

Reactivity of olefins in the hydrodesulfurization of FCC gasoline over CoMo sulfide catalyst

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Available online 21 June 2006

Abstract

To achieve selective hydrodesulfurization (HDS) of fluid catalytic-cracked (FCC) gasoline for producing sulfur-free gasoline ($S < 10$ ppm), the reactivity of various olefins contained in FCC gasoline on CoMoP/Al₂O₃ sulfide catalysts was investigated. Isomerization of the C=C double bond from the terminal position to an internal position was observed. The steric hindrance around the C=C double bond suppresses the reactivity of olefin hydrogenation. The sulfidation temperature of the catalyst has a major influence on olefin hydrogenation active sites. Addition of the appropriate amount of cobalt (Co/Mo ratio approximately 0.6) contributes to the suppression of olefin hydrogenation at high reaction temperature (260 °C). From the comparison of catalytic performance and characterization of our CoMoP/Al₂O₃ catalyst with an analogous commercial catalyst, it is suggested that the hydrogenation of olefins depends not only on the state of the Mo CUS but also on the steric effects of both olefin structure and MoS₂ crystalline structure.

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Keywords: FCC gasoline; Hydrogenation; Olefin; Cobalt molybdenum catalyst; Hydrodesulfurization

1. Introduction

FCC gasoline, which is one of the major components of motor gasoline, contains high levels of sulfur derived from heavy gas oil and atmospheric residues used as FCC feedstock. More than 90% of the sulfur content in gasoline blendstocks derives from FCC gasoline. Reduction of sulfur content in FCC gasoline is the most effective strategy for sulfur-free ($S < 10$ ppm) 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 the hydrotreating reaction. Therefore, selective HDS which minimizes octane loss is highly desired in response to ever-tightening controls on sulfur content [1–3].

To clarify the structure of the active sites responsible for olefin conversion, the hydrogenation of typical olefins in model feedstock containing sulfur compounds has been extensively studied. Stevens and Edmonds showed by using edge-plane-rich and basal-plane-rich MoS₂ that the hydro-

genation of butenes is a highly structure-sensitive reaction [4]. Okamoto et al. reported that HDS selectivity depends on the S/Mo ratio and surface structure of MoS₂ catalyst [5]. Based on the inhibiting effect of H₂S and various olefins, Hatanaka et al. [1] proposed that on the sulfided CoMo/Al₂O₃ catalyst there are three types of active sites for: (1) HDS, (2) *n*-olefin hydrogenation and (3) isoolefin hydrogenation. However, the authors did not mention the structure of the active sites. Choi et al. [6] examined the hydrogenation of 2,3-dimethyl-2-butene and 1-hexene in the presence of 3-methylthiophene over sulfided CoMo/Al₂O₃ with different tin loadings. They proposed that interfacial sites between the sulfide phase and the hydroxyl groups of the support play an important role in olefin hydrogenation. However, the results obtained by these kinds of experiments using a model feedstock do not always adequately represent the real catalytic system. In fact FCC gasoline contains complex mixture of olefins whose reactivity towards hydrogenation might be influenced by the presence of other olefins, hydrocarbons and sulfur compounds.

In this study, the reactivity of various olefins contained in FCC gasoline in selective HDS over CoMo/Al₂O₃ catalyst was investigated to clarify the relationship among reaction conditions, active sites of catalysts and selectivity of HDS.

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2. Experimental

CoMoP/Al₂O₃ sulfide catalysts were prepared by incipient wetness impregnation of γ -alumina (surface area: 195 m²/g) with a mixed solution obtained from molybdenum oxide, cobalt carbonate, a phosphate salt and a special ligand. CoO and MoO₃ contents were 2.3 and 12.0 wt.% (Co/Mo = 0.36 (mol/mol)), 3.1 and 12.0 wt.% (Co/Mo = 0.50 (mol/mol)), 3.9 and 12.0 wt.% (Co/Mo = 0.62 (mol/mol)) and 5.4 and 12.0 wt.% (Co/Mo = 0.85 (mol/mol)), respectively. A commercial CoMoP/Al₂O₃ sulfide catalyst (3.1 wt.%CoO and 12.0 wt.%MoO₃ (Co/Mo = 0.50 (mol/mol))) was used for comparison purpose. All catalysts were sulfided in situ under of 5%H₂S/H₂ flow (200 ml/min) between 298 and 360 °C for 3 h before being used in the reaction.

