Available online at www.sciencedirect.com

SCIENCE DIRECT®

Catalysis Today 104 (2005) 64–69

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Selective hydrodesulfurization of FCC gasoline over $CoMo/Al_2O_3$ sulfide catalyst

Makoto Toba *, Yasuo Miki, Yukio Kanda, Takashi Matsui,
Masaru Harada, Yuji Yoshimura

National Institute of Advanced Industrial Science and Technology, Tsukuba Central-5,
1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

Abstract

In order to achieve selective hydrodesulfurization (HDS) of fluid catalytic cracked (FCC) gasoline for producing $S < 10$ ppm sulfur-free gasoline, we developed $CoMoP/Al_2O_3$ catalysts by using a special ligand and examined their catalytic performances. The developed $CoMoP/Al_2O_3$ catalyst showed higher HDS activity and more depressed olefin hydrogenation than commercial catalyst. The HDS selectivity of the developed catalysts depended on their sulfidation conditions. From the results of NO pulse adsorption and FT-IR of adsorbed NO, the organic residues derived from a ligand have influence on the formation of catalytically active sites such as coordinatively unsaturated molybdenum sites (Mo CUS) and seem to result in the differences of catalytic performance between developed and commercial catalysts.

Keywords: Hydrodesulfurization; FCC; Sulfide catalyst; Cobalt; Molybdenum

1. Introduction

The demand to reduce exhaust emissions requires high specifications for gasoline. Many refiners in Japan already meet the 50 ppm sulfur specification and some already meet the 30 ppm specification. However, Japanese regulation of gasoline sulfur will drop to 10 ppm in 2008. In order to meet the new regulation, it is necessary to develop the new technology for producing $S < 10$ ppm sulfur-free gasoline. FCC gasoline is one of the major components of motor gasoline. It contains high level of sulfur derived from heavy gas oil and atmospheric residue used as FCC raw materials. More than 90% of sulfur in gasoline blendstocks derives from FCC gasoline. Reduction of sulfur content in FCC gasoline is the most effective for sulfur-free gasoline production. FCC gasoline also contains valuable olefins which contribute to the octane number of the motor gasoline. Octane-boosting olefins in the FCC gasoline are often saturated during hydrotreating. Therefore, the selective HDS which minimizes octane loss is highly desired to meet the severe limitation of sulfur content [1–3].

It is well known that Co and Ni which coordinate the edge site of MoS_2 (Co(Ni)–Mo–S structure) promote HDS activity of supported molybdenum sulfide catalysts [4]. Strong MoS_2–support interaction suppresses HDS activity (Type-I MoS_2) [4]. According to the proposed olefin hydrogenation active site, olefin hydrogenation occurs at molybdenum coordinatively unsaturated sites (Mo CUS) [5]. These results indicate that effective coordination of promoters (effective formation of Co(Ni)–Mo–S structure and suppression of the number of unpromoted Mo sites) and suppression of Mo–support interaction contribute to HDS selectivity. On the basis of these results, we prepared $Co(Ni)MoP/Al_2O_3$ sulfide using a special ligand which promote formation of Co(Ni)–Mo complexes. In this study, the selective HDS of FCC gasoline over these developed sulfide catalysts was investigated.

2. Experimental

CoMo and NiMo sulfide catalysts were prepared by incipient wetness impregnation of γ-alumina (surface area:

---

* Corresponding author. Tel.: +81 29 861 4741; fax: +81 29 861 4740.
E-mail address: m.toba@aist.go.jp (M. Toba).

0920-5861/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2005.03.027

195 m^2/g) with a mixed solution obtained from molybdenum oxide, cobalt(nickel) carbonate, a phosphate salt and a special ligand. A commercial $CoMoP/Al_2O_3$ catalyst was used for comparison. All catalysts were sulfided in the stream of 5% H_2S/H_2 gas for 3 h before reaction.

