R&D on Catalyst for Catalytic Cracking of Heavy Oil with High Metal and High Residual Carbon Content

(High residual carbon catalytic cracking catalyst group)
Sodegaura 404 Laboratory
Toshio Itoh, Hideyuki Hara, Masao Miyaoka

1. Contents of Empirical Research

Over the medium and long term, huge changes in the structure of demand for petroleum products are forecast, namely a sharp drop in demand for heavy oil and an increase in demand for gasoline. In the petroleum industry, the question of how to efficiently decompose heavy oil fraction, which is forecast to be in surplus, and satisfy demand for gasoline, which is forecast to be inadequate in supply, has become an urgent issue. In addressing this issue, there are countermeasures in terms of hardware, namely the addition of new and/or expanded cracking facilities and stepped up efficiency in existing processes. But it is also important to have new developments and improvements in catalyst so as to adapt flexibly to changes in feedstock properties that come with diversification of treated crude oil, and so as to bring out latent processing potential to the maximum.

Amid these conditions, further development and/or improvement of residual fluid catalytic cracking (RFCC) process catalyst has become a major objective. Attention is now being focused on development of catalyst from coarse feedstock (low-priced feedstock which could not be treated up to the present) containing large amounts of residual carbon believed to be metals and coke precursors, and on development of catalyst for treatment of RFCC feedstock in which metals, residual carbon and sulfur have increased in the course of continuous treatment over two years with direct desulfurization units.

When useful FCC gasoline and LCO are obtained from this coarse RFCC feedstock, the economy of RFCC equipment improves, the range of crude oil selection at refineries expands, and international competitiveness is strengthened. It is suspected that in the future, crude oil will be heavy and large quantities of coke will be produced, but in obtaining FCC gasoline and LCO, the volume of CO₂ discharged from RFCC equipment regeneration tower can be drastically reduced by using catalyst that produces little coke. This approach would also contribute to the prevention of global warming.

In light of these conditions, the objective of the present research is to develop an RFCC catalyst which exhibits the following performance in the RFCC process when desulfurized heavy oil, or even heavier oil, has been passed through. It is assumed that this oil is a mixture of Arabian heavy and Wafra containing 15 ppm or more of metal and 5 wt% or more of residual carbon.

- FCC gasoline + LCO 64 wt% or more
- Coke 8 wt% or below

Other objectives include greater operational efficiency in the RFCC process, reduced volumes of CO₂ generation, and countermeasures against global warming.
1.1 Highly Active Catalyst Search and Improvement

With RFCC catalyst, feedstock containing heavy fraction and large quantities of sulfur and metals such as V or Ni must be processed so that the yield of FCC gasoline and LCO is 64 wt% or more and the coke yield is 8 wt% or less. For this purpose, studies have been done on spherical alumina, which is believed to generate little coke, to be used as a substitute for the conventional needle alumina. In addition, catalysts comprised of spherical alumina combined with substances of different properties and compositions have been trial-produced and examined.

1.1.1 Preparation of spherical alumina

Spherical alumina with homologous pores was prepared for improving catalyst reactivity, and this was used to prepare catalyst.

1.1.2 Activity of catalyst to which spherical alumina has been added

The reactivity of catalyst to which spherical alumina had been added was evaluated, together with reaction results.

1.1.3 Optimization of zeolite addition to catalyst

The amount of zeolite to be added to spherical alumina was optimized for obtaining catalyst that yields high FCC gasoline + LCO and low coke.

1.1.4 Catalyst in which the level of spherical alumina pulverization has been changed

In order to improve catalyst reactivity, catalyst was prepared in which the level of spherical alumina pulverization had been changed, and the reactivity of such catalyst was evaluated.

1.1.5 Optimization of catalytic constituents

Spherical alumina of high acid volume, spherical alumina of low acid volume, and zeolite volume, all of which are catalytic constituents, were optimized for the purpose of improving catalytic activity.

1.2 Factors Affecting Catalyst Activity

With the aim of attaining high yields of FCC gasoline and LCO, the relationships between catalyst pore distribution, acid volume, OH base and catalytic activity were investigated. Also investigated were the relationships between the distribution in catalyst of spherical alumina, a catalyst raw material, the level of spherical alumina pulverization and pore distribution.

1.2.1 Catalyst pore distribution

In examining catalyst structure, the relationships between the pulverization level of spherical alumina, a catalyst raw material, and catalyst pore distribution were investigated, as were the relationships between uniformity in catalyst meso (intermediate) pores and reactivity.