The selective HDS of FCC gasoline was carried out in a high-pressure fixed-bed continuous-flow reactor as described previously [7]. The products were collected using a liquid–gas separator at –15 °C and atmospheric pressure. The reaction was performed under 1–2 MPa of hydrogen pressure, at 220–260 °C, liquid hourly space velocity (LHSV) 4 h⁻¹, and a volumetric ratio hydrogen (NTP) to feed of 100.

The hydrocarbon compositions of feedstock and products were analyzed using a PIONA-GC (Agilent 6890N (JIS K2536) Yokogawa Analytical Systems Co. GPI system). The total sulfur content was measured by elemental analysis (Mitsubishi Chemicals Co., TS-100V). Sulfur compounds were analyzed using a GC-SCD (Agilent 6890-Sievers 355).

The HDS and conversion of olefin (HDO) were calculated as follows:

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

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

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

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

Three kinds of FCC gasoline were used: (a) full-range FCC gasoline, (b) heavy A (60 °C + distillate of full-range FCC gasoline (a)) and (c) heavy B (heavy FCC gasoline supplied from another refinery). Their properties are summarized in Table 1. High sulfur FCC gasoline was prepared by mixing thiophene ($S = 480.2$ wt. ppm), 2-methylthiophene ($S = 480.2$ wt. ppm) and benzothiophene ($S = 960.4$ wt. ppm) with heavy FCC gasoline (heavy B).

3. Results and discussion

3.1. Composition of olefins contained in FCC gasoline

The distributions of olefins contained in the three kinds of FCC gasoline were determined by GC analysis. C5 (8.6 vol.% in total hydrocarbon) and C6 (6.7 vol.% in total hydrocarbon) olefins are the main components in the full-range FCC gasoline. Most C5 olefins are removed by distillation and C6 (5.9 vol.% (heavy A) and 5.8 vol.% (heavy B) in total hydrocarbons) and

Table 1
Properties of FCC gasoline

	Full range	Heavy A	Heavy B
Density (g/cm ³ , 15 °C)	0.733	0.771	0.780
Sulfur (wt. ppm)	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
T90 (°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.

C7 (7.2 vol.% (heavy A) and 9.1 vol.% (heavy B) in total hydrocarbons) olefins are the main components in the two kinds of heavy FCC gasoline. Table 2 shows in details the composition of the C6 olefin contained in the three kinds of FCC gasoline. Internal olefins prevailed on the terminal ones. The compositions of C5 and C7 olefin compositions are similar to that for C6 olefins. Four kinds of C6 olefins (2-hexene, 3-hexene, 4-methyl-2-pentene and 3-methyl-2-pentene) have *trans* and *cis* isomers. Due to steric effect it is expected that the

Table 2
C6 olefins contained in three kinds of FCC gasoline

Olefin	Composition (% in total acyclic C6 olefins)		
	Full range	Heavy A	Heavy B
Terminal olefins			
RCH=CH ₂	9.9	6.3	7.6
1-Hexene	5.0	4.3	5.2
3-Methyl-1-pentene	2.7	1.2	1.5
4-Methyl-1-pentene	1.8	0.8	0.9
3,3-Dimethyl-1-butene	0.3	0	0
R ¹ R ² C=CH ₂	11.3	8.1	8.5
2-Methyl-1-pentene	8.7	6.8	7.1
2-Ethyl-1-butene	0	0	0
2,3-Dimethyl-1-butene	2.7	1.3	1.4
Internal olefins			
R ¹ CH=CHR ²	40.0	40.9	41.8
<i>trans</i> -2-Hexene	14.6	16.3	16.6
<i>cis</i> -2-Hexene	8.4	9.9	10.0
<i>trans</i> -3-Hexene	7.4	8.0	8.0
<i>cis</i> -3-Hexene	2.6	2.6	2.9
<i>trans</i> -4-Methyl-2-pentene	5.3	3.3	3.3
<i>cis</i> -4-Methyl-2-pentene	1.7	0.9	1.0
R ¹ R ² C=CHR ³	38.8	44.7	42.1
2-Methyl-2-pentene	16.1	17.2	17.5
<i>trans</i> -3-Methyl-2-pentene	13.9	17.7	15.5
<i>cis</i> -3-Methyl-2-pentene	8.8	9.8	9.1
R ¹ R ² C=CR ³ R ⁴	0	0	0
2,3-Dimethyl-2-butene	0	0	0

