obvious advantages, especially for increased production of propylene by blending with additive in the FCC unit.

4. Conclusion

Investigation of the addition of phosphoric compounds to FCC catalyst showed that monoaluminum phosphate, [Al-P], induced enhanced cracking activity and zeolite stability. In the presence of additive, [Al-P]-containing catalyst simultaneously achieved high propylene and low SLO yields, which are not possible using catalysts modified with RE only. The [Al-P]-containing catalyst is thus very effective for the production of petrochemicals such as propylene when blended with additive in the FCC unit.

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要 旨

FCC 触媒の性能に対する ZSM-5系アディティブと第一リン酸アルミニウムの併用効果

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国内のガソリン需要の減退傾向に対し、石油化学基礎原料の一つであるプロピレンの需要量は年々増加傾向にある。プロピレンはナフサクラッカーの副生成物もしくは流動接触分解(FCC)装置から得られる液化石油ガス(LPG)に含まれている。FCC装置におけるプロピレン含有LPG増産のための一手法として、FCC触媒にアディティブとしてZSM-5等を含む触媒を物理混合する方法が用いられている。本研究では、まずアディティブの添加により、主にガソリン留分中のC7～C11オレフィンが過分解され、LPGへ変換されることを見出した。また、アディティブ添加量の増大に伴い、FCC触媒の割合が低下するため、分解活性が低下し、スラリー油(SLO)等の重質

な燃料油の収率が増加する課題を確認した。一方、ゼオライトの安定化効果が高いことが分かっている第一リン酸アルミニウム([Al-P]と表記)を配合したFCC触媒は、水素移行反応の抑制などの影響で、オレフィン含有量の多いガソリン留分を与える。種々検討の結果、アディティブを添加した場合、[Al-P]を配合したFCC触媒は、LPG収率の向上とSLO収率の抑制を両立することが明らかとなった。これは、従来型希土類配合FCC触媒では達成できなかったことである。したがって、[Al-P]配合FCC触媒は、アディティブ添加による石油化学基礎原料の増産に適合すると言える。

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