1. Introduction

1.1. Background

Fluid catalytic cracking (FCC) is an important process to convert heavy raw oil into light fractions with high additional value such as FCC gasoline. In recent years, heavy fuel oil, such as slurry oil (SLO) which is a by-product of the FCC process, has tended to be in surplus due to the reduction in demand for heavy oils such as C fuel oil. On the other hand, gasoline fractions must have increased octane number to enhance energy efficiency with the greater need for environmental preservation. Therefore, FCC units which operate at much higher cracking yields and efficiencies are very desirable. Furthermore, world supply will include heavier types of crude oil, so FCC units must process heavier crude oil. However, FCC processing of heavier crude oil will require modification of the units. The reactivity of the crude oil is decreased because of the increased content of aromatic compounds with poor reactivity. New types of FCC unit can process much heavier feedstocks, and FCC units can be remodeled to enhance cracking activity\(^1\)\(^2\). However, these developments are costly and difficult to introduce, so techniques not involving the introduction of new equipment or remodeling of the FCC unit are very desirable. Previously, the FCC catalyst has included rare earth metals to increase the cracking activity with stability enhancement of the zeolite structure. However, the octane number is decreased due to promotion of the hydrogen transfer reaction\(^3\). We found that mono aluminum phosphate (Al-P) induces higher cracking activity than rare earth metal and inhibits the decrease in octane number\(^4\)\(^5\).

The present study evaluated the activity of Al-P catalyst in the commercial FCC unit, and examined the additional effects of Al-P.

Keywords
FCC catalyst, Hydrothermal stability, Commercial FCC unit, Mono aluminum phosphate

1.2. FCC Unit

Figure 1 shows a schematic view of the FCC unit\(^6\). In general, the FCC unit is comprised of a riser (reaction column), regenerator column and distillation sec-
tion. The catalyst used in the FCC unit (FCC catalyst) makes contact with the feedstock introduced from the bottom of the riser, and the cracking reaction proceeds inside the riser. Coke produced by the cracking reaction and secondary reaction of the products accumulates on the catalyst, resulting in gradual reduction of the cracking activity of the FCC catalyst. The post-reaction catalyst is transferred into the regenerator, and regenerated by burning and removing the coke. The heat obtained from coke burning is used for operations such as heating the feedstock, and maintaining the temperature of the reaction column. Consequently, the FCC catalyst passes through repeated reaction and regeneration cycles, and circulates through the inside of the unit. As the catalyst circulates inside the unit, mechanically worn catalyst (fine catalyst) is produced by contact with unit pipe walls and between the FCC catalyst particles, and this fine catalyst is collected by a dust collector called a cyclone installed at the top of the riser, so that the fine particles are not scattered into the system.

The FCC unit also suffers decreases in cracking activity due to poisoning of the catalyst by deposition of nickel and vanadium contained in the feedstock, and in the steam produced by the combustion of hydrocarbons (coking) not separated at the top of the riser and brought into the regenerator. Therefore, the catalyst is replenished to compensate for the losses due to removal of fine catalyst. Therefore, the FCC unit can be operated to maintain a fixed cracking activity by removing a certain amount of catalyst with reduced cracking activity (equilibrium catalyst), and supplying fresh catalyst in the same amount as the equilibrium catalyst.

The products of cracking by the FCC catalyst are separated at the distillation section to produce: (1) Dry gas (H₂, C₁, C₂), (2) LPG (Liquefied Petroleum Gas: C₃-C₄), (3) Gasoline, (4) LCO (Light Cycle Oil), and (5) SLO (Slurry Oil).

1.3. Present Investigations

We previously discovered that Al-P is as effective as rare earth metals in improving the stability of the zeolite crystal structure, and inhibits reduction in octane number⁷). Blending in Al-P may be responsible for improving cracking activity because more zeolite crystal structure and cracking activity sites remain even after deactivation treatment. Therefore, the present study evaluated the use of catalyst containing Al-P in the commercial FCC unit to verify catalytic activity and product properties such as octane number and confirm operational availability. Zeolite deterioration is caused by vanadium contained in the raw oil (metal deterioration), and steam (hydrothermal deterioration). Addition of Al-P is likely to suppress one or both types of deterioration.

2. Experimental

2.1. Operation of Developed Catalyst in Commercial FCC Unit

2.1.1. Preparation and Manufacture of Catalyst

To verify catalyst performance in the commercial FCC unit, the catalyst manufacturing process was scaled up and catalyst was manufactured on the industrial scale with commercial equipment based on the catalyst preparation method and catalyst composition indicated below.

