

Development of highly-active hydrodesulfurization catalyst for sulfur-free diesel production

— Full research from in-house laboratory catalyst to commercial catalyst —

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Clean transportation fuels, particularly with significantly reduced sulfur content, are effective in reducing tailpipe emissions and lead to the development of novel high-performance exhaust treatment devices. We have developed a hydrodesulfurization catalyst for sulfur-free diesel with a sulfur content below 10 ppm as well as a catalyst preparation method, and succeeded in commercializing it as a novel desulfurization catalyst through joint research with a catalyst manufacturer.

Keywords : Sulfur-free diesel, hydrodesulfurization catalyst, catalyst preparation, characterization

1 Background of Research

With enhanced urban air quality control, further reductions are required in tailpipe emissions, particularly nitrogen oxides (NO_x) and particulate matter (PM) emissions from diesel vehicles, and various emission reduction efforts are being made involving improvements to engines, exhaust treatment, and fuels. The first two issues are mainly being addressed by the automotive industry, while the third issue is being addressed by the petroleum refining industry. Exhaust-gas treatment devices include diesel oxidation catalysts, nitrogen oxide removal (deNO_x) catalysts, and diesel particulate filters (DPFs). However, noble metals and basic oxides used as catalysts are susceptible to sulfur poisoning, which can lead to increased fuel consumption due to increased catalyst combustion regeneration frequency. Because of this, sulfur reduction in diesel fuel has been required in order to accelerate the development of innovative exhaust treatment catalysts.

In Japan, the supply of sulfur-free diesel with a sulfur content reduced to below 10 ppm began on a limited scale in 2005 and was subsequently introduced nationwide in 2007. Conventionally, however, the hydrodesulfurization of diesel (sulfur content < 10 ppm) was carried out in an integrated manner through a combination of partial modifications to refinery equipment and the use of a high-performance catalyst, as well as changes in the feedstocks used for hydrotreatment (reduction in hard-to-desulfurize sulfur compounds and nitrogen-rich, high-boiling-point fractions, and reduction in aromatic-compound-rich light-cycle oil (LCO) mixed in), changes in hydrodesulfurization conditions (reduction in oil throughput per unit weight of catalyst), and changes in the hydrodesulfurization process. Consequently,

there are high expectations for replacing the conventional hydrodesulfurization catalysts with high-performance and long-life hydrodesulfurization catalysts that minimize feedstock conditioning and process changes leading to feedstock restrictions and decreased throughput, in order to reduce the production cost of sulfur-free diesel.

The use of sulfur-free diesel is a global trend (Fig. 1). There is rapidly growing demand from overseas refineries for a high-performance hydrodesulfurization catalyst that makes the production of sulfur-free diesel possible without the need to modify existing refinery equipment or change operating conditions when introducing it. Gas oil used in Japan is heavier than that in Europe and the U.S., and contains large amounts of hard-to-desulfurize sulfur compounds. If a hydrodesulfurization catalyst is developed in Japan, this hydrodesulfurization technology has the potential to be used throughout the world. We have therefore been engaged in research and development to commercialize a hydrodesulfurization catalyst for sulfur-free diesel, to meet the social need for clean transportation fuels.

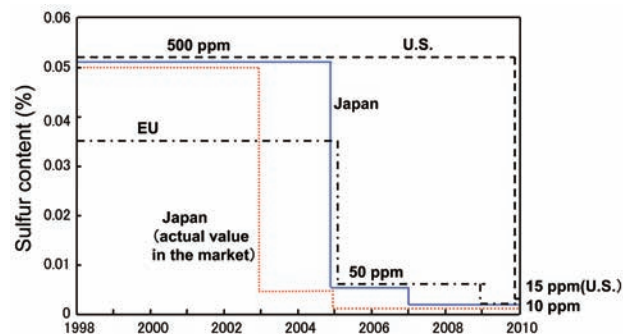


Fig. 1 Trends in diesel sulfur regulation.

2 Objectives and Outcomes of Research

Diesel fuel is produced by the hydrodesulfurization process in which sulfur (1 to 1.5 wt%) in organic sulfur compounds contained in the gas oil is removed as a hydrogen sulfide by reacting it with hydrogen over a hydrodesulfurization catalyst, thereby converting it to hydrogen sulfide (Fig. 2). With the stringent regulation of sulfur content, the performance of hydrodesulfurization catalysts has gradually improved, resulting in a significant improvement in hydrodesulfurization activity over the past 10 years.

