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Development of ultra-deep HDS catalyst for production of clean diesel fuels

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Abstract

Cosmo Oil has successfully developed a new CoMo HDS catalyst, C-606A, for production of ultra-low sulfur diesel fuels. This catalyst was prepared by an impregnation method using a solution containing Co, Mo, P, and citric acid on a HY-Al_2O_3. The resulting catalyst air-dried only without calcination. The HDS activity was measured with straight-run light gas oil feedstocks under industrial hydrotreating conditions. C-606A had a three times higher HDS activity compared with the conventional CoMoP/Al_2O_3 catalyst. Commercial operation with C-606A has successfully demonstrated high performance. This catalyst has superior activity, which enables <10-ppm sulfur content in products in a commercial hydrotreater designed to produce 500-ppm sulfur diesel fuels.

Keywords: Hydrodesulfurization; Ultra-deep HDS; Ultra-low sulfur; Cobalt molybdenum catalyst; Co–Mo–S phase; ULSD

1. Introduction

Worldwide, refiners are challenging to provide clean transportation fuels to meet increasingly demanding environmental regulations [1,2]. In particular, sulfur removal in diesel fuels is now strongly desirable because sulfur may adversely affect the durability of the catalytic converter for exhaust emission treatment. Indeed, in Japan, while proposed official legislation in diesel to <10-ppm sulfur content comes into effect in 2007, most Japanese refiners voluntarily began <10-ppm sulfur diesel before January 2005. Furthermore, many other countries are planning to begin implementing ultra-low sulfur diesel (ULSD, <10-ppm sulfur) fuel supply in the near future. In view of the demands for ULSD fuels, the development of technology for ultra-deep hydrodesulfurization (HDS) to remove most of the sulfur compounds in the diesel fractions will become extremely important.

Removal of the sulfur content is possible by using modified operating conditions for hydrotreaters with respect to the reaction temperature and liquid hourly space velocity (LHSV). However, higher reaction temperature results in coke formation on the catalyst and rapid catalytic deactivation, and lower LHSV results in reduced hydrotreating efficiency, thus, requiring additional reactor or larger reactor replacement. Consequently, the best way of achieving the ultra-deep HDS without changing the operating conditions and in a cost-effective manner is to develop a catalyst having a super high HDS activity.

In order to address this increased demand of ultra-deep HDS, the Japan Petroleum Energy Center (JPEC) was commissioned by the New Energy and Industrial Technology Development Organization (NEDO) in Japan. From October 1999 to March 2004, Cosmo Oil Co., Ltd., joined this NEDO research project and challenged to develop a highly active HDS catalyst.

The objective of this paper is to introduce our latest developed catalyst, C-606A, which has a higher HDS activity than any other commercially available CoMo HDS catalyst.

2. Experimental

2.1. Preparation of catalysts

C-606A was prepared by wet incipient pore-volume coimpregnation using an aqueous solution containing the required amounts of $CoCO_3$, MoO_3, orthophosphoric acid and

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citric acid monohydrate on a support consisting of HY (ca. 5 mass%) including Al_2O_3 (specific surface area > 300 m^2/g). Small addition of 5 mass% HY to the Al_2O_3 support improves the HDS activity by 1.2 times compared with only Al_2O_3-supported CoMo HDS catalyst [3]. The preparation procedure has been previously described in detail [4].

For comparison, a conventional Al_2O_3-supported CoMoP catalyst was evaluated. The catalyst was prepared by wet incipient pore-volume impregnation using an aqueous solution containing the required amounts of $CoCO_3$, MoO_3, and orthophosphoric acid on a support consisting of Al_2O_3 (specific surface area 364 m^2/g). After impregnation, this sample was air-dried and calcined at 500 °C. The Co/Mo molar ratio was ca. 0.3 and the loading of Mo was 13 mass% Mo.

Prior to the activity measurements, the fresh catalysts were presulfided in situ with gas oil under normal hydrotreating conditions.