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 after stirring well, this mixture was added with stirring to 98.7 g of 25 wt% sulfuric acid solution (LOI: 7.8 mass%) in a thermostatic chamber at constant 50 °C (binder slurry). Separately, 173.6 g of pure water was added to 86.8 g of Y zeolite, and stirred well (zeolite slurry). Then 76.3 g of kaolin clay (LOI: 86.5 mass%), 4.3 g of mono aluminum phosphate (LOI: 46.2 mass%) and 34.5 g of Al₂O₃ (LOI: 75.3 mass%), which acts as the matrix component, were added into the zeolite slurry, then this mixture was added with stirring to the binder slurry (mixed slurry). After stirring the mixed slurry well, drying was performed using a spray dryer (FOC-20 made by Ohkawara Kakohki Co., Ltd.). The spray dried catalyst was added to a 5 % aqueous solution of ammonium sulfate to remove Na remaining in the catalyst. After stirring for 30 min at 60 °C, rinsing and filtration were performed with hot water at 60 °C, and the catalyst was obtained by drying for 12 h in a dryer at 120 °C. A catalyst not containing Al-P was used as the reference catalyst, and a catalyst blended with Al-P was used as the catalyst containing Al-P. In order to introduce the specified amount of rare earth metal to the reference catalyst, lanthanum nitrate hex hydrate (made by Wako Pure Chem. Ind., Ltd.) was used, and ion exchange was performed in a hot water bath at constant 60 °C.

2.1.2. Verification of Catalyst Performance in Commercial FCC Unit

Verification of catalyst performance in the commercial FCC unit was carried out by replacing the conventional FCC catalyst with the developed catalyst, and then loading the catalyst into the FCC unit. The FCC unit was not expanded or modified to evaluate the cracking activity of the Al-P containing catalyst under the same conditions as the commercial catalyst. The feedstock characteristics and operating conditions vary to a certain degree day by day in the commercial FCC unit. Therefore, the equilibrium catalyst was obtained from the commercial FCC unit, and catalyst performance was compared under the same conditions using the Advanced Cracking Evaluation Micro Activity Test (ACE-MAT) made by Kayser.
2.2. Verification of Al–P Addition

2.2.1. Model Catalyst Preparation
To further clarify the effects of adding Al–P in detail, two model catalysts were prepared: a sample containing zeolite only, and a sample containing 3 mass% of Al–P added to zeolite. The model sample containing Al–P was made by first physically mixing zeolite and Al–P, and then drying at 120 °C. The two model samples were characterized after the hydrothermal deactivation treatment described in section 2.2.2.

2.2.2. Metal Deactivation Treatment
FCC catalyst is deactivated by metal poisoning such as Ni and V which are contained in the feedstock. In particular, vanadium promotes zeolite collapse. To confirm that Al–P suppresses such zeolite collapse, fresh catalyst was first deactivated with metal and steam. The flow of metal impregnation was as follows. After drying the catalyst at 600 °C for two hours, dried catalyst was mixed into a solution prepared by adding the specified amounts of nickel naphthenate (Nihon Kagaku Sangyo Co., Ltd.) and vanadium naphthenate (Nihon Kagaku Sangyo Co., Ltd.) to cyclohexane, to obtain the loading of Ni and V on the catalyst of 1000 mass ppm and 2000 mass ppm. After stirring, the cyclohexane was vaporized at 100 °C, and Ni and V were impregnated into the sample with drying at 600 °C for 2 h.8)

2.2.3. Hydrothermal Deactivation Treatment
Hydrothermal deactivation treatment was performed by inducing hydrothermal deactivation for an arbitrary time at 800 °C with circulation of 100 % steam at 800 °C and catalyst in the absence of the poisoning metal described in 2.2.2.

2.2.4. Catalyst Characterization
To verify the improvement of zeolite stability due to adding Al–P, crystallinity was evaluated as an indicator of the amount of zeolite structure after deactivation treatment, and the lattice constant as an indicator of the number of Al sites (cracking activity sites), using the Ultima IV made by Rigaku Corp. The crystallinity and the lattice constant (Unit Cell Dimension) conformed to ASTM D 3942-97, which is defined as the method for determination of crystallinity, and the U.C.D. of a faujasite type zeolite. In addition, to verify the effectiveness of Al–P in suppressing vanadium deactivation, mapping between Al–P and vanadium (determination of locations of each metal) was investigated using EPMA (electron probe micro analysis, JXA-8200 made by JEOL Ltd.) with the aim of confirming the vanadium passivation effect. To verify the effectiveness of improving zeolite stability due to hydrothermal deactivation, 29Si-NMR (nuclear magnetic resonance) measurement was performed (JNM-ECA-400 made by JEOL Ltd.) on the model catalyst subjected to hydrothermal deactivation only, and the zeolite crystal structure was analyzed in detail. In addition, the signal area ratio of each component was calculated by spectral waveform analysis. The Si/Al ratio was estimated based on the following equation9).