1.2.2 Catalyst acid volume

Among catalysts yielding outstanding reaction results, the relationship between acid volume and reaction results was investigated.

1.2.3 Alumina distribution in catalyst

The relationship between catalytic reaction results and the distribution of spherical alumina in catalyst was investigated.
1.2.4 Spherical alumina pulverization level versus pore distribution

In order to develop catalyst of high activity, the relationship between spherical alumina pulverization level and catalyst pore distribution and activity was investigated.

1.2.5 Coke yields of new catalysts

When the amount of new catalyst loaded into an RFCC unit is large, the impact of the new catalyst becomes readily apparent especially in its coke yield. For this reason, the relationship between coke yield and catalytic acidity with new catalyst was investigated.

1.3 Catalyst Industrial Production Methods

Industrial production methods were investigated in order to establish a method for production, on an industrial scale, of catalyst developed on the laboratory scale. In the investigation of industrial production methods, attention was focused on catalyst composition and on uniformity in catalyst structure during catalyst production tests, and on stability during catalyst spray drying.

1.4 Catalyst Practical Performance

Metal tolerance, hydrothermal stability and attrition resistance of production test catalyst, prepared by the industrial production method, were investigated. Moreover, in order to evaluate such things as the stripability (desorption of adhered oil) of catalyst used in practical equipment, short-term operations for verification were conducted. The metal tolerance and hydrothermal stability of improved catalyst were also examined.

2. Results and Analysis of Research and Development

2.1 High Active Catalyst Development and Improvement

2.1.1 Preparation of spherical alumina

In commercial catalyst, as shown in Figure 2.1-1, because there are few meso pores, primary cracked oil produced by cracking of heavy feedstock stagnates in the pores and coke is generated. In order to prevent coke production and increase production of FCC gasoline + LCO, as shown by the same figure of development target catalyst, it is important to increase uniform meso pores so that primary cracked oil, produced by cracking feedstock, does not stagnate and can be quickly cracked into gasoline and LCO in the catalyst pores. For this reason, preparation of spherical alumina was investigated for the purpose causing smooth production of primary cracked oil, as well as an increase in uniform macro pores together with an increase in meso pores. As shown in Figure 2.1-2, uniform particles produce the meso pores. This production can take place because when particles have accumulated, the cavities which uniform particles can make also become uniform.
As a result of various changes made in gel preparation time period, temperature, etc., using aluminum sulfate, for instance, as raw material of spherical alumina, alumina with sharp peaks at 100Å and 150Å could be prepared. The pore distribution of prepared alumina having pores at 100Å is shown in Figure 2.1-3. It can be seen that in the prepared alumina, meso pores can be produced at 100Å as targeted.

Next, catalyst was prepared using spherical alumina with pore diameter at 100Å (10 wt%), USY zeolite (30 wt%), clay mineral kaolin (40 wt%) and binder (20 wt%). The pore distribution of prepared catalyst is presented in Figure 2.1-4. It can be seen that the meso pores reach a peak at around 100Å.
2.1.2 Activity of catalyst to which spherical alumina has been added

The activity of the aforesaid catalyst, to which spherical alumina had been added at 10 wt%, was evaluated by means of microactivity testing (MAT). The results appear in Figure 2.1-5. In terms of the standard conversion rate, catalyst with spherical alumina satisfied the target values of 64 wt% or more for FCC gasoline + LCO and coke yield at 8 wt% or less. The properties of feedstock used in the evaluation of activity are given in Table 2.1-1. The feedstock satisfies final targets of properties.

<table>
<thead>
<tr>
<th>Item / Feedstock</th>
<th>Reaction evaluation feedstock</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur content</td>
<td>(wt%) 0.51</td>
</tr>
<tr>
<td>Residual carbon</td>
<td>(wt%) 5.9</td>
</tr>
<tr>
<td>Metal content</td>
<td>(ppm) 15</td>
</tr>
</tbody>
</table>
2.1.3 Optimization of zeolite additive to catalyst

With the aim of developing catalyst of low coke yield by high yields of FCC gasoline + LCO, within the range of practical equipment conversion rates, the impact of zeolite additive amount to catalyst was investigated. In the prepared catalysts, as compared to conventional catalyst, the zeolite content was lowered 14% (I4-20 catalyst) or 23% (I4-19 catalyst).

