1. Introduction

Fluid catalytic cracking (FCC) has been the most important and flexible conversion process in petroleum refineries. It is economically beneficial that low-value residues having high molecular weights can be cracked into valuable constituents, such as gasoline, diesel, and petrochemicals. Therefore, an understanding of the reaction mechanism of FCC of heavy molecules is critical for increasing the selectivity of valuable products.

In order to improve FCC performance, therefore, identifying the major factors that influence the FCC reaction, such as the catalyst structure, feed properties, and operating conditions, is crucial. This article describes the investigation of active sites of FCC catalysts, particularly for optimization of zeolite acidity, because acidic sites are recognized to be the major active sites for catalytic cracking.

Commercial FCC catalysts are made from 1-2 μm Y-type zeolites and silica and/or alumina sols or gels to form 75 μm particles with kaolin clay as a filler. Zeolites are extremely active, particularly in hydrocarbon conversion reactions, and their regular pore structures make them selective for certain molecules, which are adsorbed or converted. Among them, Y-type zeolites are the active, and thus the most important, component in FCC catalysts. They provide the major portion of the surface area and active sites, and control both the catalyst activity and selectivity.

The formation of coke also influences the catalyst activity as the formed coke can cover some of the active sites and/or block the zeolite channels, which can make the inner active sites inaccessible for the reactant molecules. In FCC reactions, coke formation takes place rapidly (in less than a second), causing a decline in the catalyst activity. Consequently, catalyst deactivation is a significant issue in catalytic cracking, and numerous studies have been carried out on this reaction.

The catalytic activity of Y-type zeolites is mainly determined by the unit cell size (UCS), which can be controlled through steaming and/or acid treatment. Al-Khattaf reported that the product distribution of vacuum gas oil (VGO) cracking could be controlled by using FCC catalysts prepared from Y-type zeolites with different UCS. Sahoo et al. studied the effect of steam dealumination on the acidity and strength distribution of ZSM-5. They reported that the density of acid sites decreased with an increase in the steaming severity, and that coke formation was mainly a function of the acid site density rather than the acid strength distribution.
tribution. They considered that strong acid sites catalyze not only cracking, but also hydrogen transfer reactions, which convert paraffin to aromatics, and even coke\(^{2,3,5}\).

Although the effect of the UCS upon VGO conversion has been reported by many researchers, the effect of the UCS on the FCC of residual oil is scarcely reported in the open literature. This article describes the relationship between the acid properties of catalytic active sites of FCC catalysts and their catalytic cracking ability using desulfurized atmospheric residue (DSAR) and desulfurized vacuum gas oil (DSVGO) feeds.

2. Experimental

2.1. Catalyst Preparation

Typically, HSZ-H330 (UCS = 2.456 nm) from Tosoh Corp. was used as the parent Y-type zeolite. Alumina, silica, and silica-alumina matrixes and silica sol binder were purchased from JGC Catalysts and Chemicals Ltd. Kaolin clay (ASP-170, Tsuchiya Kogyo Co., Ltd.) was used as the filler. These materials were mixed in a slurry, spray dried, and carried through the series of procedures shown in Fig. 1 to produce the FCC catalysts. Each catalyst contained 10-30 wt% of the Y-type zeolite, 40-60 wt% of kaolin clay, 0-20 wt% of alumina, 0-20 wt% of silica-alumina, and 0-20 wt% of the silica sol binder. The prepared catalysts were spray dried and then washed three times with 1 wt% ammonium nitrate in water to exchange the sodium (Na) ions and then with ion-exchanged water to remove the ammonium nitrate. The washed catalysts were dried at 393 K for 3 h and then calcined in air at 773 K for 2 h.

Typical catalysts examined in this study are named CAT1-CAT4, all of which contained the same number of Y-type zeolite and the original Y-type zeolite, HSZ-H330, was treated in different steaming conditions in order to give systematic decreases in UCS in the order of CAT1 to CAT4 as shown in Table 1. To extend the number of acid sites wider, supplementary catalysts were prepared and listed in Table 2, where CatA to CatF contained different Y-type zeolites in origin.

2.2. Catalyst Characterization

X-ray diffraction (XRD) patterns were recorded with an Ultima III diffractometer (Rigaku Corp.) using CuK\(\alpha\) radiation (\(\lambda = 1.5418 \text{ Å}, \ 1 \text{ Å} = 10^{-10} \text{ m}\) ). The unit cell size of the Y-type zeolite component was determined from the average 2\(\theta\) values of the (642) and (555) peaks, which were corrected for the 2\(\theta\) of Si (111) as 24.443\(^\circ\) using Si (NIST 640a) as an internal standard.

Nitrogen adsorption measurements were carried out with a Quantachrome Autosorb-6 at 77 K. The total surface areas were determined by the multi-point B.E.T. method from 0.01 to 0.1 \(P/P_0\). The surface areas of the micropores and the (meso + macro) pores were determined using the T-plot method.