The selective HDS of FCC gasoline was carried out in a high-pressure fixed-bed continuous flow reactor. The reaction conditions were hydrogen pressure of 1–2 MPa, reaction temperature of 220–260 °C, liquid hourly space velocity (LHSV) of 4 h^{-1}, and a volume ratio of hydrogen (NTP) to feed of 100.

The hydrocarbon composition and octane number (GC-RON and GC-MON) in feedstock and products were analyzed by using PIONA-GC (Agilent6890N (JIS K2536)-Yokogawa Analytical Systems Co., GPI system). The content of total sulfur was measured by elemental analysis (Mitsubishi Chemicals Co., TS-100V). Sulfur compounds were analyzed by a GC-SCD (Agilent6890-Sievers355).

The HDS, conversion of olefin (HDO) and octane loss (GC-RON loss) were calculated as follows:

$$\mathrm{HDS}(\%) = [(S_{\mathrm{feed}} - S_{\mathrm{product}})/S_{\mathrm{feed}}] \times 100$$

where S_{feed} and S_{product} indicate the amount of sulfur in the feed and products, respectively.

$$\mathrm{HDO}(\%) = [(T_{\mathrm{feed}} - T_{\mathrm{product}})/S_{\mathrm{feed}}] \times 100$$

where T_{feed} and T_{product} indicate the olefin composition determined by PIONA analysis in the feed and products, respectively.

$$\text{GC-RON loss} = \text{GC-RON}_{\mathrm{product}} - \text{GC-RON}_{\mathrm{feed}}$$

where GC-$\mathrm{RON}_{\mathrm{feed}}$ and GC-$\mathrm{RON}_{\mathrm{product}}$ indicate the research octane number calculated by GPI system in the feed and products, respectively.

The amount of NO uptake was determined by nitrogen monoxide (NO) pulse adsorption measurements (Ohkura Riken). The sample was sulfided in a hydrogen sulfide/hydrogen stream (5% H_2S/H_2 (balance)) at 360 °C for 1 h (sulfidation step). After the sulfidation, the sample was reduced in a hydrogen stream for 1 h, followed by purging by helium at the same temperature for 3 min (post-reduction step). After these pretreatments, a NO pulse was injected into the sample several times at 50 °C.

The FT-IR spectra of adsorbed NO were measured by Nexus 670 FT-IR spectrometer (Thermo Electron). Prior to the adsorption experiments, the sample was sulfided in a hydrogen sulfide/hydrogen stream (500 ppm H_2S/H_2 (balance)) for 1 h in situ in the IR cell. After the sulfidation, the sample was reduced in a hydrogen stream for 1 h, followed by purging by helium at the same temperature for 30 min.

Three kinds of FCC gasoline (A (full-range FCC gasoline), B (60 °C+ distillate of A) and C (heavy FCC gasoline supplied from another refinery)) were used here. The properties of them are summarized in Table 1.

Table 1
Properties of FCC gasoline

	A (full-range)	B (60 °C+)	C (heavy)
Density (g/cm^3, 15 °C)	0.733	0.771	0.780
Sulfur (wtppm)	158.9	234.1	61.8
H/C (atom/atom)	1.93	1.83	1.80
Average molecular weight	101.5	111.5	114.6
GC-RON[a]	90.5	88.9	89.5
GC-MON[b]	79.5	78.2	78.6
T_{90} (°C)	165.9	176.6	182.3
Hydrocarbon (vol.%)			
Paraffins (P)	5.5	4.8	4.4
Isoparaffins (I)	37.6	32.4	25.8
Olefins (O)	26.3	19.7	25.5
Naphthenes (N)	9.2	12.4	12.6
Aromatics (A)	21.4	30.8	31.7

[a] GC-RON: research octane number calculated by the result of GC analysis.

[b] GC-MON: motor octane number calculated by the result of GC analysis.

