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Two stage upgrading of middle and heavy distillates over newly prepared catalysts

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Abstract

Two kinds of catalysts, designed and prepared based on fundamental research, showed superior catalytic activities in the first-stage and second-stage upgrading of unconventional middle and heavy distillates, resulting in considerable improvements in overall activity (hydrogenation, HDN, HDS and hydrocracking) and initial deactivation of two stage upgrading.

Keywords: Middle and heavy distillates; Hydrocracking

1. Introduction

There is a strong need to produce fuels from conventional and synthetic crudes, because fuel consumption is continuously increasing [1]. On the other hand, the regulation for aromatics and hetero atoms in fuels is becoming severe for environment protection [2]. These two trends clearly show that production of clean fuel with less amounts of aromatics and hetero atoms is now required [3–5].

Two stage upgrading of middle and heavy distillates over newly prepared catalysts was investigated in this work. Production of clean fuel from unconventional feedstocks proceeded via two fundamental steps. In the first step aromatics were hydrogenated. Then two types of reactions were carried out in the second step. One is hydrocracking of reduced aromatics for producing lighter fractions. The other is deep hydrogenation for reducing aromatics. Hetero atoms removal was carried out during both first and second steps.

Based on fundamental studies, two kinds of practical catalysts were designed for the first-stage and second-stage upgrading. In order to understand the relationship between the catalysts functions and their properties, each catalyst was evaluated by model test reactions and fully characterized spectroscopically. These were prepared by optimizing the hydrogenation (HY) and hydrocracking (HC) activities of the catalysts.

2. Experimental

Coprocessing oil from CANMET process [6], light cycle oil from FCC process and coal-derived oil from Wandoan coal [7] were used as test feedstocks of the two stage upgrading. Table 1 shows

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Table 1
Characteristics of unconventional feedstocks

		Coprocessing oil	Light cycle oil	Coal liquids
Fraction	< 180°C	2.5%	13.2%	2.5%
	180–250°C	40.6%	45.3%	93.6%
	250–350°C	53.4%	37.2%	3.9%
	> 350°C	3.4%	4.3%	
Hetero atoms	S	20 700 ppm	490 ppm	160 ppm
	N	4040 ppm	68 ppm	5480 ppm

Table 2
Characteristics of catalysts prepared for two stage upgrading

Catalyst	Active metal loading (wt.-%)[a]				Support
	CoO	NiO	MoO_3	WO_3	
Co-Mo/Al	0–6		10–30		Al_2O_3
Ni-Mo/Al		0–6	10–30		Al_2O_3
Ni-W/Al		0–6		16–48	Al_2O_3
Ni-Mo/SiAl		0–3	0–15		$SiO_2 \cdot Al_2O_3$[b]
Ni-Mo/TiAl		0–3	0–15		$TiO_2 \cdot Al_2O_3$[c]
Co-Mo/USY	0–5		10–25		USY-Al_2O_3[d]
Ni-Mo/USY		0–5	10–25		USY-Al_2O_3
Ni-W/USY		0–5		16–40	USY-Al_2O_3
Ni-Mo/ZSM		0–3	0-15		ZSM-5-Al_2O_3[e]
Ni-Mo/Mor		0–3	0–15		Mor-Al_2O_3[f]

[a] The amount of metal loading was calculated as metal oxide.

[b] Double oxides of SiO_2 (50 wt.-%) and Al_2O_3 (50 wt.-%).

[c] Double oxides of TiO_2 (50 wt.-%) and Al_2O_3 (50 wt.-%).

[d] The amount of USY (ultra stable Y zeolite) was varied from 20 to 80 wt.-%, while Al_2O_3 was used as the balance.

[e] A support consisting of ZSM-5 zeolite (60 wt.-%) and Al_2O_3 (40 wt.-%) was prepared.

[f] A support consisting of mordenite (60 wt.-%) and Al_2O_3 (40 wt.-%) was prepared.

typical characteristics of middle and heavy distillates of the unconventional feedstocks. These distillates contain larger amounts of aromatics and nitrogen-containing compounds as compared to conventional petroleum distillates.