2.2. Feedstock properties

Middle East straight-run light gas oils (SRLGO) with sulfur contents between 1.05 and 1.74 mass% were used as the feedstock for the pilot plant test. The feedstock properties are shown in Table 1.

2.3. Activity measurements

HDS runs were carried out with the pilot plant consisting of an isothermal fixed-bed reactor operating in a down-flow mode. Thirty milliliter of catalyst was loaded with 15 ml of fine inactive carborundum particles in the reactor. The HDS of the diesel fractions was carried out under the conditions shown in Table 2. The amount of sulfur was measured by a trace sulfur analyzer (TS-100, Mitsubishi Kagaku) for sulfur levels below 100 ppm and by energy-dispersive X-ray fluorescence spectroscopy (RX-600SA, Mitsubishi Kagaku) for higher sulfur levels. The amount of nitrogen was measured by a chemiluminescent nitrogen analyzer (9000 NS, ANTEK Instruments). Sulfur containing compounds were analyzed by use of a gas chromatograph (GC) (Hewlett Packard 5890 II plus) equipped with a capillary column (HP-1, 25 m, 0.32 mm diameter) and an atomic emission detector (AED) (Hewlett Packard 5921A).

Table 1
Properties of feedstocks

	Feedstock		
	A	B	C
Density (g/cm^3)	0.8609	0.8623	0.8529
Sulfur (mass%)	1.37	1.74	1.06
Nitrogen (ppm)	210	120	90
Boiling range (°C)			
IBP	211.5	186.0	202.0
50%	314.0	316.0	313.0
90%	365.0	355.5	345.5
FBP	383.5	371.5	363.5

Table 2
Reaction conditions

	Pilot plant
H_2 pressure (MPa)	4.9
H_2/oil ratio (Nm^3/kl)	200
LHSV (h^{-1})	1.3, 1.5
Temperature (°C)	330–390

Commercial operation requires frequent changes in the feed quality and the process conditions such as crude source, distillation property, feed sulfur content, product sulfur content, reaction temperature, LHSV, and H_2 pressure. The precise catalytic activity is, thus, difficult to assess just by plotting commercial operating data. As an index of the catalytic activity, the normalized weight bed average temperatures (WABT) were obtained by normalizing the commercial operation data to a set of standard feedstock and operating conditions.

Prediction of catalyst deactivation during the commercial operation was calculated by a kinetic model using simultaneous equations assuming first-order decrease of active sites on the catalyst.

2.4. Characterization of catalysts

2.4.1. TEM observations

Transmission electron microscopic (TEM) measurements were carried out using an electron microscope (JEM-2010, JEOL), with an accelerating voltage of 200 keV.

The catalyst was placed in the reactor and 5% H_2S/H_2 (100 ml/min (STP)) was introduced into the reactor at room temperature. Under a flow of 5% H_2S/H_2, the catalyst was heated at 5 °C/min to 400 °C and maintained at that temperature for 1 h. After sulfidation, the reactor was cooled to 200 °C under the flow of 5% H_2S/H_2, then N_2 was introduced into the reactor to purge the 5% H_2S/H_2, and cooled to room temperature. The catalyst was then taken out from the reactor.

The presulfided sample was finely ground and suspended in acetone, then placed on a collodion film mounted on a specimen grid. The direct magnification was 200,000 diameters, and five fields of view were examined. The electron micrographs were enlarged to provide a magnification of 2,000,000 diameters. The number of MoS_2 laminated layers visually recognized on the photograph was counted, and the lateral direction length of the layers was measured.

2.4.2. XPS measurements

The X-ray photoelectron spectra (XPS) of the catalysts were measured on an XPS-7000 (Rigaku Corp.) photoelectron spectrometer using monochromated Al Kα radiation (14 kV, 350 W). Spectra were recorded with a constant pass energy of 23.5 eV. In order to prevent a sulfided catalyst from contacting the oxidative atmosphere before the XPS measurement, the following pretreatment was carried out.