In order to produce sulfur-free diesel under the same conditions as those for producing one-generation-older diesel fuel with a sulfur content below 50 ppm, a highly active catalyst (with about double the activity) is required; in other words, comparable hydrodesulfurization activity can be obtained even at a reaction temperature about 10 °C lower. In the hydrodesulfurization reaction, as the time on stream elapses, the desulfurization activity gradually decreases. Therefore, the quality of the diesel is compensated to ensure a sulfur content below 10 ppm by gradually increasing the reaction temperature; e.g., about 1 °C increase/month. However, carbon deposition on the catalyst surface and structural changes in the catalyst's active components become significant at higher reaction temperatures. Therefore, there are limits to temperature compensation in the high-temperature range. Increasing hydrodesulfurization activity even under lower temperatures is essential for the stable production of sulfur-free diesel (expansion of the temperature compensation range). Hydrodesulfurization catalysts for sulfur-free diesel production have already been developed and commercialized by catalyst manufacturers such as Criterion Catalyst, Haldor Topsøe A/S, and Albemarle Catalyst, as well as oil companies such as Exxon Mobil, IFP/Axens, Cosmo Oil, and Nippon Oil. However, they may be subject to constraints in terms of gas oil types and the operating conditions of hydrodesulfurization facilities. Research and development of high-performance hydrodesulfurization catalysts, i.e., catalysts offering activity enhancement under lower reaction temperatures and longer life, is still ongoing.

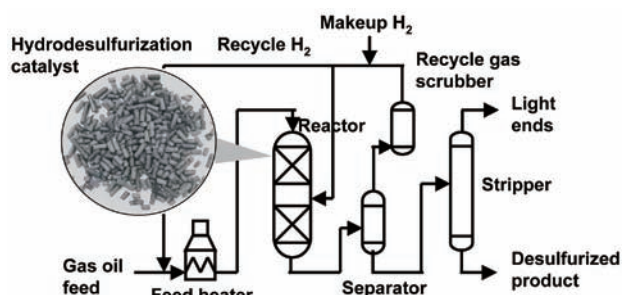


Fig. 2 Schematic diagram of the hydrodesulfurization process in refineries.

We considered that in developing hydrodesulfurization catalysts for sulfur-free diesel, the key to high performance would be the catalyst preparation technology, and conducted full research to refine the developed catalyst preparation technology into “a catalyst preparation technology that can be applied to existing hydrodesulfurization catalyst production lines without the need for modifications.” Specifically, the following research objectives were formulated as representative examples.

Issues related to performance and use of hydrodesulfurization catalysts:

- (1) Hydrodesulfurization catalysts with an activity more than double that of conventional desulfurization catalysts (for diesel with a sulfur content below 50 ppm)
- (2) Hydrodesulfurization catalysts with a lifetime longer than two years (temperature compensation rate for catalyst deactivation: approx. <math><1\text{ }^\circ\text{C/month}</math>), comparable to that of conventional hydrodesulfurization catalysts
- (3) Desulfurization catalysts with handling characteristics and safety comparable to those of conventional hydrodesulfurization catalysts

Issues related to production of hydrodesulfurization catalysts:

- (4) Upscalable catalyst preparation method (from a beaker scale of a few tens of grams to an industrial scale of tons per day) that can use inexpensive catalyst materials as with conventional hydrodesulfurization catalysts
- (5) Technique to identify and control determining factors in the catalyst preparation process
- (6) Industrial-scale production technology for the developed hydrodesulfurization catalyst

We were not able to address all of the above issues by ourselves, and therefore focused on issues (1), (4), and (5), for which we possess strong research potential. In particular, we focused on issues (4) and (5) involving new preparation methods for hydrodesulfurization catalysts, and jointly developed other items with a catalyst manufacturer.

The research outcomes include the commercialization of a new hydrodesulfurization catalyst for sulfur-free diesel and support for the supply of sulfur-free diesel to the market. The new hydrodesulfurization catalyst can indirectly contribute to the market penetration of diesel vehicles equipped with a high-performance exhaust-gas treatment catalyst. Such a shift to diesel engines can be expected to have a ripple effect leading to CO₂ reduction in the transportation sector.