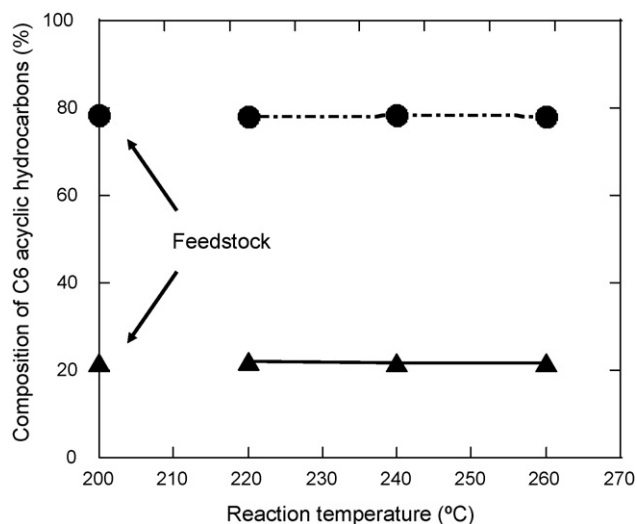


Fig. 1. Effect of temperature on isomerization of carbon skeleton of C6 acyclic hydrocarbons contained in the full-range FCC gasoline: (●) branched C6 acyclic hydrocarbons; (▲) linear C6 acyclic hydrocarbons; catalyst, CoMoP/Al₂O₃ (3.1 wt.%CoO–12.0 wt.%MoO₃ (Co/Mo = 0.50 (mol/mol))); reaction pressure, 1 MPa; feedstock, FCC gasoline (full-range).

reactivity of internal olefin and *trans* isomers is lower than that of terminal olefin and *cis* isomers, respectively. Therefore, it is expected that the olefin composition of FCC gasoline, which is rich in internal olefins and *trans* isomers, improves the selectivity of hydrodesulfurization reaction (selective HDS).

3.2. Reactivity of olefins in the hydrodesulfurization of FCC gasoline

Fig. 1 shows the effect of temperature on the skeletal isomerization of the C6 acyclic hydrocarbons contained in the full-range FCC gasoline. The ratio between linear (the sum of *n*-hexane, 1-hexene, 2-hexene (*trans*, *cis*) and 3-hexene (*trans*, *cis*)) and branched C6 acyclic hydrocarbons did not depend on the reaction temperature and remained almost constant. This result indicates that skeletal isomerization did not occur under this set of reaction conditions. Fig. 2 shows the effect of temperature on the composition of C6 acyclic hydrocarbons contained in full-range FCC gasoline. At 220 °C the percentage of the saturated acyclic hydrocarbons, such as paraffins and isoparaffins, is slightly increased (from 61.7 to 62.5% of the total amount of C6 acyclic hydrocarbon) at 220 °C. This means that the hydrogenation of olefins occurred to a minor extent. At 220 °C, the percentages of terminal olefins are decreased, while the amounts of internal olefins are increased. These results suggest that the C=C double bond is isomerized from the terminal position to an internal position. As in general, the octane value of an internal olefin is higher than that of its corresponding terminal olefin (e.g. 1-hexene: RON = 76.4, *trans*-2-hexene: RON = 92.7, *cis*-2-hexene: RON = 92.7), the isomerization of the C=C double bond from the terminal position to an internal position may contribute to octane-boosting and depression of olefin hydrogenation. Hydrogenation of internal olefins increased with increasing reaction