\[
(Si/Al)_{\text{NMR}} = \frac{\sum_{n=4}^{4} A_n}{\sum_{n=4}^{4} n A_n}
\]

3. Experiment Results and Discussion

3.1. Confirmation of Catalyst Performance with Commercial FCC Unit
The developed catalyst containing Al–P was manufactured on the industrial scale, and catalyst performance was examined using our company’s FCC unit.

3.1.1. Catalyst Operability, Circulation Performance and Catalyst Scattering
As indicated in section 1.2., the FCC catalyst is circulated throughout the unit, leading to concerns that changing the catalyst from the conventional to the newly developed type will result in reduced catalyst fluidity or catalyst level at the regenerator and reactor due to changes in the catalyst physical properties and form. Figure 2 shows the rate of replacement with the newly developed catalyst, catalyst level at the regenerator and reactor, and variation in pressure of the slide valve, which is an indicator of circulation performance. If catalyst circulation performance is poor, hunching of the slide valve pressure of the reaction column and regeneration column will occur, but even after switching to high replacement of the developed catalyst, the same slide valve pressure was maintained as with the conventional catalyst. The catalyst level is not increased at
the regenerator and reactor after switching from the conventional to the newly developed catalyst. Consequently, no problems in terms of catalyst circulation performance are anticipated.

3.1.2. Verification of Developed Catalyst Performance

Figure 3 shows variation in cracking activity (conversion), FCC gasoline yield, FCC gasoline octane number, and coke yield after switching to the developed catalyst. Figure 4 shows the amount of feedstock, catalyst/feedstock ratio, and reaction temperature. Figure 5 shows the density of feedstock and the carbon residue content in feedstock. The amounts of feedstock, catalyst/feedstock ratio, reaction temperatures, and density of feedstock were almost the same level using the conventional and newly developed catalysts. On the other hand, the carbon residue content in feedstock tended to increase using the newly developed catalyst. Carbon residue is thought to be converted into coke in the FCC unit because carbon residue has low reactivity. Therefore, the coke yield tended to increase using the newly developed catalyst.

The yield and properties of each product are described below. Operation over the entire period was constrained by the amount of coke burning at the regenerator. The developed catalyst achieved higher conversion than the base catalyst with almost the same coke yield, regardless of the high coke residue content in the feedstock. That is to say, the newly developed catalyst shows lower coke selectivity calculated as the coke yield against the conversion. The FCC gasoline yield was also confirmed to improve. Possibly more zeolite crystal structure and more cracking activity sites persisted as a result of improved zeolite stability associated with suppression of hydrothermal deactivation due to the added Al-P. The octane number of FCC gasoline was also increased. Table 1 shows the composition of the gasoline fraction at high replacement ratio of catalyst. The product of the newly developed catalyst had high octane number because the olefin content was higher and the paraffin content was lower than the product of the base catalyst. In the conventional technology, the rare earth metal forms an acid site, so the distance between acid site in zeolite is reduced and the hydrogen
The transfer reaction is promoted. The Al–P does not act as an acid site but suppresses shortening of the distance between the acid sites of zeolite. Consequently a higher octane number is achieved without promoting the hydrogen transfer reaction.

The commercial FCC unit shows variations in factors such as feedstock properties and unit operating conditions, which were evaluated with ACE-MAT using samples of base catalyst and newly developed catalyst at high replacement ratio, in order to compare catalyst activity under the same conditions. Table 2 shows the amount of deposited metal on the evaluation samples. The newly developed catalyst contained more vanadium than the conventional catalyst, so that the catalytic activity was likely to easily decrease. The possible amount of coke combustion acts as a bottleneck point for operation in the commercial FCC unit. Figure 6 shows the catalytic activities measured with ACE-MAT at the same coke yield. The newly developed catalyst blended with Al–P achieved increases of about 2 vol% in conversion, about 1 vol% in FCC gasoline yield, and about 1.5 in octane number of FCC gasoline, despite the higher amount of deposited V compared to the conventional catalyst. Therefore, the newly developed catalyst containing Al–P can be operated in the commercial FCC unit without problems with higher cracking activity and improved octane number compared to the conventional catalyst.