3. Results and discussion

3.1. Effect of catalyst species on properties of product oil

Table 2 shows effect of catalyst species on properties of product oil in the hydrotreatment of FCC gasoline. Both $NiMoP/Al_2O_3$ and $CoMoP/Al_2O_3$ catalysts showed very high HDS activities. $NiMoP/Al_2O_3$ catalyst gave a much higher olefin hydrogenation activity than $CoMoP/Al_2O_3$ catalyst. Corresponding to the olefin hydrogenation activity, the octane loss (GC-RON loss) for $NiMoP/Al_2O_3$ is larger than $CoMoP/Al_2O_3$. This result indicates that $CoMoP/Al_2O_3$ is more suitable for selective hydrogenation of FCC gasoline than $NiMoP/Al_2O_3$.

Table 2
Effect of catalyst species on HDS and olefin hydrogenation

	Feedstock	$NiMoP/Al_2O_3$	$CoMoP/Al_2O_3$
Density (g/cm^3, 15 °C)	0.771	0.766	0.768
Sulfur (wtppm)	234.1	5.6	7.1
HDS (%)	–	97.6	97.0
HDO (%)	–	80.3	37.2
H/C (atom/atom)	1.83	1.87	1.85
Average molecular weight	111.5	112.2	111.5
GC-RON[a]	88.9	85.6	87.1
GC-MON[b]	78.2	75.9	76.9
Hydrocarbon (vol.%)			
Paraffins (P)	4.8	9.6	7.3
Isoparaffins (I)	32.4	41.8	36.9
Olefins (O)	19.7	3.8	12.3
Naphthenes (N)	12.4	14.8	13.4
Aromatics (A)	30.8	30.1	30.1

Reaction conditions: temperature, 240 °C; pressure, 2 MPa; LHSV, 4 h^{-1}; H_2/feed, 100 NL/L; feedstock, FCC gasoline-B.

[a] GC-RON: research octane number calculated by the result of GC analysis.

[b] GC-MON: motor octane number calculated by the result of GC analysis.

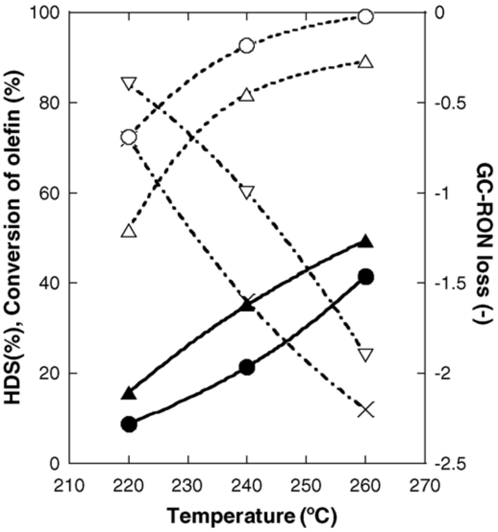

Fig. 1. Effect of hydrogen pressure on HDS and HDO. 1MPa: (○) HDS, (●) HDO, (▽) GC-RON loss; 2MPa: (△) HDS, (▲) HDO, (×) GC-RON loss. Reaction conditions: LHSV, 4 h^{-1}; H_2/feed ratio, 100 NL/L; feedstock, FCC gasoline-B, catalyst, $CoMoP/Al_2O_3$ (3.1 wt.%CoO–12.0 wt.%MoO_3–0.5 wt.%P, sulfidation, 340 °C for 3 h).