3 Research Scenario to Achieve the Objectives

As shown by the GC-SCD chromatogram in Fig. 3, obtained by gas chromatography (GC) with sulfur chemiluminescence detector (SCD), gas oil contains various sulfur compounds

such as benzothiophenes and dibenzothiophenes. C-S bonds in these compounds are broken over the sulfide catalyst, and sulfur is removed in the form of hydrogen sulfide (Eq. 1):



This hydrodesulfurization reaction takes place under high-pressure and high-temperature conditions; e.g., a reaction temperature of 330 to 360 °C and a reaction pressure of 3 to 7 MPa. After being loaded with the hydrodesulfurization catalyst, the reactor continues operation for about two years. Most hydrodesulfurization catalysts have metal species (mainly metal oxides) such as Mo, W, Co, and Ni on the surface of porous oxides, and are presulfided before hydrodesulfurization.

The structure of active sites on a hydrodesulfurization catalyst has been a subject of discussion for many years. Today, a structure model is widely supported in which, for example, in the case of a sulfided CoMo-Al₂O₃ catalyst, MoS₂ particles are present on the porous γ-Al₂O₃ support in a highly dispersed state, the Co species is coordinated with the S-edge of the MoS₂ particles, and the Co-Mo-S phase with highly active hydrodesulfurization is formed (Fig. 4).

Topsøe *et al.* [1] classified this Co-Mo-S phase into Type I, which has a significant interaction with the support, and Type II, which has a less significant interaction with the support, and showed that the hydrodesulfurization activity of Type II per unit weight of Co is higher than that of Type I. Consequently, in order to improve the performance of hydrodesulfurization catalysts, a catalyst preparation method was developed to selectively create a Type-II Co-Mo-S structure.

Cosmo Oil [2][3] developed a catalyst preparation method to multilayer the Type-II Co-Mo-S phase (① in Fig. 5: citric acid is used as a chelating agent in the catalyst preparation process). It was found that high activity could be obtained

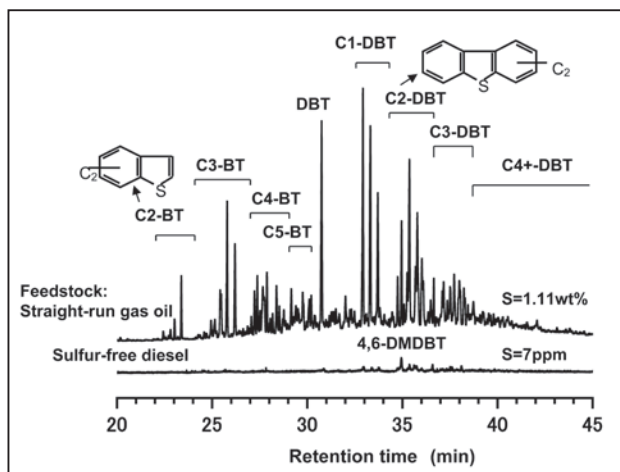


Fig. 3 Sulfur compounds contained in gas oil (straight-run gas oil).

with an average of about 3.8 layers of the MoS₂ phase, and the developed catalyst was commercialized. (It is reported that an alumina support containing zeolite is used as the support for the commercialized catalyst to enhance isomerization activity, in order to avoid steric hindrance by alkyl substituents in sulfur compounds.) AIST [4]-[6] developed a catalyst preparation method to lower the number of stacked layers of the Type-II Co-Mo-S phase (② in Fig. 5). In CoMo/Al₂O₃ or NiMo/Al₂O₃ catalysts used for hydrodesulfurization for an extended period of time, hydrodesulfurization activity is maintained to some extent, but there is lower stacking of layers (mostly single layers) and many MoS₂ particles with the grown (002) face of MoS₂ are present. We therefore considered that they would perform well with lower stacking of layers.

Furthermore, we focused on the crystallinity of the Type-II Co-Mo-S phase with the expectation of the following benefits: (1) As a result of increased crystallinity, the sulfur chemical potential of the catalyst is high and sulfur coordinatively unsaturated sites (hydrodesulfurization active sites) on the Co-Mo-S phase are less susceptible to absorptive inhibition by hydrogen sulfide. (2) The basicity of the coordinated sulfur increases, facilitating its promotion of hydrodesulfurization by removing protons from sulfur compounds and activating hydrogen. (3) Due to the increased

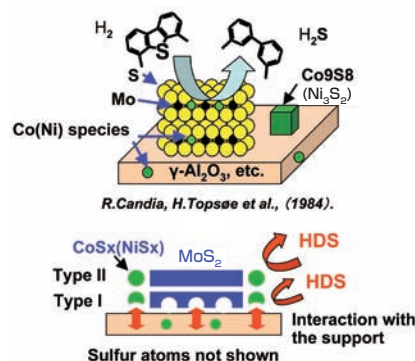


Fig. 4 Model for the active-phase structure of a molybdenum sulfide-based hydrodesulfurization catalyst.