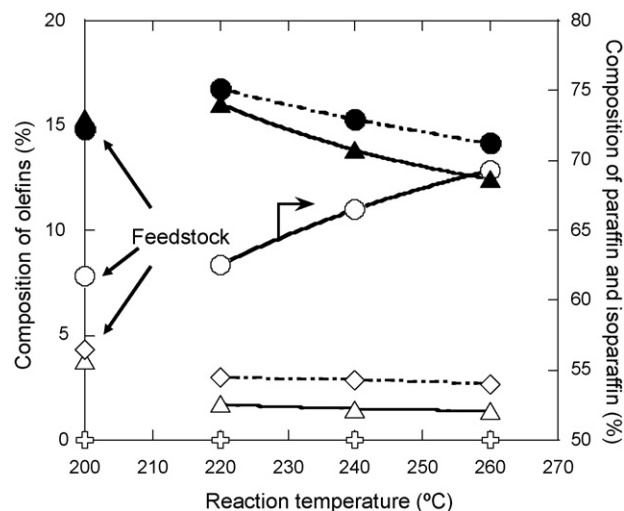


Fig. 2. Effect of temperature on composition of C6 acyclic hydrocarbons contained in the full-range FCC gasoline: (○) paraffins and isoparaffins; (◇) RCH=CH₂ type olefins; (△) R¹R²C=CH₂ type olefins; (●) R¹CH=CHR² type olefins; (▲) R¹R²C=CHR³ type olefins; (□) R¹R²C=CR³R⁴ type olefin; catalyst, CoMoP/Al₂O₃ (3.1 wt.%CoO–12.0 wt.%MoO₃ (Co/Mo = 0.50 (mol/mol))); sulfidation temperature of catalyst, 319 °C; reaction pressure, 1 MPa; feedstock, FCC gasoline (full-range).

temperature, while conversion of terminal olefins remained almost constant in the range of 220–260 °C.

Table 3 shows the effects of olefin structures on their hydrogenation activity in the hydrodesulfurization of full-range FCC gasoline over CoMoP/Al₂O₃ catalyst. The conversion rates of total C6 olefin hydrogenation at 220, 240 and 260 °C are 2.2%, 12.6% and 19.9%, respectively. The conversions of terminal olefins (*x*-methyl-1-pentene) and *cis* olefins are much higher than those of total C6 olefin conversions. ‘Negative conversion’ means formation of less reactive olefins, such as internal and *trans* olefins, from more reactive olefins such as terminal and *cis* olefins through C=C isomerization. The

Table 3

Effect of olefin structures on their hydrogenation activity in the hydrodesulfurization of full-range FCC gasoline

Olefin	Conversion of each temperature (%)		
	220 °C	240 °C	260 °C
<i>x</i> -Methyl-1-pentene			
<i>x</i> = 2	30.4	32.9	37.8
<i>x</i> = 3	58.6	67.1	67.8
<i>x</i> = 4	50.8	60.4	64.4
<i>x</i> = 5 (=1-Hexene)	56.9	58.8	60.7
<i>y</i> -Methyl-2-pentene			
<i>y</i> = 2	–11.9	–0.8	9.0
<i>y</i> = 3 (<i>trans</i>)	–17.2	–7.5	–1.1
<i>y</i> = 3 (<i>cis</i>)	–7.8	–0.3	5.5
<i>y</i> = 4 (<i>trans</i>)	–1.9	16.8	27.9
<i>y</i> = 4 (<i>cis</i>)	19.9	37.4	45.6
<i>z</i> -Hexene			
<i>z</i> = 2 (<i>trans</i>)	–18.4	–2.5	8.0
<i>z</i> = 2 (<i>cis</i>)	7.0	18.8	25.1
<i>z</i> = 3 (<i>trans</i>)	–8.2	4.9	14.4
<i>z</i> = 3 (<i>cis</i>)	25.5	32.7	36.2

conversion of 2-methyl-1-pentene is lower than those of 3-methyl-1-pentene, 4-methyl-1-pentene and 1-hexene. The conversions of 2-methyl-2-pentene and 3-methyl-2-pentenes (*trans*, *cis*) are lower than those of 4-methyl-2-pentenes (*trans*, *cis*). These results indicate that a methyl group bonded to olefinic carbons depresses the reactivity of olefin hydrogenation. The conversions of *trans* isomers are lower than the corresponding *cis* isomers. If the adsorption of a C=C double bond to the active site of the catalyst is inhibited, the hydrogenation of the olefin should be depressed. As previously expected, it is suggested that steric hindrance around C=C double bond influences the reactivity of olefin hydrogenation.