Various kinds of catalysts were prepared by impregnation. The active metal combinations selected were Ni-Mo, Co-Mo and Ni-W with various active metal loadings. Alumina, titania, silica, zirconia and double oxides such as $SiO_2 \cdot Al_2O_3$ and $TiO_2 \cdot Al_2O_3$ were prepared as supports of the catalysts for the first-stage upgrading. USY (Ultra Stable Y) type zeolite was used as the support of the second-stage catalysts. Characteristics of catalysts prepared for the two stage upgrading are summarized in Table 2. All the catalysts were presulfided with 5 vol.-% H_2S and 95 vol.-% H_2 gas for 2 h at 400°C before reaction.

Model test reactions were done using batch type microreactors (50 cm^3) to evaluate catalytic functions (HY, HC, HDS and HDN) of the catalysts prepared (initial H_2 pressure, 6.9 MPa; reaction temperature, 310–400°C; reaction time, 1 h; catalyst, 0.3 g). After selecting catalysts of the first and second-stage upgrading, two stage upgrading of the unconventional feedstocks was carried out over newly prepared catalysts using continuous flow reactors. Fig. 1 shows the flow diagram of the two stage upgrading. Reaction conditions used are as follows: H_2 pressure, 6.9–11.8 MPa; reaction temperature, 350–400°C; LHSV, 1–2 h^{-1}; H_2/oil, 1000 Nl/l. Reaction products were analyzed using gas chromatography and mass spectrometry. Liquid products were also analyzed by an elemental analyzer (C,H,N, Yanagimoto MT-03; N, S, Mitsubishi chemicals TN-02). Simulated distillation was carried out according to

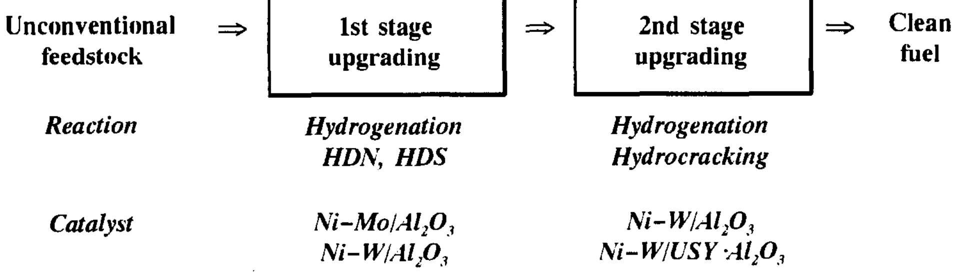

Fig. 1. Flow sheet of two stage upgrading of middle and heavy distillates.

ASTM-D2287 by means of gas chromatography. We carried out characterization of the catalysts using XPS, XAFS and TEM for designing highly active catalyst.

3. Results and discussion

3.1. Catalyst design and preparation

Model test reactions showed that HY and HC activities of sulfide catalysts were influenced to a large extent by types of supports. Since each support possesses a different physical or chemical property, the interaction between active metal and support might be distinct on each support. In fact, XAFS and TEM measurements showed separate local structures and dispersions of active metals on various supports. Concerning the HY, HDS and HDN activities of the catalysts, the catalysts supported on Al_2O_3 were more active than those based on other oxides, double oxides and Y-type zeolite. This is mainly due to a large surface area and proper acidity of Al_2O_3 support as compared to other supports. Although SiO_2 support possesses larger surface area than Al_2O_3 support, less interaction between support and active metal tends to lead more sintering of active metal on the catalyst, resulting in lower HY activity [8]. In the case of TiO_2 and ZrO_2 supports, proper control of physical properties such as pore volume and surface area to meet practical requirement was difficult, while there still remains further possibilities for improving physical properties of these supports.