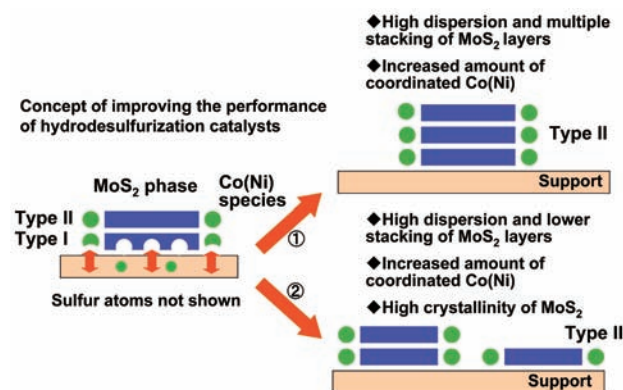


Fig. 5 Approach to high-performance hydrodesulfurization catalysts.

basicity of the coordinated sulfur (reduced Lewis acidity of adjacent sulfur coordinatively unsaturated sites), the hydrodesulfurization reaction is less susceptible to absorptive inhibition by basic aromatic compounds and nitrogen compounds in feedstock oil.

Therefore, we considered that the key to the high dispersion, lower stacking of layers, and high crystallization of MoS₂ and the proper coordination of Co species with the MoS₂ edge sites would be a metal-containing impregnation solution, and focused on establishing the preparation method for such a solution (Fig. 6). The effectiveness of chelating agents (nitrilotriacetic acid, citric acid [7], CyDTA [8], etc.) in preparing an impregnation solution containing Mo-polyanions and Co ions has already been confirmed.

We found a new chelating agent, identified the controlling factors in catalyst preparation, and confirmed that the preparation of highly active Mo-based catalysts is reproducible, although on a laboratory scale.

4 Deepening and Integration of Element Technologies as an Approach

Usually, a catalyst research approach consisting of three parts (a “three-in-one” type of research approach: catalyst design and preparation technique – catalyst structure analysis/evaluation technique – catalytic reaction evaluation technique) as shown in Fig. 7 is used if a proof of principle approach is used for Section 3. This approach is a process in which, as this three-part relationship revolves, the catalyst develops into a high-performance catalyst (evolving in a spiral like a helical spring). It is a series of processes: the latest analytical machines are incorporated to characterize a catalyst that, for example, was trial-produced for specific purposes or purchased on the market; the obtained catalyst structure is correlated to active sites on the catalyst; and design guidelines for an advanced catalyst are proposed.

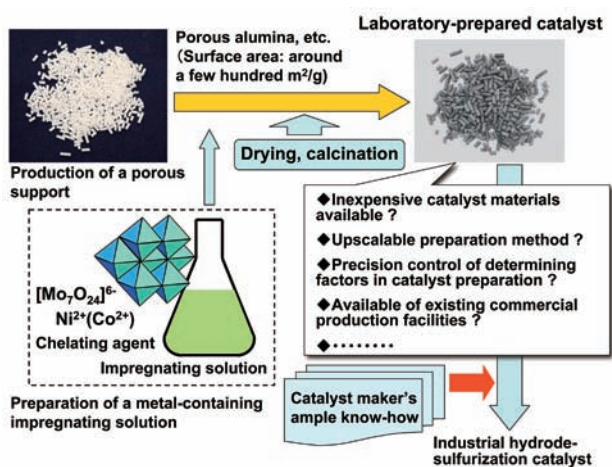


Fig. 6 Catalyst preparation method based on the conventional impregnation method using the new impregnation solution.

With advances in catalyst analysis techniques and theoretical support for catalyst structures (density functional theory (DFT) calculation, etc.), atomic- and molecular-level information on catalysts is constantly updated, and the three-part relationship is evolving and successful. However, for the wet catalyst preparation method, which is the mainstream industrial catalyst preparation method and is widely used for catalyst preparation in the laboratory, information on the prepared catalyst is not necessarily fed back to the preparation stage. This might be due to the limited information available on the properties of metal ions, metal complex, or colloids in the impregnation solutions. It is more appropriate to say that information to help link information on the prepared catalyst to that on catalyst preparation is not disclosed because the preparation process is directly linked to intellectual property. Another feature of this study is that the three-part relationship for solid catalysts, such as preparation of a metal-containing impregnation solution used for catalyst preparation and structural analysis of metal ions in the impregnation solution, was investigated at the solution level, and the catalyst preparation process was reviewed from a chemical as well as engineering perspective.