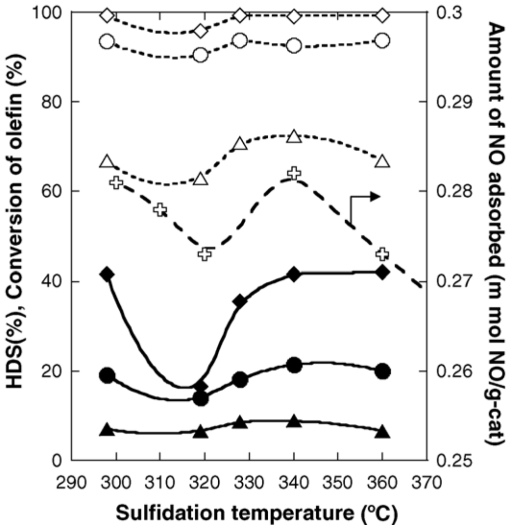

Fig. 2. Effect of sulfidation temperature of catalyst on HDS and HDO. Reaction temperature: 220 °C ((△) HDS, (▲) HDO), 240 °C ((○) HDS, (●) HDO), 260 °C ((◇) HDS, (◆) HDO),(✙) amount of NO adsorbed. Reaction conditions: pressure, 1 MPa; LHSV, 4 h^{-1}; H_2/feed ratio, 100 NL/L; feedstock, FCC gasoline-B, catalyst, $CoMoP/Al_2O_3$ (3.1 wt.%CoO–12.0 wt.%MoO_3–0.5 wt.%P).

3.2. Effect of hydrogen pressure on HDS and HDO

Fig. 1 shows effect of hydrogen pressure on HDS and olefin hydrogenation activity. A higher hydrogen pressure causes higher HDO and lower HDS. At higher hydrogen pressure, acceleration of recombination reaction (addition of H_2S to olefins) seems to be responsible for lower HDS [6]. A lower hydrogen pressure is preferable to achieve deep HDS of FCC gasoline, selectively.

3.3. Effect of sulfidation temperature of catalyst on HDS and HDO

Fig. 2 shows effect of sulfidation temperature of catalyst on HDS, olefin hydrogenation activities and amounts of NO adsorbed. It is noted that olefin hydrogenation activity of the catalyst sulfided at 319 °C is much lower than those of other catalysts, while HDS activity showed almost same level. These results suggest that sulfidation temperature have larger influence on olefin hydrogenation active sites than the HDS active sites. These phenomena appeared more remarkably at higher reaction temperature. According to the proposed olefin hydrogenation active site, olefin hydrogenation occurs at Mo coordinatively unsaturated sites (CUS) [5]. It is well known that NO is a useful selective probe molecule for elucidating the nature of the Mo species present in sulfided hydrotreating catalysts [7–9]. The amount of NO uptake showed the minimum value at 320 °C and decreased in the range of 340–380 °C. The conversion of olefin agrees with the amount of NO uptake in the range of 300–340 °C. Organic residues derived from ligands coordinated molybdenum and cobalt still remain in the catalysts sulfided at lower temperature. These organic residues seem to have influence on the formation of molybdenum sulfide crystalline and Mo CUS located at molybdenum sulfide edge sites. Perhaps, formation of CUS Mo sites of the catalyst sulfided at 319 °C seems to be selectively suppressed by the influence of the organic residues. The decrease in the amount of NO uptake at higher temperature seems to be caused by the aggregation of molybdenum sulfide crystalline.

3.4. Effect of Co/Mo ratio of catalyst on HDS and HDO

As previously described, HDS activity is promoted by formation of Co–Mo–S structure [4] and olefin hydrogenation occurs at Mo CUS [5]. According to these hypotheses, disappearance of Mo CUS by addition of cobalt and formation of Co–Mo–S structure may contribute to HDS selectivity improvement. As shown in Fig. 3, Co/Mo ratio has influence on hydrogenation of olefin especially at higher temperature. Inamura and Prins [10] and Hatanaka et al. [1] also reported that olefin hydrogenation decreases with increasing Co/Mo ratio. They have explained about the phenomena that Co ions block the Mo CUS on the edge of MoS_2. Addition of cobalt contributed to suppression of olefin hydrogenation and retainment of octane value.