The catalyst disk was sulfided under the same conditions as for the TEM measurements in a glass reactor connecting with the XPS pre-chamber. After sulfiding, the inside of the reactor was evacuated at ambient temperature by a turbo molecular pump. Then, the sulfided catalyst disk was transferred from the reactor to the XPS pre-chamber in high vacuum (1×10^{-5} Pa). The base pressure of the spectrometer was better than 1×10^{-6} Pa during the measurements. Sample charging was compensated using the Al 2p line of Al_2O_3 at 74.7 eV as the internal standard [5]. Background signals were removed using the Shirley-type integral [6]. The ratios of Mo^{6+}, Mo^{5+}, and Mo^{4+} were quantitatively calculated from the peak deconvolution of the Mo 3d XPS spectrum. The S 2p/Mo 3d peak area intensity ratios (S 2p binding energy, 162.0 eV, referenced to Al 2p, 74.7 eV) were converted to the S/Mo molar ratio based on the ideal atomic sensitivities.

2.4.3. FT-IR measurements of adsorbed NO

To evaluate the amount of adsorbed NO on the coordinatively unsaturated Co and Mo sites, a sulfided catalyst after NO adsorption was analyzed by diffuse-reflectance FT-IR. The FT-IR was measured using an FT-IR-8100M (Shimadzu Corp.) and an in situ diffuse-reflectance type cell (Spectratech Co.). The finely ground catalyst was sulfided in an in situ diffuse-reflectance type cell in a gas flow consisting of 5% H_2S in H_2 at 400 °C for 2 h, followed by He flush treatment at 400 °C for 30 min. After cooling to room temperature, NO was introduced for adsorption for 30 min. After flushing with He for 30 min, the IR spectra were recorded.

3. Results and discussion

3.1. Alkyldibenzothiophenes HDS reactivity

Fig. 1 shows the sulfur compound distributions of straight-run gas oil (feedstock A) before and after the HDS with a conventional $CoMoP/Al_2O_3$ catalyst. The sulfur distributions were determined using a GC–AED. Feedstock contains a large variety of different sulfur compounds, that is, benzothiophene, alkylbenzothiophenes, dibenzothiophene, and mono, di, and trialkyldibenzothiophenes. The reactivities of the various species significantly differ. In particular, when hydrotreating to an ultra-low sulfur level, it can be seen that benzothiophene, alkylbenzothiophenes and dibenzothiophene completely disappeared, while the refractory sulfur compounds, e.g., 4,6-dimethyldibenzothiophene (4,6-DMDBT) and the higher molecular weight alkyldibenzothiophenes with side chains in sterically hindering positions still remain in product.

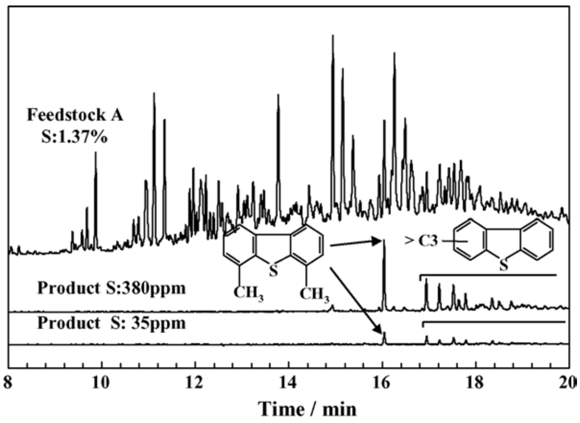

Fig. 1. GC–AED charts of straight-run gas oil before and after desulfurization.

In order to achieve ultra-deep HDS, it is necessary to significantly increase the active site density and to raise the intrinsic catalytic activity per active site compared to conventional catalysts. Additionally, it becomes necessary to add a function of converting the refractory sulfur compounds to sulfur compounds that are easy to desulfurize.