We assumed that the following were essential to move smoothly from beaker-scale to industrial-scale catalyst production:

- (1) Industrial catalyst materials are inexpensive, the impregnation solution preparation method can correspond to variations in industrial catalyst material lots, and quality control can be applied to a large-scale catalyst preparation process.
- (2) The catalyst preparation method can be used in existing commercial hydrodesulfurization catalyst production facilities.

As a result of studying various aspects, we identified controlling factors in catalyst preparation, although for laboratory preparation; undertook an in-depth study on techniques to control controlling factors; and developed a recipe for catalyst preparation. Subsequently, based on the results obtained at AIST, we conducted joint research with a catalyst manufacturer. It was found that AIST’s recipe required improvements, but the overall direction of our

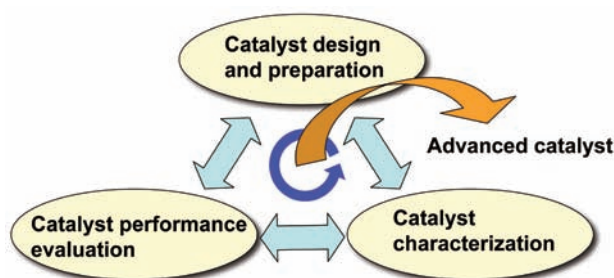


Fig. 7 Three-in-one technology in catalyst development.

research was confirmed to be correct. Through the joint research, we were able to directly learn the requirements for industrial production of catalysts and address them from an academic perspective at AIST. This is probably the foremost reason why it was possible to scale up from the laboratory scale relatively easily.

5 Research Results

5.1 Performance of the Developed Catalyst

The hydrodesulfurization performance of the NiMo/Al₂O₃ catalyst developed by AIST was evaluated under the normal hydrodesulfurization conditions of a refinery (reaction temperature: 340 °C, reaction pressure: 4.9 MPa, LHSV: 1.5 h⁻¹, H₂/Oil feed ratio: 250 NI/l) using a high-pressure continuous-flow reactor. The evaluation showed that sulfur-free diesel (S < 10 ppm, N < 1 ppm) can be produced from straight-run gas oil (S: 1.11 wt%, N: 105 ppm).

5.2 Structural Characteristics of the Developed Catalyst

Figure 8 shows a TEM image of the developed NiMo/Al₂O₃ catalyst (sulfide). The average layer length of MoS₂ particles is about 4.4 nm and the average number of stacked layers is about 1.7. The MoS₂ particles observed by TEM have a smaller basal plane length than a conventional NiMo catalyst and are highly dispersed. The number of stacked layers of MoS₂ particles is smaller than in the conventional NiMo catalyst. Thus, it was confirmed that as initially intended, MoS₂ particles on the γ-Al₂O₃ support were highly dispersed and supported in a lower stacking of layers.

Atomic-level analysis of the MoS₂ phase was conducted through extended X-ray absorption fine structure (EXAFS) analysis of the developed NiMo/Al₂O₃ (sulfide). Figure 9 shows a Fourier transform of the Mo K-edge EXAFS spectra for the conventional NiMo/Al₂O₃ catalyst (conv.) and the developed NiMo/Al₂O₃ catalyst (lab.). The table at top right shows the coordination number, N, of the sulfur atom around the Mo

atom of each catalyst and the interatomic distance, R, of the Mo-S bond, as well as the coordination number, N, of the Mo atom around the Mo atom and the interatomic distance, R, of the Mo-Mo bond, which were obtained by the curve-fitting method. In both catalysts, the interatomic distance of the Mo-S and Mo-Mo bonds was 2.41 and 3.17 Å, respectively, and comparable MoS₂ nanostructures were obtained. In the developed catalyst, however, the coordination number of the Mo-Mo and Mo-S bonds increased. The increase in the former suggests an increased size of the highly crystallized domain in the (002) face of MoS₂. The increase in the latter suggests that the unit cell of MoS₂ is closer to the cell structure of single crystals. The TEM image in Fig. 8 shows that MoS₂ particles have a smaller basal plane size in the developed catalyst than in the conventional catalyst. These findings suggest very high crystallinity (nanocrystal state) of the MoS₂ sheet in the developed NiMo/Al₂O₃ (sulfide), despite the smaller MoS₂ basal plane size. From the above, it was confirmed that as initially intended, MoS₂ particles on the γ-Al₂O₃ support existed in a highly crystalline state.