The results of an evaluation of activity by I4-19 catalyst, in which zeolite content was lowered, are presented in Figure 2.1-6. It can be seen that as a result of the reduction in zeolite, the conversion rate range becomes equivalent to the practical equipment range, and target values are reached in FCC gasoline + LCO yield and in coke yield.

![Figure 2.1-6: Reactivity of Zeolite Optimized Catalyst](image)

2.1.4 Catalyst in which spherical alumina pulverization level was changed

Pulverization of spherical alumina was investigated from the standpoint of increasing meso pores, together with uniform macro pores, and smoothly producing primary cracked oil. In spherical alumina pulverization, a wet pulverizer was used to set the mean particle diameter of spherical alumina at 4\(\mu\)m (I4-23 catalyst) or 1\(\mu\)m (I4-24 catalyst), and each was then used to prepare catalyst. It is apparent that when the pulverization level of spherical alumina has been raised, there is an increase in the cubic capacity of both meso pore and macro pore. The results of an evaluation of catalyst reaction appear in Figure 2.1-7. We find that the results with catalyst employing spherical alumina of high pulverization level satisfy the target values for FCC gasoline + LCO yield at 64 wt% or above and for coke yield at 8 wt% or less. We also note that the results from I4-24 catalyst, with high spherical alumina pulverization level, are good in comparison to those of the previous I4-05 catalyst. This can be ascribed to the fact that pulverization of spherical alumina produced an increase in FCC gasoline + LCO yield because meso pores, of medium size, and large macro pores increased and heavy oil, the feedstock, decomposed smoothly in the pores.

The coke yield increased only slightly, despite the increase in FCC gasoline + LCO yield, and this can be ascribed to the fact that the feedstock gradually decomposes more smoothly in the increased number of macro pores and meso pores, so that primary cracked oil does not stagnate in the pores.

![Figure 2.1-7: Reactivity of Spherical Alumina Pulverized Catalyst](image)
2.1.5 Optimization of catalyst compositional constituents

In order to develop catalyst of even higher activity, the magnitudes of spherical alumina of high acid content, spherical alumina of low acid content and zeolite were optimized. The relationship between conversion rate and FCC gasoline + LCO yield appears in Figure 2.1-8 while the relationship between conversion rate and coke yield appears in Figure 2.1-9. The magnitude of spherical alumina with abundant acid and zeolite was reduced while that of spherical alumina with low acid amount was increased. Through optimization, catalyst of even higher activity could thus be realized.

2.2 Factors Affecting Catalyst Activity

2.2.1 Catalytic pore distribution

The impact of pore distribution on catalytic reactions was investigated. The pore distribution of a typical developed catalyst is illustrated in Figure 2.2-1. It was found that catalysts having a meso pore peak at around 100Å produce favorable results. Table 2.2-1 shows the percentages of pore capacity in I4-10 catalyst, which produced the best reaction results, and in catalysts on the market with pore sizes ranging from 40 - 400Å, 400 - 2000Å and 2000 - 18000Å. It was found that catalyst with large meso pore capacity between 40 - 400 Å produced favorable results.
2.2.2. Catalyst acid volume

In order to investigate the factors behind catalytic activity, the acid volume of developed catalyst was measured by ammonia adsorption heat; the results are given in Figure 2.2-2. In light of these results and the results of a search for catalyst, no clear relationship between acid amount and yield of FCC gasoline + LCO, or coke yield, could be recognized. However, in view of the fact that the greatest adsorption heat volume is in the I4-10 catalyst, which produces the highest yield of FCC gasoline + LCO, it is evident that acid must be added to catalyst to some extent in order to improve upon a yield of 64 wt% or more for FCC gasoline + LCO.
2.2.3 Alumina distribution in catalyst

An investigation was undertaken to discover how alumina becomes distributed in catalyst when spherical alumina has been added. Measurements by EPMA of alumina distribution in I4-10 catalyst revealed that larger alumina clusters are distributed in I4-10 catalyst, to which spherical alumina has been added, than in commercial catalyst, and that pores effective in reactions are formed.

2.2.4 Spherical alumina pulverization level versus pore distribution

It was discovered that reaction results become favorable when the level of spherical alumina pulverization is elevated, but the relationship between pulverization level and pore distribution was also investigated. This relationship is depicted in Figure 2.2-3. It was found that as the pulverization level is raised, meso pores increase and reaction results become favorable (I4-23 catalyst mean particle diameter: 4 µm; I4-24 catalyst mean particle diameter: 1 µm).