3.2. Effect of Addition of Al–P

As mentioned in section 3.1., the newly developed catalyst containing Al–P shows higher cracking activity than the conventional catalyst in the commercial FCC unit. Zeolite stability was enhanced with the addition of Al–P7). In this study, the effect of addition of Al–P was examined in more detail.

3.2.1. Inhibition of Metal Deactivation with Addition of Al–P

Figure 7 illustrates collapse of the zeolite crystal structure by vanadium10). Vanadium contained in the feedstock reacts with steam in the regenerator, forming vanadic acid and causing breakdown of the zeolite crystal structure due to reaction with Al in the zeolite

| Table 1 Composition of Gasoline Fraction |
|----------------------------------------|
| Base catalyst | Developed catalyst |
| Paraffin [vol%] | base | −5.8 |
| Olefin [vol%] | base | +6.2 |
| Naphthene [vol%] | base | −0.2 |
| Aromatics [vol%] | base | −0.2 |

| Table 2 Amount of Deposited Metal on Each Catalyst |
|----------------------------------------|
| Base catalyst | Developed catalyst |
| Ni [mass ppm] | base | ±0 |
| V [mass ppm] | base | +200 |

(a) Comparison of conversion, (b) comparison of octane number, (c) comparison of gasoline yield. All data are values with the same amount of coke production. Equilibrium catalyst was extracted from a refinery using the newly developed catalyst. Evaluation conditions: evaluation unit = ACE-MAT unit, reaction temperature = 510 °C, catalyst/oil ratio = 3-6. Analysis conditions: conversion, gasoline yield and RON are calculated with the regression calculation based on the results of cracking activity at different catalyst/oil ratios.

Fig. 6 Catalytic Activities at the Same Coke Yield
framework. Consequently, vanadic acid collapses the crystal structure in some of the zeolite and part of the zeolite is dealuminated at the regenerator.

Elimination of active sites on the zeolite due to vanadium has been suppressed by blending in basic materials such as manganese and magnesium, and passivating (trapping) vanadium through the acid-base reaction with vanadic acid\(^{11}\). If metal deactivation is suppressed by adding Al–P and passivating vanadium, then Al–P and vanadium are likely to be colocated. Therefore, we used EPMA to examine the metal passivation effect in catalyst blended with manganese (a conventional basic material) and catalyst containing Al–P. Since Al is also contained in zeolite and clay minerals, the position of Al–P was examined by mapping P. The results in Fig. 8 confirmed that the mappings of manganese and vanadium matched, and that vanadium was trapped due to the acid-base reaction. On the other hand, the mappings of phosphorus and vanadium showed no match. In other words, vanadium was not trapped by Al–P, so Al–P did not contribute to suppression of metal deactivation.

3.3 Suppression of Hydrothermal Deactivation Due to Al–P

Figure 9 shows the changes in crystallinity and lattice constant with variation in hydrothermal deactivation treatment time. Even for the catalyst containing Al–P with longer hydrothermal deactivation treatment time than the reference catalyst, decreases in the crystallinity and lattice constant were moderate, and durability was high against hydrothermal deactivation.

To examine hydrothermal deactivation durability due to Al–P in more detail, zeolite only and a sample containing Al–P were used as model catalysts as described in section 2. 1. 2., and the crystal structure of zeolite after hydrothermal deactivation treatment was investigated using \(^{29}\)Si-NMR. The degree of degeneracy \((Q^3 - Q^4)\) can be evaluated with \(^{29}\)Si-NMR, and \(Q^3\) indicates the bonding state of Si and Al in the zeolite framework. With lower value of \(n\), Si in zeolite framework increasingly bonds to Al, so collapse in the zeolite crystal structure can be inferred. Figure 10 shows the spectra of \(^{29}\)Si-NMR, (a) the results of whole chemical shifts, and (b) the abstraction of \(Q^2\) and \(Q^3\). Table 3 shows the area ratio and estimated Si/Al ratio of each spectrum obtained with \(^{29}\)Si-NMR. According to a previous report\(^{12}\), the peaks were attributed as follows: \(-89\) ppm to \(Q^1(\text{Si}(3\text{Al}))\), \(-95\) ppm to \(Q^1(\text{Si}(2\text{Al}))\), \(-102\) ppm to \(Q^1(\text{Si}(1\text{Al}))\), and \(-107\) ppm to \(Q^1(\text{Si}(0\text{Al}))\), where in the notation Si\((n\text{Al})\), \(n\) means the number of Al bonded to Si. The area ratio was calculated based on these assignments. Compared to samples of zeolite, samples with a mixture of zeolite and Al–P had a high area ratio of \(Q^2\) and \(Q^3\), which signifies Si species bonded to Al, a low area ratio of \(Q^4\) where Al is de-
sorbed, and $Q^0$ and $Q^1$ were not observed in any model catalyst because USY zeolite underwent hydrothermal treatment and was dealuminated. Therefore, Al-P is likely to suppress Al elimination of zeolite, even after hydrothermal deactivation treatment, so Si species bonded with Al persist.