5.3 Performance of a New Desulfurization Catalyst, LX-NC1

A new hydrodesulfurization catalyst (product name: LX-NC1) was developed by the catalyst manufacturer, with the design concept of improving the functionality of the nanocrystal structure of this low-stacked-layer MoS₂. Figure 10^[9] shows the performance of the developed LX-NC1 NiMo hydrodesulfurization catalyst. In order to produce sulfur-free diesel using existing facilities in refineries, a highly active catalyst with a reaction temperature about 10 °C lower is required rather than a hydrodesulfurization catalyst for producing diesel with a sulfur content below 50 ppm; e.g., CDS-LX6 hydrodesulfurization catalyst, produced by the joint research partner. It was confirmed that the developed LX-NC1 catalyst exhibits high activity at a reaction temperature nearly 17 °C lower, and that sulfur-free diesel can be easily produced.

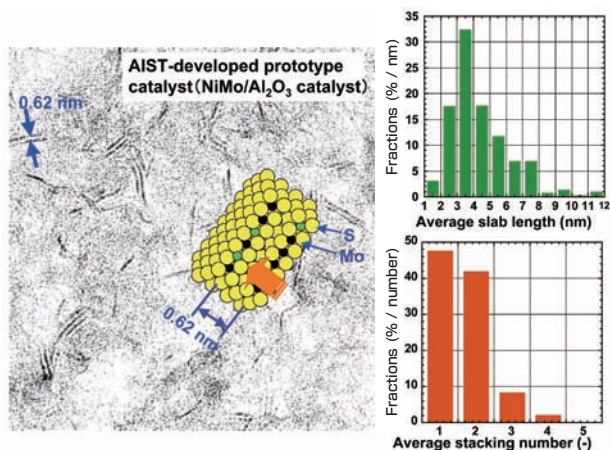


Fig. 8 TEM image of the developed NiMo/Al₂O₃ catalyst (sulfide) and dispersed state of MoS₂ particles.

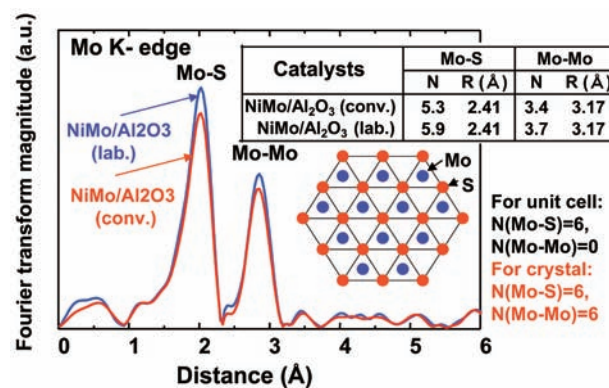


Fig. 9 Local structure of MoS₂ particles on the developed NiMo/Al₂O₃ catalyst.

The stability of activity of the developed catalyst is the most important element of an industrial catalyst. A lifetime test of the developed LX-NC1 catalyst using bench apparatus confirmed very high stability; i.e., during operation to produce diesel with a sulfur content of 7 ppm, the activity reduction rate was less than 1.0 °C/month after a time on stream of two months.

6 Future Plans

The LX-NC1 catalyst for sulfur-free diesel, developed using a new design concept and an advanced catalyst preparation method, can reduce sulfur content from straight-run gas oil both economically and efficiently to produce sulfur-free diesel, and can adequately meet the requirements for sulfur-free diesel production by refineries both in Japan and overseas. It is expected that after the introduction of sulfur-free diesel in Japan and overseas, market introduction of new automotive technologies, including new exhaust post-treatment technologies with the problem of sulfur poisoning mitigated or solved, will be accelerated, resulting in reduced diesel exhaust-gas emissions and improved fuel consumption of diesel engines (reduced CO₂ emissions).

On the other hand, with the stringent regulation of sulfur in gasoline, sulfur-free gasoline was introduced in 2008 in Japan. The sulfur content of premium gasoline had been below 10 ppm, and the issue was to also reduce sulfur in regular gasoline to below 10 ppm.