![Figure 2.2-2: Measurements of Ammonia Heat Adsorption in Catalyst](image)

![Figure 2.2-3: Spherical Alumina Pulverization Level vs Pore Distribution](image)
2.2.5 Coke yields of new catalyst

When the amount of new catalyst loaded into an RFCC unit is large, the impact of new catalyst of high activity becomes readily apparent especially in its coke yield. For this reason, the relationship between coke yield and catalytic acidity with new catalyst was investigated. It was discovered that in the new catalyst state, catalysts containing large amounts of zeolite, of great acid volume, had high rates of coke yield. Figure 2.2-4 illustrates the relationship between coke yield and conversion rate of new catalyst in which spherical alumina and zeolite magnitudes have been optimized. By optimizing the amount of spherical alumina and zeolite, catalyst of lower coke yield than conventional developed catalyst, even in the new catalyst state, could be developed.

![Figure 2.2-4: Coke Yield vs Conversion Rate of New Catalyst](image)

2.3 Catalyst Industrial Production Methods

Industrial production tests were conducted in order to establish a method for production, on an industrial scale, of catalyst developed on a laboratory scale. In the production tests, investigation focused on catalyst composition and on uniformity in catalyst structure. During test production of catalyst for verification operations, the conditions for industrial production of catalyst were studied. In examining industrial production methods, stability, etc., during the catalyst spray drying was also considered.

2.3.1 Examination of catalyst composition and structure during test production

An investigation was made to determine if catalyst can be produced on an industrial scale without problems and according to specifications. As a result of the catalyst search, I4-10 catalyst, which yielded the best results, was used as a basis in test production of catalyst. The composition and property values of the test-produced catalyst fell within the permissible range of variance from specifications and there were no problems in uniformity.

2.3.2 Stability in catalyst spray drying during catalyst test production

If conditions change during spray drying of catalyst, cavities are created in the catalyst and catalyst particle diameters become disparate. When large cavities are produced in the catalyst and particle diameters become disparate, the catalyst becomes weak in mechanical strength, and the flow condition of catalyst in practical equipment becomes poor, which in turn adversely affects reaction results. When cavities form in catalyst, apparent bulk density becomes low, and when particle diameters are disparate, mean particle diameters become larger and smaller so that specifications cannot be satisfied.
So as to investigate stability during catalyst spray drying, attention was focused on apparent bulk density of catalyst and on mean particle diameter. Temporal changes in apparent bulk density and in particle diameter of catalyst during catalyst test production are presented in Table 2.3-1. At each stage of catalyst test production, changes were within permissible limits, so it was concluded that during spray drying, catalyst physical properties are stable and there are no problems.

Table 2.3-1 Temporal Changes in Apparent Bulk Density and in Particle Diameter During Catalyst Test Production

<table>
<thead>
<tr>
<th></th>
<th>Apparent bulk density (g/ml)</th>
<th>Mean particle diameter (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Early term</td>
<td>Standard + 0.02</td>
<td>Standard + 2</td>
</tr>
<tr>
<td></td>
<td>Standard + 0.02</td>
<td>Standard + 2</td>
</tr>
<tr>
<td>Middle term</td>
<td>Standard ± 0</td>
<td>Standard + 2</td>
</tr>
<tr>
<td></td>
<td>Standard + 0.02</td>
<td>Standard + 2</td>
</tr>
<tr>
<td>Late term</td>
<td>Standard − 0.01</td>
<td>Standard + 3</td>
</tr>
<tr>
<td></td>
<td>Standard + 0.01</td>
<td>Standard + 3</td>
</tr>
</tbody>
</table>

2.4 Catalyst Practical Performance

In order to investigate the practical performance of test-produced catalyst, metal resistance, hydrothermal resistance and attrition resistance were investigated from the standpoint of catalyst application in practical equipment, and it was confirmed that there are no problems. For a secure evaluation of developed catalyst, short-term verification operations were conducted using practical equipment for catalyst stripability, for instance, which cannot be evaluated with laboratory-scale equipment. In addition, catalyst was further improved, and the metal resistance and hydrothermal resistance of developed catalyst were evaluated.