The conversion of olefin versus the HDS conversion in the hydrotreating of full-range FCC gasoline is shown in Fig. 3. The conversion of olefins decreased in the order of $RCH=CH_2 > R^1R^2C=CH_2 > R^1CH=CHR^2 > R^1R^2C=CHR^3$. It is evident that the structure of olefins influences the hydrogenation activity. For HDS conversion above 93%, the conversion of internal olefins abruptly increased. These phenomena suggest that it is possible to depress olefin hydrogenation by steric inhibition of the olefin molecules' approach to the active site on the HDS catalyst.

Table 4 shows the effect of sulfur content of feedstock on C6 olefin conversions contained in heavy FCC gasoline. Except for linear $R^1CH=CHR^2$ type C6 olefins, most C6 olefin conversions increased with increasing sulfur content in the feedstock. Owens and Amberg reported that both thiophene and butene hydrogenation are retarded by H_2S [8]. Hatanaka et al. reported that H_2S retarded the hydrogenation of 1-octene and 1-hexene and accelerated the hydrogenation of 2,4,4-trimethyl-2-pentene [1]. Our results obtained using real FCC gasoline, are different from those obtained with model feedstock. The reason for the

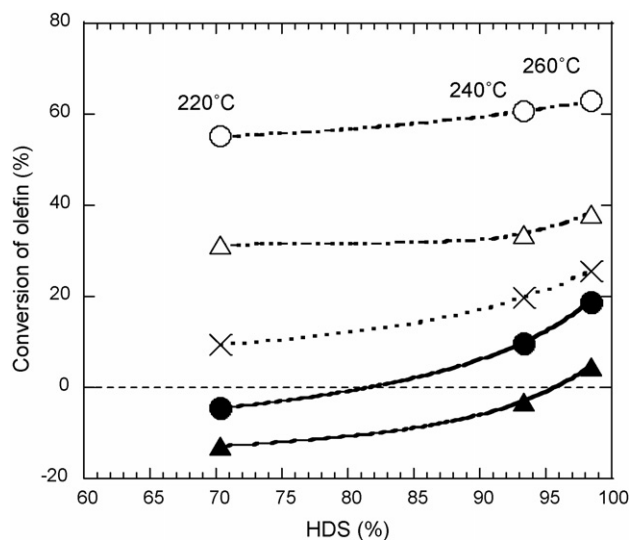


Fig. 3. Selectivity for olefin conversions versus HDS in the hydrotreating of full-range FCC gasoline: (×) total olefin conversion calculated by PIONA analysis; (○) $RCH=CH_2$ type olefins; (△) $R^1R^2C=CH_2$ type olefins; (●) $R^1CH=CHR^2$ type olefins; (▲) $R^1R^2C=CHR^3$ type olefins; catalyst, CoMoP/Al₂O₃ (3.1 wt.%CoO–12.0 wt.%MoO₃ (Co/Mo = 0.50 (mol/mol))); sulfidation temperature of catalyst, 319 °C; reaction temperature, 220–260 °C; reaction pressure, 1 MPa; feedstock, FCC gasoline (full-range).

Table 4

Effect of sulfur contents of feedstock on C6 olefin conversions contained in heavy FCC gasoline at 260 °C

Olefin	Olefin conversion (%)	
	Heavy B (S = 61.8 ppm)	High sulfur heavy FCC gasoline (S = 1982.6 ppm)
Total acyclic C6 olefins	18.9	19.9
Terminal olefins		
$RCH=CH_2$	51.3	54.8
1-Hexene	57.0	59.2
3-Methyl-1-pentene	38.1	44.2
4-Methyl-1-pentene	42.6	48.9
$R^1R^2C=CH_2$	31.3	33.9
2-Methyl-1-pentene	36.5	38.8
2,3-Dimethyl-1-butene	4.8	9.1
Internal olefins		
$R^1CH=CHR^2$	16.3	15.7
<i>trans</i> -2-Hexene	9.7	8.2
<i>cis</i> -2-Hexene	28.5	28.8
<i>trans</i> -3-Hexene	11.4	9.3
<i>cis</i> -3-Hexene	35.0	34.0
<i>trans</i> -4-Methyl-2-pentene	6.9	11.3
<i>cis</i> -4-Methyl-2-pentene	20.4	23.9
$R^1R^2C=CHR^3$	13.1	14.9
2-Methyl-2-pentene	21.8	24.0
<i>trans</i> -3-Methyl-2-pentene	7.0	8.5
<i>cis</i> -3-Methyl-2-pentene	6.8	8.4