3.2. Catalyst design

In CoMo HDS catalysts, the so-called Co–Mo–S phase, which consists of sulfided Co atoms decorating the edges and corners of the MoS_2 slabs [1], which is generally accepted as active phase at the present time. The density of Co–Mo–S phases on the catalyst directly influences the catalytic activity. On the other hand, the morphology of the MoS_2 phase is also important to the HDS activity. In the ultra-deep HDS region, there still remain only large molecular alkyldibenzothiophenes, as shown in Fig. 1. The Co–Mo–S Type II [7], which is located at the edges of the multi-layers of MoS_2 would be much more accessible to large molecules than the Co–Mo–S Type I, which is located at the edges of the single layer of MoS_2 [8–10]. Therefore, it is necessary to find effective preparation methods for the high density Co–Mo–S Type II on the catalyst.

Significant improvements in catalytic activity can be obtained by the addition of chelating agents or phosphate to the impregnation solution during the preparation of the HDS catalyst. The addition of chelating agents, such as nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA), cyclohexanediaminetetraacetic acid (CyDTA) and ethylenediamine (EN), to the impregnation solution during catalyst preparation increases the catalytic activity of the $NiMo/SiO_2$, $NiMo/Al_2O_3$, and $CoMo/Al_2O_3$ catalysts [11–20]. Phosphate also improves the catalytic properties by promoting the formation of the Co–Mo–S Type II phase [21–25]. However, no HDS catalyst containing both a chelating agent and a phosphate has yet been commercialized [26].

General chelating agents, such as NTA, EDTA, CyDTA, and EN, were very expensive and economically less attractive, so inexpensive citric acid easily forming stable complexes with transition metal ions was selected as the chelating agent. Consequently, we found that when a support was impregnated with a solution containing Co, Mo, P, and citric acid and dried, then, the Co–Mo–S Type II could be precisely regulated without producing any inactive forms of Co species. At last, we successfully developed a highly active HDS catalyst, C-606A. The physical and chemical properties of C-606A are listed in Table 3.

3.3. Catalyst characterization

To investigate the characteristics of the active sites on C-606A and the conventional $CoMoP/Al_2O_3$ catalyst, TEM measurements were carried out. Fig. 2 shows TEM micrographs

Table 3
Properties of C-606A, which is Cosmo Oil's ultra-deep HDS catalyst

Active phase	Co–Mo
Metal content	C-606A: Co 4 mass%, Mo 15 mass%
Additive	Citric acid, phosphorus
Support	HY-Al_2O_3
Surface area (m^2/g)	>200
Pore volume (ml/g)	>0.4
Extrudate shape	Cylinder
Diameter (mm)	1.5
Side crushing strength (kg/mm)	>1.4

Table 4
Percentage abundance of the Mo species, Mo^{6+}, Mo^{5+}, and Mo^{4+}, on C-606A and conventional CoMoP/Al_2O_3

Catalyst	Mo^{6+} (%)	Mo^{5+} (%)	Mo^{4+} (%)
C-606A	10	0	90
Conventional CoMoP/Al_2O_3	16	0	84

of the sulfided catalysts. C-606A has multi-layers of MoS_2 slabs, the number of the observed layers being more than two. It is assumed that these layers of MoS_2 formed on the support, not only served to increase the contact area of the catalyst but also had active sites, e.g., the Co–Mo–S phase [9,10]. Furthermore, because the number of such laminating layers on the conventional catalyst is less than two on average, this catalyst has a larger proportion of the lower active Type I sites of the Co–Mo–S phase and, hence, would not have a high activity.

The sulfiding behavior of Mo on the catalyst was investigated by in situ XPS. Table 4 shows the distribution of the Mo species, Mo^{6+}, Mo^{5+}, and Mo^{4+}, on C-606A and the conventional CoMoP/Al_2O_3. The fraction of Mo^{4+} on C-606A was 90%, while that of Mo^{4+} on the conventional CoMoP/Al_2O_3 catalyst was 84%. Generally, there is an agreement that a sulfided Mo^{4+} species attributed to MoS_2 is present. The XPS results suggest that C-606A was easily sulfided compared with the conventional catalyst. Mo^{6+} species are probably still present in low concentrations as Mo–O–Al linkages. Since Mo species on C-606A had only weak interaction with the Al_2O_3 support, so the sulfidation degree was larger compared with the conventional catalyst.