The order of HY activity of the catalysts was Ni-W > Ni-Mo > > Co-Mo. Measurements of XPS, XAFS and TEM revealed that sulfiding behavior of W on Ni-W catalysts was quite different from that of Mo on Ni-Mo catalysts. Ni-W catalysts showed the highest HY activity at less sulfiding of W, while the highest HY activity of Ni-Mo catalysts was obtained at more sulfiding of Mo. In fact HY activities of Ni-W catalysts decreased rapidly when sulfur-containing compounds were added into the feed, indicating that the choice of catalyst in the first-stage upgrading depends on the concentration of sulfur in feedstock. The correlation between the HY activity and catalytic structure was investigated using the model test reactions and the spectroscopic techniques. Physical and chemical properties of Al_2O_3 were optimized to give most effective HY active sites [9]. Then the optimization of active metal loadings was carried out [10]. Two kinds of catalysts (4.2 wt.-% NiO-18 wt.-% MoO_3/Al_2O_3 and 4.2 wt.-% NiO-29 wt.-% WO_3/Al_2O_3) were finally prepared as the catalysts for the first stage upgrading. These two kinds of catalysts, designed and prepared based on the fundamental research, showed superior HY and HDN activities and catalytic performance as compared to the reference catalyst which was selected among commercially available catalysts because of the highest catalytic performance (Fig. 2 and Fig. 3).

Since Y-type zeolite gave much higher HC activity of hydrogenated aromatic rings than other zeolites and double oxides, catalysts based on Y-type zeolite were selected for the second-stage upgrading. Dealuminated USY-type zeolite was applied to prepare a support consisting of USY and Al_2O_3, because the Y-type zeolite must be stable during upgrading reaction. Ni-W/zeolite catalysts were more active than Ni-Mo/zeolite

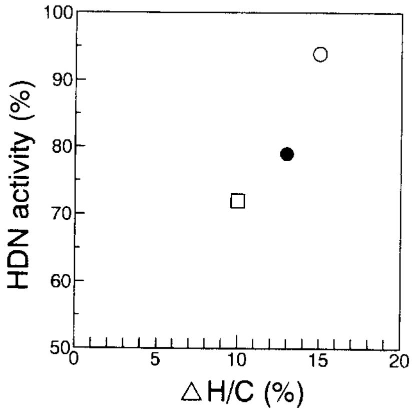

Fig. 2. Hydrogenation and hydrodenitrogenation activities of Ni-W and Ni-Mo catalysts for the first-stage upgrading. ○, Ni-W/ Al_2O_3 catalyst; ●, Ni-Mo/Al_2O_3 catalyst; □, a reference catalyst. 4.2 wt.-% NiO-29 wt.-% WO_3/Al_2O_3 catalyst, 4.2 wt.-% NiO-18 wt.-% MoO_3/Al_2O_3 catalyst and a reference catalysts were tested for upgrading of coal-derived liquids. Reaction conditions are as follows: H_2 pressure, 6.9 MPa; reaction temperature, 380°C; LHSV, $2h^{-1}$; H_2/oil, 1000 Nl/l.

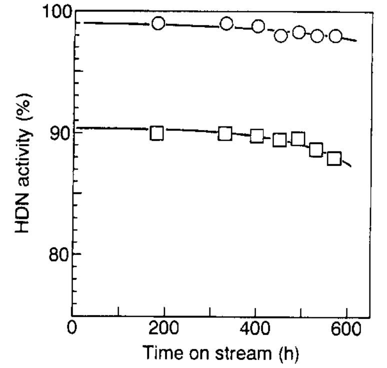

Fig. 3. Short-time life test of the Ni-W catalyst used for the first-stage upgrading. ○, Ni-W/ Al_2O_3 catalyst; □, a reference catalyst. 4.2 wt.-% NiO-29 wt.-% WO_3/Al_2O_3 catalyst and a reference catalysts were used for upgrading of coal-derived liquids. Reaction conditions are as follows: H_2 pressure, 11.8 MPa; reaction temperature, 370°C; LHSV, 2 h^{-1}; H_2/oil, 1000 Nl/l.