inconsistency of results between FCC gasoline and model feedstock is still unclear. It is known that H_2S , which is a product of the HDS reaction of organic sulfur compounds, reacts with olefins and forms thiols (the so-called “recombination reaction”) [1,9]. The concentration of H_2S is thus likely to affect the formation of thiols. The thiols formed are desulfurized and produce saturated hydrocarbons which are the same as the products of olefin hydrogenation. The reactivities of thiol formation from olefins and formed thiol HDS may influence olefin saturation. It is thought that depression of thiol formation is effective not only for deep HDS but also for depression of olefin saturation.

3.3. Relationship between catalyst properties and depression of olefin hydrogenation

Before reaction, a catalyst such as CoMoP/Al₂O₃ is usually presulfided by H_2S or sulfur containing compounds to obtain the activated sulfide form. It has been suggested that olefin hydrogenation occurs at Mo coordinatively unsaturated sites (CUS) [10,11] located at edge sites of the MoS₂ crystalline. This hypothesis suggests that modification of Mo edge sites enables olefin hydrogenation to be depressed.

Fig. 4 shows the effect of the sulfidation temperature of the catalyst on HDS and olefin hydrogenation activities. As previously described, conversion of olefins at 220 °C are mostly caused by C=C bond isomerization. As shown in Fig. 4(A), the isomerization activity was not affected by the sulfidation

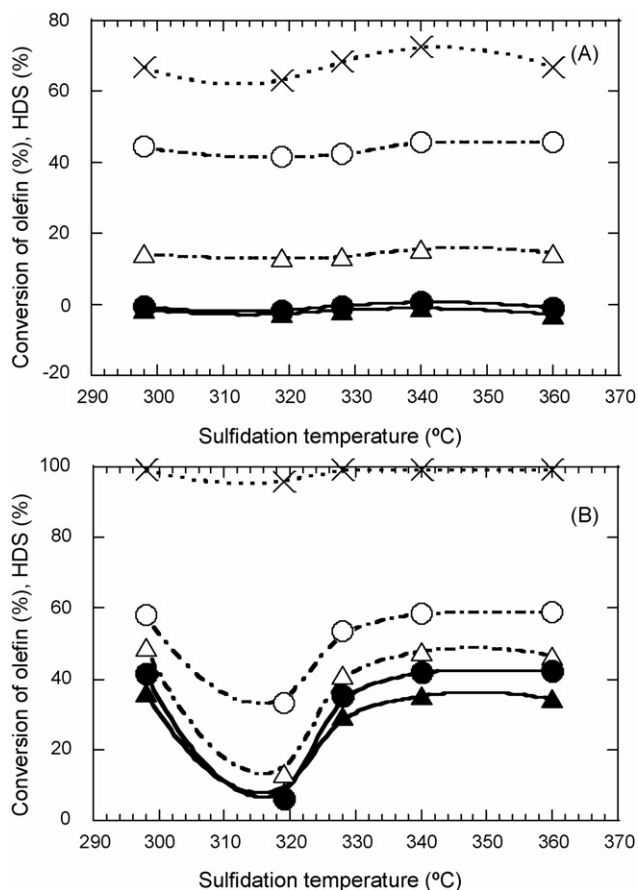


Fig. 4. Effect of sulfidation temperature of catalyst on HDS and olefin hydrogenation activities: (x) HDS; (○) RCH=CH₂ type olefins; (△) R¹R²C=CH₂ type olefins; (●) R¹CH=CHR² type olefins; (▲) R¹R²C=CHR³ type olefins; catalyst, CoMoP/Al₂O₃ (3.1 wt.%CoO–12.0 wt.%MoO₃ (Co/Mo = 0.50 (mol/mol))); reaction temperature: (A) 220 °C, (B) 260 °C; reaction pressure, 1 MPa; feedstock, FCC gasoline (heavy A).