To investigate the dispersion of the Co–Mo–S phases, the FT-IR experiments by analyzing the adsorption of NO on the sulfided catalysts were carried out. NO is the one of the most frequently used molecules to characterize HDS catalysts [27,28]. Fig. 3 shows the IR spectra of NO adsorbed on the sulfided catalysts. Compared with the conventional CoMoP/Al_2O_3 catalyst, C-606A shows a strong intensity of the Co-associated symmetric NO vibration (1840 cm^{-1}) but shows a very weak intensity of the Mo-associated symmetric NO vibration (1700 cm^{-1}). This indicates that the edges of MoS_2 on C-606A are likely to be occupied to a great extent by the Co–Mo–S phases.

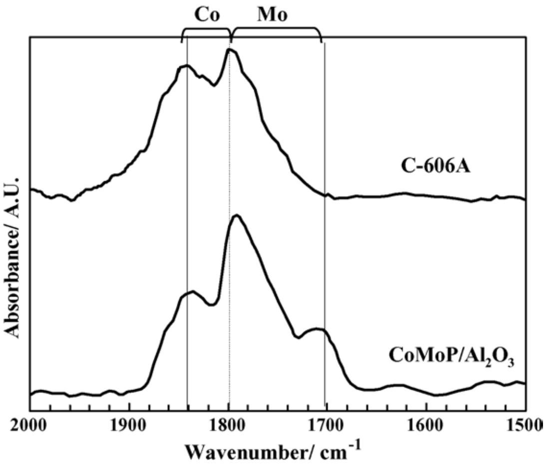

Fig. 3. FT-IR spectra of NO adsorbed on sulfided catalysts.

Our new catalyst preparation method leads to an increased number of the Co–Mo–S phases and provide more highly active Co–Mo–S Type II, which is located at the edges of the MoS_2 multi-layers.

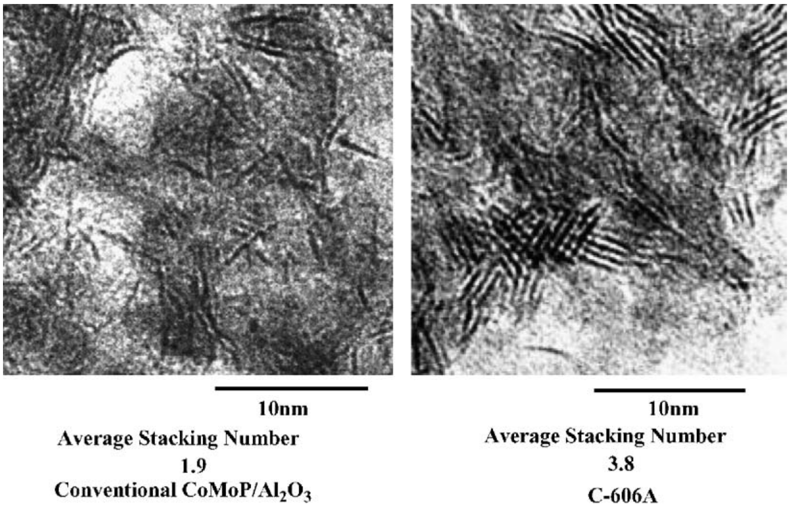

Fig. 2. High resolution TEM micrograph of the conventional CoMoP/Al_2O_3 and C-606A after sulfidation. Dark lines represent edges of MoS_2.