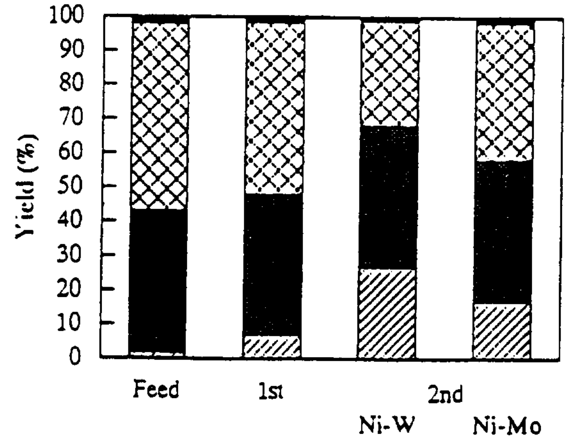

Fig. 4. Hydrocracking activities of Ni-W and Ni-Mo zeolite catalysts in the second-stage upgrading. Shaded, − 180°C; dotted, 180–250°C; double shaded, 250–350°C; filled, + 350°C. 4.2 wt.-% NiO-18 wt.-% MoO_3/Al_2O_3 catalyst was used for the first-stage upgrading of coprocessing oil. Reaction conditions of the first-stage upgrading are as follows: H_2 pressure, 9.8 MPa; reaction temperature, 380°C; LHSV 1.5 h^{-1}; H_2/oil, 1000 Nl/l. 2.8 wt.-% NiO-19 wt.-% WO_3/USY-Al_2O_3 catalyst and 2.8 wt.-% NiO-12 wt.-% MoO_3/USY-Al_2O_3 catalyst were used for the second-stage upgrading. Reaction conditions of the second-stage upgrading are as follows; H_2 pressure, 9.8 MPa; reaction temperature, 280°C; LHSV, 1.5 h^{-1}; H_2/oil, 1000 Nl/l.

catalysts for the second-stage upgrading when high sulfur removal was achieved in the first-stage upgrading (Fig. 4). Research concerning the preparation of well crystallized Y-type zeolite with a high framework Si/Al ratio has been done for developing a highly active catalyst with a long life. The catalyst prepared for the second-stage upgrading was 3.5 wt.-% NiO-24 wt.-% WO_3/USY-Al_2O_3 (60 wt.-% USY and 40 wt.-% Al_2O_3). This catalyst showed higher HC activity and superior catalytic performance as compared to the reference hydrocracking catalyst which was selected among commercially available catalysts (Fig. 5). For reducing aromatics in the feedstocks (deep hydrogenation), the Ni-W/Al_2O_3 catalyst, which was prepared for the first-stage upgrading, was also used for the second-stage upgrading.

3.2. *Two stage upgrading*

Various kinds of middle and heavy distillates obtained from conventional and synthetic crudes were upgraded using the newly prepared catalysts. In a one stage process, insufficient hydrocracking occurred on zeolite supported catalysts [11]. This is because the feedstocks contain larger amounts of polyaromatics which are difficult to hydrocrack. Therefore, the two stage process consisting of hydrogenation and hydrocracking was performed to obtain lighter fractions.

The Ni-Mo/Al_2O_3 catalyst was applied to the first-stage upgrading of the coprocessing oil, because the coprocessing oil contains considerable amounts of sulfur. While the Ni-W/Al_2O_3 catalyst showed higher hydrogenation activity than the Ni-Mo/Al_2O_3 catalyst for the first-stage upgrading of the coal-derived oil with a lower amount of sulfur. Nitrogen content of the first-

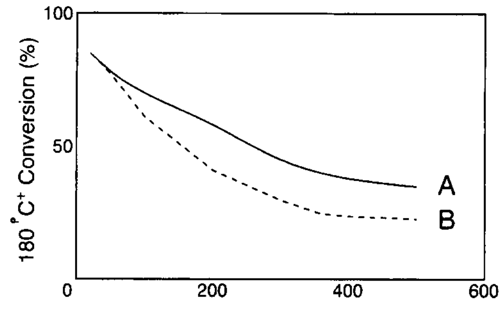

Fig. 5. Accelerated aging test of hydrocracking catalysts. A: Ni-W zeolite catalyst; B: a reference hydrocracking catalyst. 3.5 wt.-% NiO-24 wt.-% WO_3/USY-Al_2O_3 catalyst and a reference catalyst were used for the accelerated aging test. Product obtained after the first-stage upgrading of coal-derived liquids was used as the feed of the second-stage upgrading. Reaction conditions of second-stage upgrading are as follows; H_2 pressure, 6.9 MPa; reaction temperature, 370°C; LHSV, 2 h^{-1}; H_2/oil, 1000 Nl/l.

stage product was minimized for reducing the deactivation of zeolite catalysts used for the second-stage upgrading. When the optimized Ni-Mo/Al_2O_3 (Ni-W/Al_2O_3) and Ni-W/zeolite catalysts were used in the first-stage and second-stage upgrading, respectively, gasoline fractions were efficiently produced from kerosene and gas oil fractions of the light cycle oil and coprocessing oil (Fig. 6). Yields of gasoline fractions increased with increasing of the reaction temperature of the second-stage hydrocracking.