temperature of the catalyst when the HDS reaction was performed at 260 °C. On the other hand, when the HDS reaction was performed at 260 °C, the olefin hydrogenation activity reached minimum when the catalyst was sulfided at 319 °C (Fig. 4(B)). The suppression of olefin hydrogenation activity becomes more marked with increasing reaction temperature. According to the NO adsorption results, the formation of CUS Mo sites of the catalyst sulfided at 319 °C appears to be selectively suppressed by the presence of organic residues [12]. The catalysts used for this experiment were prepared by incipient wetness impregnation of alumina support with a mixed solution containing active metals and an organic ligand. Organic residues derived from the ligand-coordinated molybdenum and cobalt remain on the catalysts sulfided at lower temperatures. In addition, it is thought that Co and Mo could not be sulfided sufficiently at 298 °C because of low temperatures. In the range of 328–360 °C, the organic residues may be eliminated from the active metals. These organic residues appear to play a role in the formation of active sites such as molybdenum sulfide crystalline and Mo CUS at relatively low sulfidation temperatures.

The disappearance of Mo CUS by addition of cobalt and formation of Co–Mo–S structure may contribute to reduce the

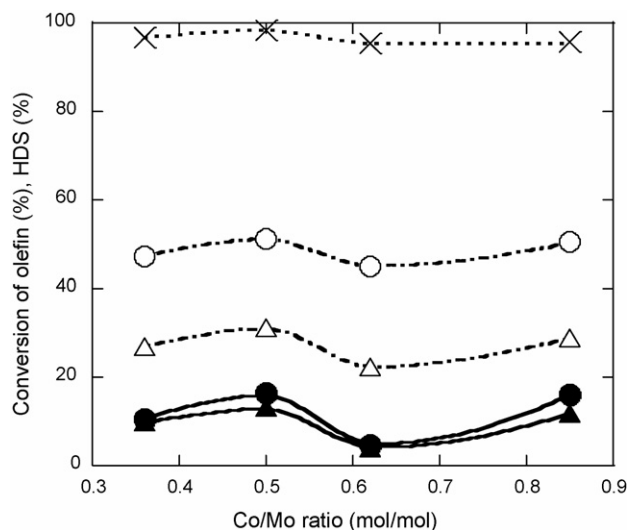


Fig. 5. Effect of Co/Mo ratio of catalyst on hydrogenation of olefin: (x) HDS; (○) RCH=CH₂ type olefins; (△) R¹R²C=CH₂ type olefins; (●) R¹CH=CHR² type olefins; (▲) R¹R²C=CHR³ type olefins; sulfidation temperature of catalyst, 319 °C; reaction temperature, 260 °C; reaction pressure, 1 MPa; feedstock, FCC gasoline (heavy B).

olefin hydrogenation activity leading to highly selective HDS [1,13]. As shown in Fig. 5, Co/Mo ratio influences the hydrogenation of olefins, while no obvious influence on isomerization was observed. Catalyst with low Co/Mo ratio (Co/Mo = 0.36) caused relatively low olefin hydrogenation activity. It is reported that the promotion of MoS₂ by addition of cobalt is related to an increase in the MoS₂ dispersion [14]. Low olefin hydrogenation activity of the catalyst with low Co/Mo ratio seems to result from the low dispersion of MoS₂ crystalline. Catalyst with extremely high Co/Mo ratio (Co/Mo = 0.85) caused high olefin hydrogenation activity. This is most likely due to elimination of cobalt from molybdenum edge sites and the appearance of Mo CUS. These results indicate that addition of cobalt contributes to the suppression of olefin hydrogenation, and that the Co/Mo ratio of the most selective catalyst is approximately 0.6.

To clarify the behavior of active site, we compared the catalytic performances of our CoMoP/Al₂O₃ catalyst with those of a conventional commercial CoMoP/Al₂O₃ catalyst. Fig. 6 shows olefin hydrogenation activity in the hydrotreatment of full-range FCC gasoline over developed and commercial catalysts. The olefin hydrogenation activity of our developed catalyst was relatively low compared with the commercial catalyst. Hydrogenation of R¹CH=CHR² and R¹R²C=CHR³ type olefins over our catalyst was markedly depressed over 95% of HDS. According to TEM analysis, the stacking numbers of MoS₂ crystalline in our catalyst are predominantly 1 or 2 [15]. Due to steric hindrance, it must be difficult for bulky olefins to be adsorbed onto active sites located at edge sites of low-stacked MoS₂ crystalline. In a previous report [12], we described how, on the basis of NO adsorption analyses, these differences are caused by selective formation of active sites involved with Co by using ligands. The results shown in Fig. 6 suggest that hydrogenation of olefins depends on not only on