3.5. Effect of metal content of catalyst on HDS and HDO

Fig. 4 shows effect of metal content of catalyst on HDS and olefin hydrogenation. The catalyst of middle metal loading showed the highest HDS selectivity less than 80% of HDS. Over 80% of HDS, HDO of lower metal loading catalysts increased remarkably, while HDO of the highest metal loading catalyst increased moderately. It is known that

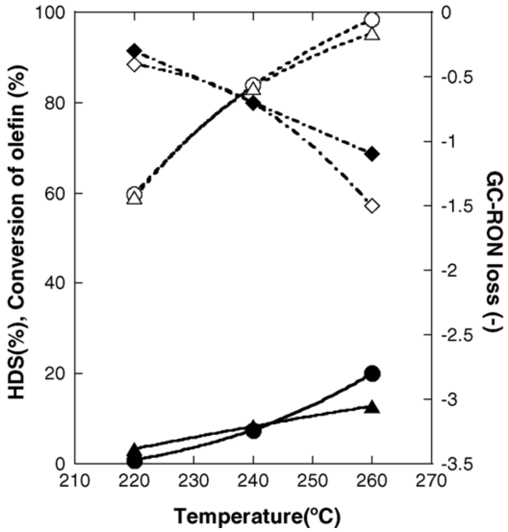

Fig. 3. Effect of Co/Mo ratio of catalyst on HDS and HDO. Co/Mo = 0.5: (○) HDS, (●) HDO, (◇) GC-RON loss; Co/Mo = 0.62: (△) HDS, (▲) HDO, (◆) GC-RON loss. Reaction conditions: pressure, 1 MPa; LHSV, 4 h^{-1}; H_2/feed ratio, 100 NL/L; feedstock, FCC gasoline-C, catalyst, CoMoP/Al_2O_3 (12.0 wt.%MoO_3–0.5 wt.%P, sulfidation, 320 °C for 3 h).

olefins are adsorbed by metal ions in the metal oxide through π coordination [11]. Choi et al. indicated that interfacial sites (support hydroxyl groups H-bonded with molybdenum sulfide phases) appeared to play an important role in olefin hydrogenation [12]. These results suggest that the adsorption of olefin to the surface of support promotes olefin hydrogenation. One of the reasons of the suppression of olefin hydrogenation over the highest metal loading catalyst may be due to covering the surface of support by molybdenum sulfide phase.

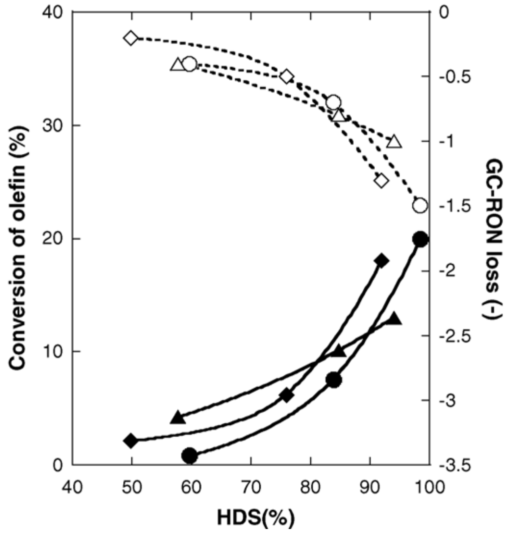

Fig. 4. Effect of metal content of catalyst on HDS and HDO. MoO_3 content (HDO: (◆) 5.9 wt.%, (●) 12.0 wt.%, (▲) 23.6 wt.%; GC-RON loss: (◇) 5.9 wt.%, (○) 12.0 wt.%, (△) 23.6 wt.%). Reaction conditions: pressure, 1 MPa; LHSV, 4 h^{-1}; H_2/feed ratio, 100 NL/L; feedstock, FCC gasoline-C, catalyst, CoMoP/Al_2O_3 (Co/Mo=0.5, P/Mo=*, sulfidation, 320 °C for 3 h).