These XRD (X-ray diffraction) and $^{29}$Si-NMR findings indicate that blending Al-P into zeolite improves durability against hydrothermal deactivation of zeolite, by preserving the zeolite crystal structure and cracking.

Fig. 9 Changes in Relative Crystallinity and Relative Lattice Constant with Variation in Hydrothermal Deactivation Treatment Time

(a) Spectra with chemical shift of $-90$ to $-110$ ppm, (b) spectra with chemical shift of $-90$ to $-105$ ppm. Model samples underwent only hydrothermal treatment ($800\degree C \times 6$ h).

Measurement conditions: probe $= 7.5$ mm $\phi$ MAS probe, MAS velocity $= 5$ kHz, temperature $= \text{room temperature}$, external standard $= \text{polydimethylsilane}$, pulse width $= 33^\circ$, repetition time $= 200$ s, cumulative number $= 360$.

Fig. 10 $^{29}$Si-NMR Measurement Results
activity sites. Cracking activity is enhanced in the commercial FCC unit with reduced hydrothermal deactivation as described in section 3.1.

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References
1) Andresson, S. I., Stud. Surf. Sci. Catal., 134, 227 (2001).
2) Fujiyama, Y., ENEOS Tech. Rev., 47, 109 (2005).
3) Watanabe, K., PETROTECH, 32, (3), 201 (2009).
4) Sakai, S., Syokubai kasei Gihou, 24, 35 (2007).
5) Kato, Y., Syokubai kasei Gihou, 9, 2 (1992).
6) Saka, Y., "Atarashii Puropiren Seizou Process," S&T Publishing Inc., Tokyo (2013), p. 72.
7) Saka, Y., Chiyoda, N., Watanabe, K., J. Jpn. Petrol. Inst., 58, 1, 40 (2015).
8) Mitchell, B. R., Ind. Eng. Chem., Prod. Res. Dev., 19, 209 (1980).
9) Schaefer, D. J., Favre, D. E., Wilhelm, M., Weigel, S. J., Chemelkaet, B. F., J. Am. Chem. Soc., 119, 9252 (1997).
10) Pine, L. A., J. Catal., 125, 514 (1990).
11) Wang, F., Zhuo, R., Qian, J., Sun, Z., Zhou, S., Prepr. Am. Chem. Soc., Div. Petrol. Chem., 43, 324 (1998).
12) van de Ven, L. J. M., Post, J. G., van Hooff, J. H. C., de Haan, J. W. J., J. Chem. Soc., Chem. Commun., 4, 214 (1985).

Table 3 Area Ratio and Estimated Si/Al Ratio of Each Spectra (with Gauss function)

| Peak area ratio | Si/Al |
|-----------------|-------|
| Q1 Si(2Al)      | 5.4   |
| Q2 Si(1Al)      | 14.1  |
| Q3 Si(0Al)      | 80.5  |
| Q4                | 11.3  |

a) Lorentzian fitting.

要 旨
第一リン酸アルミニウムによる触媒安定性向上効果および商業FCC装置における触媒性能

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燃料油の需要構造変化および環境保全の観点から高分解活性かつオクタン値の高いガソリン留分（FCC ガソリン）の製造が求められており、これまでに我々はFCC（Fluid Catalytic Cracking）装置で用いられる触媒（FCC 触媒）には第一リン酸アルミニウム（Al-P）が有効であることを見出した。本論文では、Al-P の添加による触媒安定性への影響を検討したところ、Al-P は水蒸気雰囲気下におけるゼオライトの劣化（水熱劣化）を抑制し、ゼオライト結晶構造を安定化させることが見出された。その結果、分解活性向上効果が得られ、実際の商業FCC装置においても高分解活性を示し、さらにはオクタン値の高いガソリン留分を得られることを確認した。

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