The acid properties of the catalyst were determined by ammonia temperature programmed desorption (NH\(_3\)-TPD)\(^7\). A typical NH\(_3\)-TPD profile of a Y-type zeolite consists of a low temperature peak (LP) at \(~ 473\) K and a high temperature peak (HP) at \(~ 523\) K. The LP is attributed to the desorption of physically adsorbed NH\(_3\), while the HP is due to the desorption of NH\(_3\) strongly adsorbed on the acid sites.

For the NH\(_3\)-TPD measurements, a meshed catalyst sample (16-32 mesh, \(~ 100\) mg) was charged into a tubular quartz cell. The sample was maintained at

![Simplified Manufacturing Process for Calcined FCC Catalysts](Fig. 1)
773 K for 1 h in flowing helium and then cooled down to 373 K. Next, NH₃ was adsorbed onto the sample by flowing a 0.5 % NH₃/He mixed gas at 100 mL/min for 45 min. After NH₃ adsorption, two types of pretreatments described below were applied. For case A, the sample was flushed at 373 K for 1 h in a 50 mL/min He flow to remove the excess adsorbed NH₃. For case B, after removal of the excess adsorbed NH₃ as in case A, the sample was exposed to saturated water vapor at room temperature in a 50 mL/min He flow at 373 K for 4 h, and then subsequently flushed at 373 K for 1 h in 50 mL/min He flow. The exposure to water vapor (case B) has been reported to selectively eliminate the LP⁷. After the above pretreatments, each sample was heated at a rate of 20 K/min up to 983 K and flushed in a 50 mL/min He flow. The amount of NH₃ was determined using a mass spectrometer.

2.3 Catalyst Evaluation

Evaluation of catalyst activity was carried out in a fixed fluid bed reactor known as the Advanced Catalyst Evaluation Micro Activity Testing (ACE-MAT, Kayser Technology Inc.) reactor. It is a fixed fluid bed reactor that uses nitrogen flow and is operated at atmospheric pressure and 80³ K. Conversions are adjusted by varying the catalyst to oil weight ratio (C/O), in the range of 3.75-6.0, where C/O is the amount of catalyst (9 g) divided by the total amount of oil feed in a given time on stream. In this paper, catalytic activities were expressed at C/O of 5.0. DSAR and DSVGO, as shown in Table 3, were used as the feedstocks.

The distribution of gaseous products was analyzed using a gas chromatography. The boiling point range of the liquid products was determined using simulated distillation gas. The products from the ACE-MAT unit were classified based on the boiling point range as follows:

1. Gases, C₁-C₄

2. (2) Gasoline, C₅-463 K
3. (3) Light cycle oil (LCO), 463-633 K
4. (4) Slurry oil (SLO) or clarified slurry oil (CLO), over 633 K.

The carbon deposited on the spent catalyst (the coke) was burned out at 948 K in air. The combustion flue gas was converted completely to carbon dioxide by a copper catalyst, and the amount of coke was determined using an infrared gas analyzer. The product material balances were calculated, and only runs with balances >95 wt% were accepted for data analysis. Conversion is defined as 100 wt% - (LCO + SLO).

3. Results and Discussion

3.1 Catalysts Prepared with Different UCSs

Four types of catalysts can be distinguished by their characteristic UCSs. Compared to CAT1 as a base catalyst, CAT2, CAT3, and CAT4 have lower UCSs—0.005, 0.010, and 0.015 nm, respectively.

The influences of steaming conditions of zeolite on surface areas (Table 1) and on pore size distributions (Fig. 2) of the catalysts were also investigated. The (meso + macro) pore surface area, which represents the external surface area, was nearly the same for each catalyst. This result is confirmed by the fact that all of
the catalysts show equivalent pore size distributions. On the other hand, the micro surface area decreases with decrease in the UCS.

Next, information on the number of acid sites and acid strength was obtained using NH$_3$-TPD. The number of acid sites was determined as the equivalent area of the LP + HP obtained for the catalyst prepared using the method in case A, as shown in Fig. 3 and listed in Table 1. The number of acid sites decreased with a decrease in the UCS (CAT1 > CAT2 > CAT3 > CAT4). In addition, the number of acid sites as defined by the equivalent area of the HP alone was also determined, and as can be seen in Fig. 4, follows the same trend observed for the number derived from the LP + HP. It is noteworthy that the peak top temperature of the HP is nearly the same for the four catalysts, indicating that the acid strength calculated by the method of Sawa et al. is same for all four catalysts.

The retention of a similar pore size distribution and external surface area for all four catalysts suggests that the steaming conditions were not severe enough to disintegrate the crystalline structure of the original Y-type zeolite. Furthermore, the steaming varied only the number of acid sites while keeping the acid strength constant. Based on these two results, it can be concluded that the steaming conditions may have only induced dealumination of the catalysts.

### 3.2. Catalyst Evaluation Using ACE-MAT

Figure 5 shows the product yield distributions for the FCC of DSAR in the ACE-MAT reactor using the four catalysts. Conversion is defined as 100 wt% − (LCO + SLO). CAT4 shows the lowest conversion, the lowest coke yield and the highest gasoline yield, while CAT1 shows the highest conversion, the highest coke yield and the lowest gasoline yield.