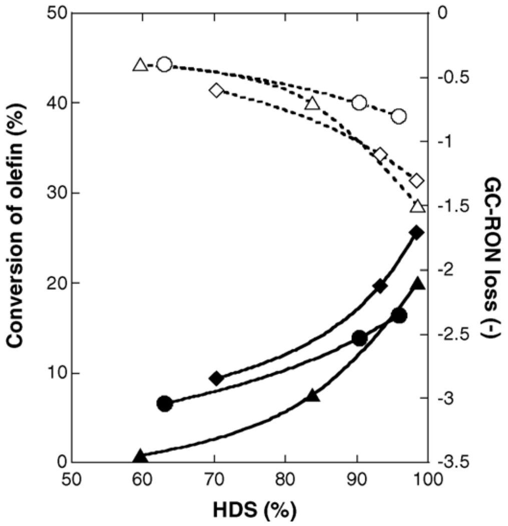

Fig. 5. Effect of feedstock on HDS and HDO. Feedstock (HDO: (◆) FCC gasoline-A, (●) FCC gasoline-B, (▲) FCC gasoline-C; GC-RON loss: (◇) FCC gasoline-A, (○) FCC gasoline-B, (△) FCC gasoline-C). Reaction conditions: pressure, 1 MPa; LHSV, 4 h^{-1}; H_2/feed ratio, 100 NL/L; catalyst, CoMoP/Al_2O_3 (3.1 wt.%CoO–12.0 wt.%MoO_3–0.5 wt.%P, sulfidation, 320 °C for 3 h).

3.6. Effect of feedstock on HDS and HDO

Fig. 5 shows HDS and olefin hydrogenation activity in the hydrotreatment of three kinds of FCC gasoline. Compared with HDO of FCC gasoline-A (full-range), HDO of its heavy fraction (60 °C+: FCC gasoline-B) is lower at the same HDS. This result indicates that removing of light fraction is effective for the suppression of olefin hydrogenation. HDO of FCC gasoline-A and FCC gasoline-C (heavy FCC gasoline supplied from another refinery) increased remarkably over 90% of HDS, while FCC gasoline-B did not show such behavior. These results suggest that HDS and HDO behaviors of FCC gasoline depend on compositions of hydrocarbons derived from raw materials and reaction conditions of fluid catalytic cracking.

3.7. Relationship between HDS, HDO performances and active sites

In order to clarify the feature of catalyst properties, we compared catalytic performances and NO adsorption profiles of developed CoMoP/Al_2O_3 catalyst with those of a conventional commercial CoMoP/Al_2O_3 catalyst. Fig. 6 shows HDS and olefin hydrogenation activity in the hydrotreatment of full-range FCC gasoline (FCC gasoline-A). Olefin hydrogenation activity of developed catalyst is relatively low and GC-RON loss is 0.6–1.3 in the range of 70–98% of HDS. On the other hand, olefin hydrogenation activity of a commercial catalyst remarkably increased over 95% of HDS. The presence of organic residues derived from a ligand, that is, the state of active sites influenced by the organic residues seems to be responsible for such difference in the olefin hydrogenation activity because both catalysts

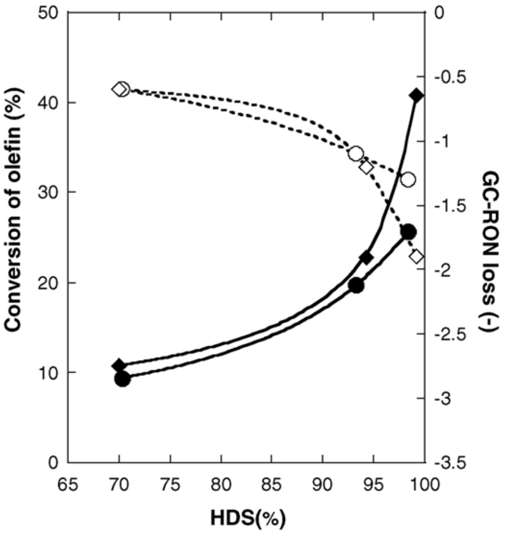

Fig. 6. Catalytic performances of developed and conventional commercial catalysts in the hydrotreating of FCC gasoline. Catalyst: HDO((●) developed, (◆) commercial), GC-RON loss ((○) developed, (◇) commercial). Reaction conditions: pressure, 1 MPa; LHSV, 4 h^{-1}; H_2/feed ratio, 100 NL/L.