The main blending stock of regular gasoline is a high-octane gasoline obtained by fluid catalytic cracking of heavy oil, known as FCC gasoline. Most of the sulfur content in regular gasoline comes from FCC gasoline, and hydrodesulfurization technology was therefore required to both reduce sulfur in FCC gasoline and maintain the high octane number. The following hydrodesulfurization processes have been studied: (1) hydrodesulfurization in the fluid catalytic cracking unit;

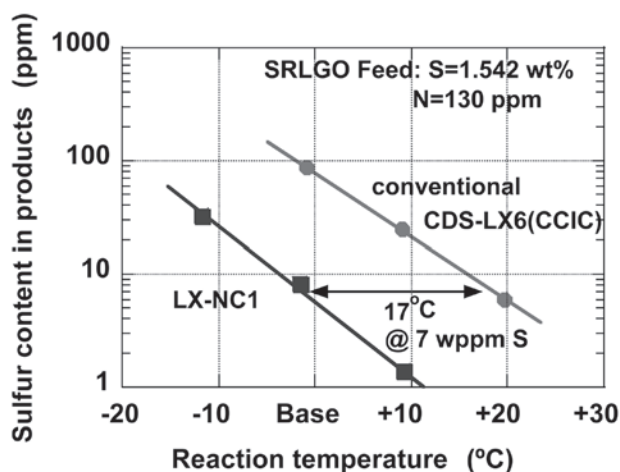


Fig. 10 Hydrodesulfurization performance of the jointly developed LX-NC1 industrial catalyst .

(2) a process in which deep hydrodesulfurization of FCC gasoline is prioritized (simultaneous deep hydrogenation of olefins) and the octane number loss is then compensated for by alkylation, etc.; (3) a selective hydrodesulfurization process in which the hydrogenation of olefins contained in FCC gasoline is minimized (minimization of octane number loss), and thiophenes and thiols are selectively hydrodesulfurized; and (4) an alkylation desulfurization process in which olefins and sulfur compounds contained in FCC gasoline are alkylated and the produced high-boiling-point sulfur compounds are removed by distillation. The hydrodesulfurization processes in (2) and (3) were commercialized. The hydrodesulfurization process in (3) was developed in Japan^[10]. However, a study on the effect of the increased octane number of regular gasoline on fuel consumption improvement has also begun in Japan. The octane number may be increased to around 95 as in the European market (it is currently around 90 in Japan). Demand may therefore increase for hydrodesulfurization catalysts that minimize the hydrogenation of olefins (for example, olefin hydrogenation rate < 15 %) and provide high hydrodesulfurization activity.

In order to improve the hydrodesulfurization selectivity of FCC gasoline, studies are mainly being conducted on the control of hydrogenation of olefins. These include the study of a method of controlling the hydrogenation and isomerization of olefins due to the movement of double bonds in olefins by controlling the acidity of the catalyst support^[10], thereby weakening the adsorption of basic olefins. However, most of the conventional hydrodesulfurization catalysts contain the Type-I Co-Mo-S phase (Fig. 4), and are susceptible to hydrogen activation and the hydrogenation of double bonds even in the presence of hydrogen sulfide. Therefore, there is presumably a limit to control of the hydrogenation of olefins. The hydrodesulfurization selectivity of FCC gasoline is expected to further improve if hydrodesulfurization catalysts contain only the Type-II Co-Mo-S phase (or the Ni-Mo-S phase) and, in addition, if hydrodesulfurization activity per sulfur coordinatively unsaturated site can be improved and the solid acidity of the support can be optimized. In other countries, the sulfur concentration of FCC gasoline is a few hundred to a few thousand ppm (higher by one to two digits than the concentration in Japan), and the need for improved hydrodesulfurization selectivity is higher than in Japan. We plan to apply the preparation method for the developed gas oil hydrodesulfurization catalyst to the production of selective hydrodesulfurization catalysts for FCC gasoline^{[11][12]} to develop applications for the developed technology.

Acknowledgements

The LX-NC1 hydrodesulfurization catalyst for sulfur-free diesel was developed for commercialization through joint research for patent commercialization with Catalysts &

Chemicals Industries Co., Ltd. (currently, JGC Catalysts and Chemicals Ltd.). We would like to thank them. The developed hydrodesulfurization catalyst was the fruit of more than 40 years of research, which was initiated at the former Industrial Laboratory of Tokyo. We would like to thank the senior members of the former institutes, as well as Dr. Akio Nishijima, Mr. Toshio Sato, Dr. Hiromichi Shimada, Dr. Nobuyuki Matsubayashi, and Mr. Motoharu Imamura of the former Nishijima Laboratory.

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Discussions with Reviewers

1 Features of this research

Comment (Koichi Mizuno)

This research work is highly evaluated, since the project is focused on catalyst performance which is one of the factors for improving desulfurization of diesel fuels. However, the desulfurization technologies are wider, and beside catalyst, there are many other improving processes such as distillation of crude oil and so forth. I, therefore, recommend the authors to clarify the potential of technical options of desulfurization processes and to explain the reason(s) for emphasizing the catalyst process.