Two stage hydrogenation was also carried out for reducing aromatics in the feedstocks. In this case the Ni-W/Al_2O_3 catalyst was used for the second stage upgrading, because sulfur was largely removed in the first-stage upgrading. After the two stage hydrogenation of the coprocessing oil, a large improvement was observed in the cetane index of reaction products as shown in Table 3.

The cetane improvement, however, remained modest for the two stage hydrogenation of the light cycle oil as compared to the two stage hydrogenation of the coprocessing oil. The two stage hydrogenation of the coal-derived oil showed insufficient cetane improvement. These different behaviors in cetane improvement are mainly due to differences in aromatics and hetero atoms in the feedstocks. The light cycle oil and coal-derived oil contain larger amounts of aromatics than the coprocessing oil. When comparing the coal-derived oil with the light cycle oil, the former contains larger amounts of hetero atoms than the latter as shown in Table 1. These results indicate that hydrocracking of hydrogenated aromatic rings (ring opening) is necessary for additional cetane improvement of the light cycle oil and coal-derived oil.

Table 3
Cetane improvement of reaction products after two stage upgrading of unconventional feedstocks

	Feed	1st stage	2nd stage
Coprocessing oil	36	51	53
Light cycle oil	30	37	43
Coal-derived oil	13	25	31

Reaction conditions of the first-stage and second-stage upgrading are the same as described in Fig. 6.

Sulfur and nitrogen in the feedstocks were reduced to a great extent during the two stage upgrading. Fig. 7 shows hydrogenation and hydrodesulfurization in the two stage upgrading of the light cycle oil and coprocessing oil. Sulfur concentrations decreased from 490 ppm to a few ppm and from 2 wt.-% to 20 ppm after the second-stage hydrocracking of the light cycle oil and the second-stage hydrogenation of the coprocessing oil, respectively. Tri- and di-aromatics were easily hydrogenated followed by aromatic saturation of mono-aromatics. Hydrogenation and hydrocracking behaviors of naphthalene in feedstock during upgrading of light cycle oil are summarized in

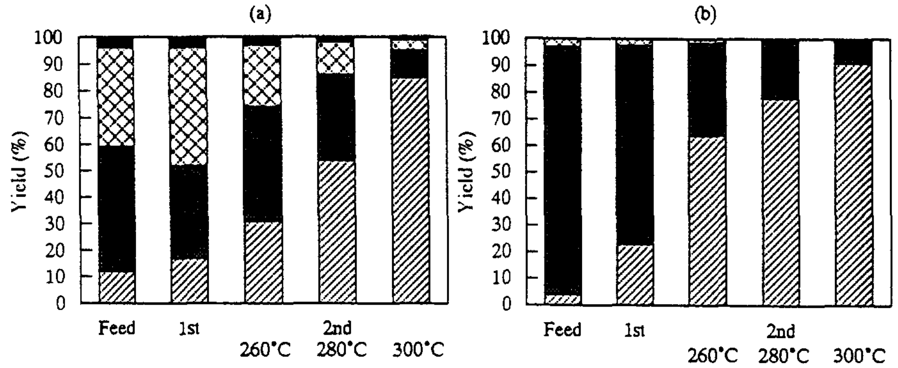

Fig. 6. Two stage upgrading of unconventional feedstocks over newly prepared catalysts: (a) light cycle oil, (b) coprocessing oil. Shaded, – 180°C; dotted, 180-250°C; double shaded, 250-350°C; filled, +350°C. 4.2 wt.-% NiO-18 wt.-% MoO_3/Al_2O_3 catalyst and 3.5 wt.-% NiO-24 wt.-% WO_3/USY-Al_2O_3 catalyst were used for first and second-stage upgrading, respectively. Reaction conditions are as follows: first-stage upgrading; H_2 pressure, 6.9–11.8 MPa; reaction temperature, 330–380°C; LHSV, 1–2 h^{-1}; H_2/oil, 1000 Nl/l; Second-stage upgrading; H_2 pressure, 6.9–11.8 MPa; reaction temperature, 260–300°C; LHSV, 1–2 h^{-1}; H_2/oil, 1000 Nl/l.