It has been the general consensus that a higher activity (conversion) correlates fairly well with a higher UCS, which is an approximate measure of the aluminum content of the zeolite framework and thus of the number of acid sites. The ACE-MAT evaluation results are consistent with the consensus. In contrast to the conversion trend, however, the gasoline yield is highest for CAT4. Because CAT4 contains the lowest number of acid sites, one might speculate that there is an optimum level of acidity for enhanced gasoline yield, especially for residual oil catalytic cracking.

In order to confirm this speculation, another set of catalysts was prepared and evaluated in the ACE-MAT reactor using both DSAR and DSVGO to consider the molecular size effect. The catalysts studied in these experiments contained CAT1-4, CatA-F and steamed CatA-C (showed in Table 2). Figure 6 depicts the relationship between the number of acid sites (as determined by NH$_3$-TPD using the case B method), and the conversion and product yields obtained in the ACE-
MAT reactor. When DSAR was used as the feed, the gasoline yield reached a maximum when the number of acid sites equaled ca. 0.10 mmol/g, while both the conversion and the coke yield increased with an increase in the number of acid sites. On the other hand, using DSVGO as the feed, the gasoline yield increased with an increase in the number of acid sites in a manner similar to that of both the conversion and the coke yield. The higher conversion for DSVGO compared with that for DSAR can be accounted for by the apparent difference in the average molecular sizes of the compounds in the DSVGO and DSAR feeds. Figure 7 suggested by Masuda10) shows a schematic image for catalytic cracking, where the DSVGO or DSAR feed compounds are sequentially converted to smaller molecules inside the different sized pore structures that are present in typical FCC catalysts. Masuda and Sato11) considered the diffusion-limited to approach of zeolite acid sites in the FCC catalysts on DSAR cracking case. Because VGO molecules are able to access the zeolite micropores more readily than AR molecules, the conversion of DSVGO is generally higher than that of DSAR.

The existence of a maximum for the gasoline yield only in the DSAR cracking may be interpreted as follows. It can be assumed that the main precursors for the cracked gasoline, which are shown as the pre-cracked oils in Fig. 7, have a similar size as the LCO molecules and are smaller than those of VGO. The population of the pre-cracked oil inside the catalyst pores for the DSAR cracking will therefore be much smaller than that for the DSVGO cracking. Sato11) suggested that it is important to have a pore diameter which is 3-6 times of a molecule size which is wanted to crack. Masuda10) also presented that Y-type zeolites are suitable for the higher gasoline selectivity compared with silica-alumina and mordenite in terms of acid strength distribution. But he did not discuss about the number of acid sites.

In such lean conditions for the pre-cracked oil reaction, the higher number of acid sites would result in over-cracking of the gasoline to gases and LPG. These results suggest that to obtain a higher gasoline yield for DSAR cracking, catalysts should be prepared with a suitable number of acid sites or a larger pore size, which would create a wider reaction area.

4. Conclusions

A series of FCC catalysts from Y-type zeolites with different UCSs were prepared by changing the steaming conditions. A decrease in the number of acid sites due to a decrease in the UCS of the Y-type zeolite was observed, while the pore size distribution did not change. The catalyst with the lowest number of acid sites exhibited the highest gasoline yield and the lowest conversion for DSAR cracking reactions.

In order to elucidate these phenomena, another set of
catalysts with a wider range of acid site number were prepared and evaluated. When DSAR was used as the feed, the gasoline yield reached a maximum when the number of acid sites was ca. 0.10 mmol/g, while both the conversion and the coke yield increased with an increase in the number of acid sites. On the other hand, using DSVG0 as the feed, the gasoline yield increased with increasing in the number of acid sites, as did the conversion and the coke yield. The existence of a maximum in the gasoline yield only for the DSAR cracking suggests that the population of pre-cracked oil molecules inside the catalyst pores determines the gasoline yield in connection with the number of acid sites.

Acknowledgments

This work was supported by the Japan Petroleum Energy Center (JPEC) as a technological development project supported financially by the Japan’s Ministry of Economy, Trade and Industry. We gratefully acknowledge Dr. K. Inamura (Idemitsu Kosan Co., Ltd.) for helpful discussions.

References

要  旨

流動接触分解触媒の酸性質が重質重油分解へ与える影響

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流動接触分解触媒の有する分解活性点である酸性質が重質重油分解へ与える影響について検討した。酸強度はアンモニア TPD のピーク位置から決定し、アンモニア吸着量から酸量を定義した。ゼオライト含有量が一定で、格子定数が異なる触媒を調製し、応応評価を行った。その結果、酸量が増えるにつれ転化率も高くなった。最も酸量が少ない触媒が最もガソリン収率が高かった。酸量の影響をより幅広く確かめるため、ゼオライト含有量、格子定数を変化させた触媒を調製し、評価した結果、ある特定の酸量においてガソリン収率は最大点を示すことが明らかとなった。減圧軽油留分を原料油と用いた場合と異なり、重質重油からガソリンを得るには適量の酸量を有していることが重要と考えられる。ガソリンは重質重油が分解し、ガスへと転換するところでの中间物質にあたるため、ガソリン収率向上のためには、適度な酸量に調整することに加え、重質重油に適した反応場を創出することが重要である。