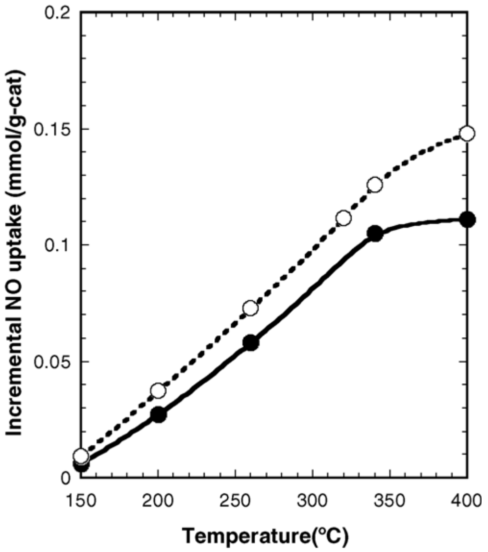

Fig. 7. NO uptakes for the developed and the conventional commercial $CoMoP/Al_2O_3$ catalysts. Catalyst: (●) developed, (○) commercial.

contain phosphorous as an additive and presulfidation conditions of the catalysts are almost same.

Before reaction, $CoMoP/Al_2O_3$ catalyst is usually presulfided by H_2S or sulfur compounds to transform the catalyst to activated sulfide state. It is thought that small amounts of Mo CUS on the edge of MoS_2 form in this step and their amounts were determined by metal content and presulfidation temperature. The amount of NO uptake of presulfided developed and commercial catalysts (V_1) were 0.168 and 0.209 mmol/g_{cat}, respectively. When the presulfided catalyst was reduced under hydrogen atmosphere, NO uptake increased. Fig. 7 shows that incremental NO uptake of reduced $CoMoP/Al_2O_3$ catalyst. The amount of incremental NO uptake (V_2) is calculated as follows: V_2 = total NO uptake (V) − V_1. V_2 increased with increasing reduction temperature. This result means that more Mo coordinatively unsaturated sites were formed by removing sulfur atoms bonded to molybdenum metals. At higher temperature, further increase in NO uptake of developed catalyst is more suppressed than that of commercial one. The relationship between V_1, V_2 and the kinds of active sites of Mo is not clear at present. Perhaps, V_1 and V_2 may correspond to the number of different Mo sites which show the different catalytic functions [13,14]. Compared reaction profiles with and NO uptake of two catalysts, the suppression of V_2 may contribute to the suppression of hydrogenation of olefin.

Fig. 8 shows FT-IR spectra of NO adsorbed on the sulfided and sulfided-reduced $CoMoP/Al_2O_3$ catalysts. The bands around 1700 and 1800 cm^{-1} are assigned to NO adsorbed on Mo and the bands around 1800 and 1860 cm^{-1} are assigned to NO adsorbed on Co [13]. For the commercial

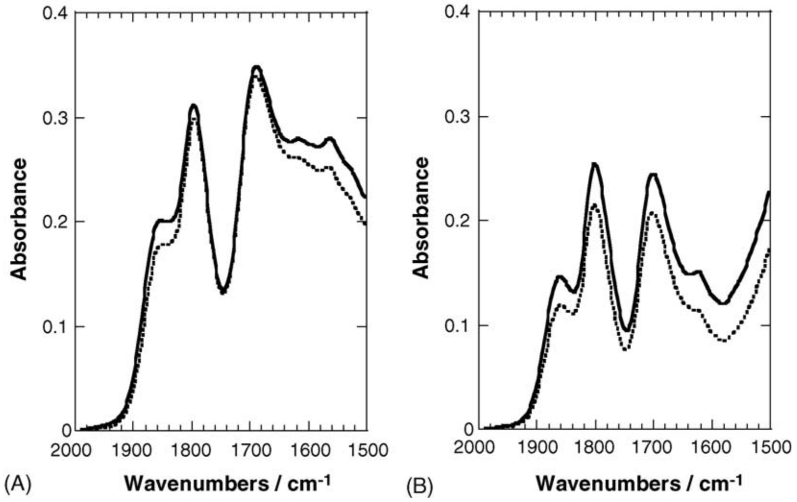

Fig. 8. FT-IR spectra of adsorbed NO on the developed and the conventional commercial $CoMoP/Al_2O_3$ catalysts. Catalyst: (A) developed, (B) commercial.