2.4.1 Evaluation of catalyst stripability

To attain a secure evaluation of developed catalyst, short-term verification operations were conducted, using practical equipment, respecting catalyst stripability, which cannot be evaluated with laboratory-scale equipment. One cause of the drop in kerosene fraction yield and the rise in coke yield with practical equipment lies in the fact that the oil remaining in catalyst pores after reaction is burnt together with catalyst in the regeneration tower. For this reason, it is essential to confirm that the oil in developed catalyst is stripped adequately in practical equipment. And to make this confirmation, the following are checked: 1) FCC gasoline + LCO yield in produced oil, 2) coke magnitude burnt in the regeneration tower, and 3) regeneration tower temperature. If oil is brought to the regeneration tower without being stripped from the catalyst, the FCC gasoline + LCO yield decreases and coke yield increases. The relationship between catalyst substitution rate in practical equipment and FCC gasoline + LCO yield is presented in Figure 2.4-1. It is believed that catalyst stripability is favorable because the FCC gasoline + LCO yield grows higher together with catalyst substitution rate and oil adhered to catalyst is not forwarded with catalyst to the regeneration tower.
If the oil content is forwarded to the regeneration tower without being stripped, the yield of coke burnt in the regeneration tower increases. Figure 2.4-2 illustrates the relationship between developed catalyst substitution rate and coke yield. The stripability of developed catalyst is considered favorable because the coke yield diminishes even though the catalyst substitution rate increases. What is more, it was learned from the relationship between catalyst substitution rate and regeneration tower temperature that the latter does not rise even if the developed catalyst is used. Given these findings, it was concluded that there are no problems with the developed catalyst in terms of stripability.

2.4.2 Evaluation of developed catalyst practical performance

With the aim of developing catalyst of even higher activity, the metal tolerance and hydrothermal stability of developed catalyst were evaluated. After 2100 ppm or 4200 ppm of V+Ni were impregnated in catalyst, steaming treatment and pseudo equipoising were performed. Then catalyst activity was evaluated, together with metal tolerance. Findings from the evaluation of metal tolerance are presented in Figure 2.4-3. We can see that the metal tolerance of developed catalyst is greater than that of commercial catalyst and that there are no problems. Similarly, there are no problems with hydrothermal stability.
3. Results of Empirical Research

3.1 Highly Active Catalyst Search and Improvement

With the aim of increasing the yield of FCC gasoline + LCO and decreasing coke yield, optimizations were done on spherical alumina pulverization level, zeolite additive amount and catalyst components. As a result, it was found that the developed catalyst satisfied the target values in the present research.

3.2 Factors Affecting Catalyst Activity

From the standpoint of attaining high yield of FCC gasoline + LCO and low coke yield, the relationships between prepared catalyst pore distribution, pulverization level of spherical alumina, the catalyst raw material, alumina distribution in catalyst and reaction results were investigated. It was discovered that reaction results of catalyst having meso (intermediate) pores near 100Å are superior, that meso pores are increased by elevating the level of spherical alumina pulverization, and that in conjunction with this, reaction results are improved.

3.3 Catalyst Industrial Production Methods

So as to establish a method of production, on an industrial scale, of catalyst developed on the laboratory scale, attention was focused on catalyst components and on uniformity in catalyst structure during catalyst production tests, as well as on stability in catalyst spray drying during test production of catalyst for verification operations. It was found that the composition and property values of developed catalyst produced on an industrial scale were stable within permissible ranges and presented no problems.
3.4 Catalyst Practical Performance

To attain a secure evaluation of developed catalyst, short-term verification operations were conducted, using practical equipment, respecting catalyst stripability, which cannot be evaluated with laboratory-scale equipment, and catalyst service life. It was found that in verification operations, the FCC gasoline + LCO yield increases together with a rise in the substitution rate of developed catalyst and that the coke yield decreases. From this, it was determined that there are no problems with the developed catalyst in terms of stripability.

Moreover, in evaluating the service life of more-improved catalyst in terms of metal tolerance and hydrothermal stability, it was confirmed that there are no problems.

4. Synopsis

Following search and improvement of catalyst for catalytic cracking of heavy oil containing high levels of metal and residual carbon, it was discovered that the performance of developed catalyst reaches target values. Short-term verification operations were conducted, using practical equipment, respecting catalyst stripability, which cannot be evaluated with laboratory-scale equipment, and catalyst service life. As a result, it was confirmed that developed catalyst roughly satisfies target values. Moreover, for the purpose of improving the performance of developed catalyst, studies were done on optimization of catalyst components and on reducing coke from new catalyst. Consequently, catalyst of superior performance could be developed.

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