3.4. Catalyst performance

The activity measurements of C-606A and the conventional $CoMoP/Al_2O_3$ were carried out with the straight-run gas oil feedstock B under the conditions of 1.5 h^{-1} LHSV, 4.9 MPa of H_2, and 200 Nm^3/kl of H_2/oil. Fig. 4A shows that ultra-deep HDS to sulfur content of 10 ppm or below can be easily achieved with the developed catalyst under the same conditions as for the conventional gas oil hydrotreating. The HDS rate constant of C-606A was about three times higher than that of the conventional catalyst. Furthermore, special attention should be paid to that the HDN activity of C-606A is significantly higher than that of the conventional catalyst in Fig. 4B. Several studies of HDN reactions of nitrogen heterocyclic compounds have shown that the major pathway involves (1) hydrogenation of the N-ring, (2) scission of C–N bond, forming an amine intermediate, and (3) hydrogenolysis of the amine to hydrocarbons and ammonia [1,29]. That is to say, the reaction pathway proceeding by hydrogenation and scission of C–N bond is much more important than direct N abstraction.

In order to achieve ultra-deep HDS, it is necessary to effectively remove refractory sulfur containing compounds such as 4,6-DMDBT. The retarding effect of methyl substituents on the 4- and 6-position of DBT on the HDS rates should be ascribed to the steric hindrance in the C–S scission of DBTs adsorbed on the HDS active sites [30] or the direct steric hindrance of DBTs adsorption on the HDS active sites [31]. In this respect, the ultra-deep HDS reaction pathway is very similar to the HDN reaction pathway, where pre-hydrogenation precedes hydrogenolysis reaction. Because C-606A indicates the excellent HDS and HDN activities, it is assumed that C-606A not only has the active sites for the direct HDS but also has the pre-hydrogenation active sites for alleviating steric hindrance of refractory sulfur containing compounds.

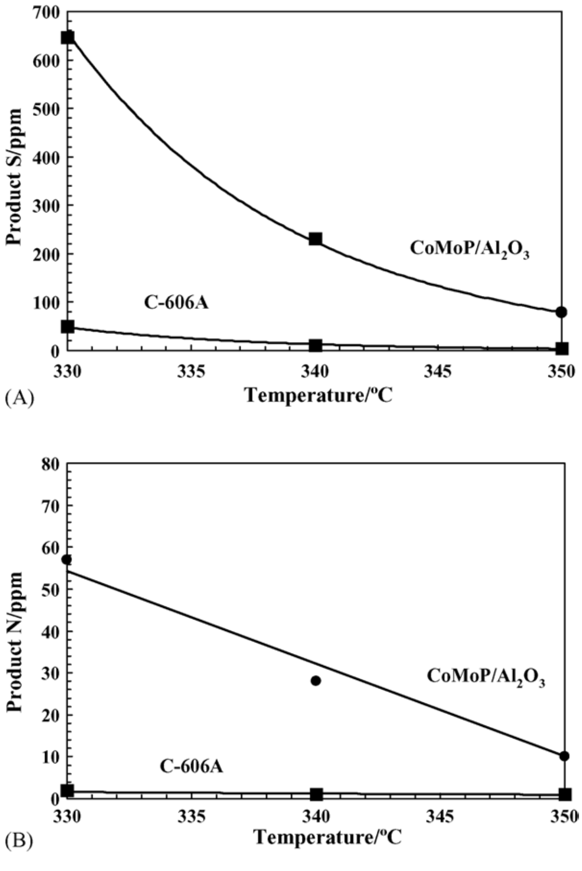

Fig. 4. Relationship between reaction temperature and (A) sulfur and (B) nitrogen in product over the conventional $CoMoP/Al_2O_3$ and C-606A.

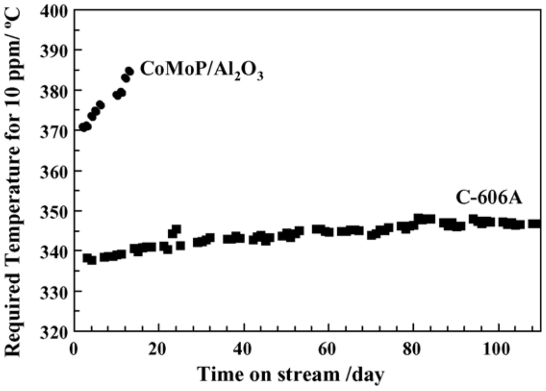

Fig. 5. Temperature required to maintain 10 ppm sulfur in product using the conventional $CoMoP/Al_2O_3$ and C-606A for HDS of SRLGO.