catalyst, intensities of NO peaks derived from both Co and Mo sites increased by reduction (Fig. 8(B)). In contrast, intensity of NO peaks derived from Co site selectively increased by reduction for developed catalyst (Fig. 8(A)). These results suggest that selective formation of active sites involved Co is effective for selective hydrodesulfurization and that such selective catalyst can bed prepared by using a special ligand.

4. Conclusions

The developed CoMoP/Al_2O_3 catalyst showed high HDS activity and depressed olefin hydrogenation. Addition of cobalt contributed to suppression of olefin hydrogenation and retainment of octane value. The HDS selectivity of the catalyst depended on their sulfidation temperature. Olefin hydrogenation activity of the catalyst sulfided at 319 °C less increased with increasing operating temperature than those of other catalysts. Compared catalytic performances and NO adsorption profiles of developed CoMoP/Al_2O_3 catalyst with those of a conventional commercial CoMoP/Al_2O_3 catalyst, the organic residues derived from a ligand is assumed to have influence on the formation of active Mo coordinatively unsaturated sites.

References

[1] S. Hatanaka, M. Yamada, O. Sadakane, Ind. Eng. Chem. Res. 36 (1997) 5110.

[2] S. Hatanaka, M. Yamada, O. Sadakane, Ind. Eng. Chem. Res. 37 (1998) 1519.

[3] J.S. Rosvoll, K. Grande, K. Moljord, P.A. Skjølsvik, B. Thorvaldsen, S. Johansen, S. Kuhnle, P.Å. Sørum, A.V. Sapre, E.M. Roundtree, Hydrocarbon Process. (2004) 55.

[4] H. Topsøe, B.S. Clausen, F.E. Massoth, Hydrotreating Catalysis, Science and Technology, Springer-Verlag, Berlin, 1996.

[5] K. Tanaka, T. Okuhara, in: H.F. Barry, P.C.H. Mitchell (Eds.), Proceedings of the Third International Conference on Chemicals and Uses of Molybdenum, Climax Molybdenum Company, 1979, p. 170.

[6] K. Hayasaka, E. Morita, S. Hatanaka, in: Proceedings of the Fourth Middle East Refining and Petrochemicals Conference and Exhibition, 2003, p. 16.

[7] N.-Y. Topsøe, H. Topsøe, J. Catal. 84 (1983) 386.

[8] Y. Okamoto, Y. Katoh, Y. Mori, T. Imanaka, S. Teranishi, J. Catal. 70 (1981) 445.

[9] J. Vaylon, W.K. Hall, J. Catal. 84 (1983) 216.

[10] K. Inamura, R. Prins, J. Catal. 147 (1994) 515.

[11] R.L. Burwell Jr., G.L. Haller, K.C. Taylor, J.F. Reed, Adv. Catal. 20 (1969) 1.

[12] J.-S. Choi, F. Maugé, C. Pichon, J. Oliver-Fourcaded, J.C. Jumas, C. Petit-Clair, D. Uzio, Prep. Pap. -Am. Chem. Soc., Div. Fuel Chem. 49 (2004) 570.

[13] Y. Okamoto, A. Maezawa, T. Imanaka, J. Catal. 120 (1989) 29.

[14] S. Kasztelan, A. Wambeke, L. Jalowiecki, J. Grimblot, J.P. Bonnelle, J. Catal. 124 (1990) 12.