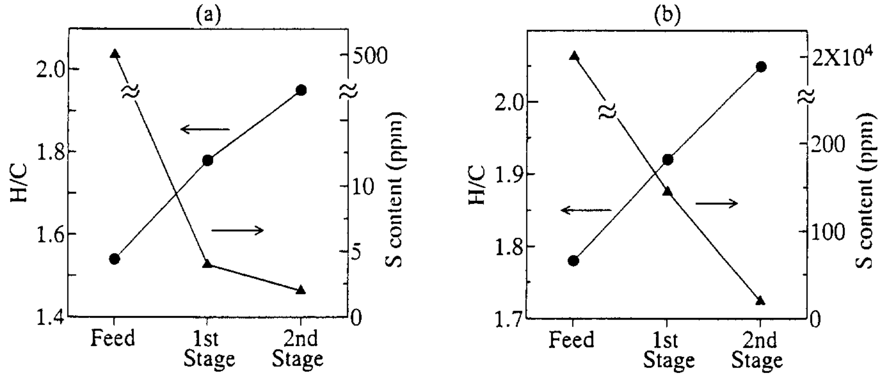

Fig. 7. Hydrogenation and hydrodesulfurization of unconventional feedstocks. (a) Light cycle oil, (b) Coprocessing oil. 4.2 wt.-% NiO-18 wt.-% MoO_3/Al_2O_3 catalyst was used for the first-stage upgrading. 3.5 wt.-% NiO-24 wt.-% WO_3/USY-Al_2O_3 catalyst and 4.2 wt.-% NiO-29 wt.-% WO_3/Al_2O_3 catalyst were used for the second-stage upgrading of light cycle oil and coprocessing oil, respectively. Reaction conditions of the first stage upgrading are as follows: H_2 pressure, 9.8–11.8 MPa; reaction temperature, 350–380°C; LHSV, 1–2 h^{-1}; H_2/oil, 1000 N*l*/*l*. While reaction conditions of second-stage upgrading are as follows; H_2 pressure, 9.8–11.8 MPa; reaction temperature, 260–300°C (hydrocracking), 350–380°C (hydrogenation); LHSV, 1–2 h^{-1}; H_2/oil, 1000 N*l*/*l*.

Table 4
Hydrogenation and hydrocracking behavior of naphthalenes in feedstock during upgrading of light cycle oil

	Naphthalene (wt.-%)	Tetralin (wt.-%)	Decalin (wt.-%)	Total[a] (wt.-%)
Feedstock	93	7	0	2.5
1st-stage upgrading[b]	2	74	24	1.9
2nd-stage hydrocracking[c]	1	53	46	0.9
2nd-stage hydrogenation[d]	0.6	20	79	1.7

[a] Total concentration of naphthalene, tetralin and decalin.
[b] Product obtained after the first-stage upgrading.
[c] Product obtained after the second-stage hydrocracking.
[d] Product obtained after the second-stage hydrogenation.
Reaction conditions of the first-stage and second-stage upgrading are the same as described in Fig. 6.

Table 4. Most of naphthalene was converted to tetralin and decalin during the first-stage upgrading. After the second-stage hydrocracking total concentration of naphthalene, tetralin and decalin was decreased from 2.5 wt.-% to 0.9 wt.-% mainly due to the ring opening reaction over the hydrocracking catalyst. In the case of the two stage hydrogenation most of naphthalene was reduced to decalin, indicating deep aromatic saturation.

Clean fuels with less amounts of aromatics and hetero atoms were successfully obtained after the two stage upgrading. These two stage processes and newly prepared catalysts mentioned above gave considerable improvements in overall activity (aromatic saturation, HDS, HDN and hydrocracking) and initial deactivation as compared to conventional process and commercially available catalysts.

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