The long-term stability test of ultra-deep HDS of C-606A was carried out with SRLGO feedstock C under the conditions of 1.3 h^{-1} LHSV, 4.9 MPa of H_2, and 200 Nm^3/kl of H_2/oil. The results obtained with C-606A in a 100-day test are shown in Fig. 5. The ordinate shows the temperature required for maintaining 10-ppm sulfur in the product. Notice that the required temperature for 10-ppm sulfur of C-606A is about 30 °C more active than that of the conventional $CoMoP/Al_2O_3$ catalyst.

C-606A enabled the HDS of the diesel fuel to a high degree and produces no significant deactivation. On the other hand, the higher reaction temperature required for 10-ppm sulfur on the conventional $CoMoP/Al_2O_3$ resulted in rapid catalytic deactivation.

Based on these results, C-606A could industrially produce ULSD (<10-ppm sulfur) fuels without modifying the existing industrial diesel hydrotreater.

3.5. Commercial operation

First application of C-606A in the diesel hydrotreater, which was designed to produce 500-ppm sulfur diesel, was started at the Cosmo Oil Chiba refinery in mid-June 2004 [4]. The feedstocks were SRLGO with sulfur of 0.8–2.0 mass%, FCC light cycle oil contents of 0–20 vol.% and DDS light gas oil contents of 0–20 vol.%. After 5 months, operation to produce diesel with maximum 50-ppm sulfur of this hydrotreater has produced diesel with maximum 10-ppm sulfur. The normalized WABT for 50- and 10-ppm sulfur in the product are presented in Fig. 6. This hydrotreater has now been in operation for about 1 year, showing no significant catalyst

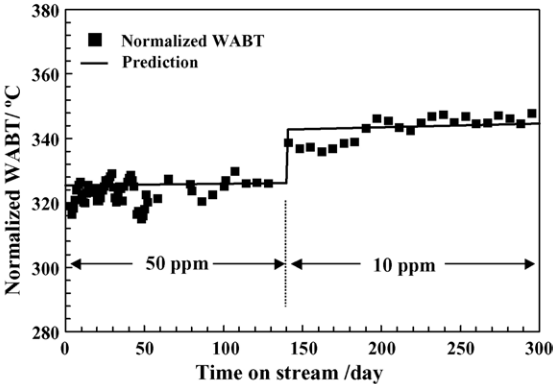

Fig. 6. Commercial operation with C-606A for production of <50-ppm sulfur and <10-ppm sulfur diesel fuels in the hydrotreater at Cosmo Oil Chiba refinery.

deactivation. This commercial operation directly demonstrates the excellent activity and stability of C-606A under industrial operating conditions. Based on the technical and economical advantages, Cosmo Oil Co., Ltd., has utilized C-606A in other diesel hydrotreaters and kerosene hydrotreaters at the Cosmo Oil refineries. High catalyst performance has been demonstrated for each application.

4. Conclusions

The main conclusions of new highly active CoMo/HY-Al_2O_3 catalyst containing a phosphate and citric acid are as follows:

1. In a new preparation method which involves impregnation of the support with a solution containing $CoCO_3$, MoO_3, citric acid, and phosphoric acid and drying (without calcination), we have successfully developed a high activity HDS catalyst, C-606A.
2. TEM measurements showed that C-606A has multiple, more than two, layers of MoS_2 slabs.
3. FT-IR measurements of adsorbed NO indicated that the edges of MoS_2 on C-606A were entirely occupied by the Co–Mo–S phase.
4. Long-term stability tests on straight-run light gas oils demonstrated the excellent stability of C-606A.
5. Commercial operations have demonstrated the high HDS activity and stability of C-606A.
6. C-606A has a super high HDS activity, which achieves <10-ppm sulfur content in products using hydrotreaters designed to produce 500-ppm sulfur content diesel fuels without major reconstruction or other investment.

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