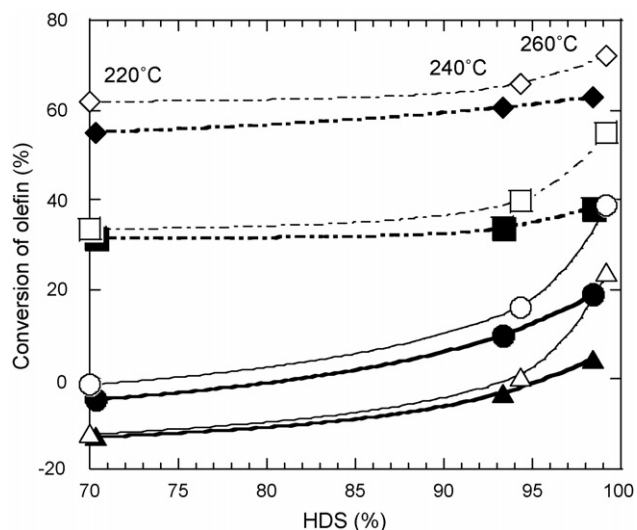


Fig. 6. Olefin hydrogenation activity in the hydrotreatment of full-range FCC gasoline over developed and commercial catalysts developed catalyst: (◆) RCH=CH₂ type olefins; (■) R¹R²C=CH₂ type olefins; (●) R¹CH=CHR² type olefins; (▲) R¹R²C=CHR³ type olefins; commercial catalyst: (◇) RCH=CH₂ type olefins; (□) R¹R²C=CH₂ type olefins; (○) R¹CH=CHR² type olefins; (△) R¹R²C=CHR³ type olefins; catalyst, developed and commercial CoMoP/Al₂O₃ (3.1 wt.%CoO–12.0 wt.%MoO₃ (Co/Mo = 0.50 (mol/mol))); sulfidation temperature of catalyst, 319 °C (developed), 360 °C (commercial); reaction temperature, 220–260 °C; reaction pressure, 1 MPa; feed-stock, FCC gasoline (full-range).

the state of Mo CUS but also on the steric effects caused by both the olefin structure and the structure of the MoS₂ crystalline.

4. Conclusions

In the selective HDS of FCC gasoline over CoMoP/Al₂O₃ catalyst, skeletal isomerization of acyclic hydrocarbon was not observed, whereas isomerization of C=C double bonds from the terminal position to an internal position took place. The shift of C=C double bonds may boost the octane number and reduce the activity in olefin hydrogenation. Methyl groups bonded to olefinic carbons depress the reactivity of olefin hydrogenation. *Trans* olefins are less active than their corresponding *cis* isomers. These results suggest that steric hindrance around C=C double bonds influences the reactivity of olefin hydrogenation. For the HDS conversion above 93%, the hydrogenation activity of internal olefin abruptly increased.

The active sites involved in the isomerization of C=C double bonds were not influenced by the sulfidation temperature of the

catalyst, whereas sulfidation temperature influenced olefin hydrogenation active sites at 260 °C. It appears that the organic residues play a role in the formation of active sites such as molybdenum sulfide crystalline and Mo CUS at relatively low sulfidation temperatures. However, the relationship between sulfidation temperature and the structure of active sites remains unclear. Addition of the correct amount of cobalt contributes to the suppression of olefin hydrogenation; the Co/Mo ratio of the most selective catalyst is approximately 0.6. The comparison of the catalytic performance and characterization of our CoMoP/Al₂O₃ catalyst with those of a conventional commercial CoMoP/Al₂O₃ catalyst suggests that hydrogenation of olefins depends on not only on the state of Mo CUS but also on the steric effects of the structures of both olefins and MoS₂ crystalline. It would thus appear to be possible to depress the olefin hydrogenation by steric inhibition of the olefin molecules that approach the active sites on the HDS catalyst.

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