Based on the above reasons, I felt some narrow viewpoint in the original first manuscript describing "However, since sulfur-free technologies until now has been solved only by replacement of deactivated catalyst with fresh catalyst, higher performance of desulfurization catalysts are highly desired." To make ordinary people understand more easily existing sulfur-free technology (sulfur content <10 ppm), I recommend the authors to describe (1) technological options other than catalyst improvement, (2) disadvantages of the other technologies, and (3) the reason(s) for improving catalyst performance.

Answer (Yuji Yoshimura)

As you have pointed out, in order to produce sulfur-free diesel using an oil refinery facility for producing conventional low-sulfur diesel (sulfur content < 50 ppm), integrated measures are required, including equipment modifications such as the installation of additional reactors, a switch to a high-performance catalyst, the use of an easy-to-desulfurize fraction as the feedstock, the use of reaction conditions to facilitate the hydrodesulfurization reaction, and a change in the blending process for the diesel blending stocks. However, issues arise, such as the increased capital investment cost for revamping facilities and the need for adjustment of the oil product balance due to changes in the feedstock and processes. The switch to a high-performance catalyst is the most economical measure, and

expectations for high-performance catalysts are rising. Therefore, first we have described diesel hydrodesulfurization methods and revised the text to clarify the role of catalyst technology in hydrodesulfurization.

2 Technological goal for gasoline desulfurization

Comment (Koichi Mizuno)

In the Future Plans section, there is a statement that you would like to apply the developed technology to the selective hydrodesulfurization of gasoline. I understand that the target of this statement requires both control of the hydrogenation of olefins as well as improvement of hydrodesulfurization performance. It is not particularly emphasized, however, that catalysts that allow the control of hydrogenation as well as the improvement of hydrodesulfurization have never been explored and are a challenging technology. For the readers' better understanding, I wonder whether you could elaborate on why the technology is challenging and how it can be turned into reality.

Answer (Yuji Yoshimura)

The main blending stock of regular gasoline is high-octane FCC gasoline obtained by the fluid catalytic cracking of heavy oil. Most of the sulfur content in regular gasoline comes from FCC gasoline, and hydrodesulfurization technology is therefore required to both reduce sulfur in FCC gasoline and maintain the high octane number. In order to improve the hydrodesulfurization selectivity of FCC gasoline, studies are mainly being conducted on the control of hydrogenation of olefins. These include the study of a method of controlling the hydrogenation and isomerization of olefins due to the movement of double bonds in olefins by controlling the acidity of the catalyst support^[10], thereby weakening the adsorption of basic olefins. However, most of the conventional desulfurization catalysts contain the Type-I Co-Mo-S phase (Fig. 4), and are susceptible to hydrogen activation and the hydrogenation of double bonds even in the presence of hydrogen sulfide. Therefore, there is presumably a limit to

control of the hydrogenation of olefins. The hydrodesulfurization selectivity of FCC gasoline is expected to further improve if desulfurization catalysts contain only the Type-II Co-Mo-S phase (or the Ni-Mo-S phase) and, in addition, if hydrodesulfurization activity per sulfur coordinatively unsaturated site can be improved and the solid acidity of the support can be optimized. We plan to apply the preparation method for the developed diesel fuel hydrodesulfurization catalyst to the production of selective hydrodesulfurization catalysts for FCC gasoline to develop applications for the developed technology.

3 Future plans for fuel refining technology

Question (Koichi Mizuno)

I understand that the results of your research on catalyst technology are intended to be used for hydrodesulfurizing diesel fuel and will be applied to the desulfurization of gasoline. Do you have a plan to develop other applications?

Answer (Yuji Yoshimura)

There are rapidly increasing expectations for biofuels (in the future, biofuels based on non-food biomass) arising from the need for diversification and secure supply of transportation fuels due to soaring oil prices, as well as compliance with the Kyoto Protocol. Expectations are increasing for new fuel production technologies, including hydrocarbon production using a hydrodeoxygenation catalyst technology, such as from *Jatropha*, a non-food oil crop, and hydrocarbon fuel production using a hydrodeoxygenation catalyst technology for pyrolysis oils (bio-oils) produced by the thermochemical conversion of biomass residue. In these reaction systems, the hydrogenation deoxidation reaction is the main reaction accompanied by the breaking of C-O bonds, unlike the hydrodesulfurization reaction accompanied by the breaking of C-S bonds. These two reactions have a similarity in the mechanism of heteroatom removal over a solid catalyst. We plan to take on the challenge of developing production technology for these new biofuels by improving the developed hydrodesulfurization catalyst.