

# Hydrodesulfurization kinetics and mechanism of 4,6-dimethyldibenzothiophene over NiMo catalyst supported on carbon

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## Abstract

4,6-Dimethyldibenzothiophene (4,6-DMDBT), one of the most refractory sulfur compounds in gas oil, was desulfurized in *n*-decane using NiMo sulfide supported on active carbons (NiMo/C) with a microautoclave installed with a sampling apparatus, to establish the hydrodesulfurization (HDS) kinetics and mechanism. The NiMo/C catalysts exhibited the higher activity for the HDS of 4,6-DMDBT at relatively higher temperatures of 340–380°C than a commercial NiMo/alumina catalyst regardless of the carbon supports. The main route was the direct desulfurization in this temperature range. The main reaction at 300°C was found to be the hydrogenative desulfurization route over the same catalyst, producing 3-(3'-methyl cyclohexyl)toluene. The direct desulfurization was significantly inhibited by the coexisting H<sub>2</sub>S regardless of reaction temperatures, although the hydrogenation route was found to be enhanced by H<sub>2</sub>S to some extent. The present desulfurization network was established by the computation curve fitting through measuring the equilibrium between 4,6-DMDBT and its tetrahydroderivative. © 2000 Elsevier Science B.V. All rights reserved.

**Keywords:** Hydrodesulfurization; Kinetics; 4,6-Dimethyldibenzothiophene (4,6-DMDBT); NiMo/carbon catalyst

## 1. Introduction

Demand for lighter and cleaner fuels to transportation engines and small-scale burner is expanding, while supply of heavier, more contaminated and more aromatic crude is increasing. Sulfur, nitrogen and even aromatic species in the petroleum products are to be deeply re-

moved to protect the environment. Hence, the hydrotreatment of petroleum products should be advanced to achieve the deeper and rapid conversion, milder operational conditions and longer term run at the same time.

The catalytic species for hydrotreating petroleum products have been nickel molybdenum or cobalt molybdenum sulfides for many years and their superior performances have been established. Alumina has been widely applied commercially as an excellent support for such sulfides. Nevertheless, the better catalysts, as well as efficient reaction configurations, have to

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be developed. Better performances of carbon or titania have been reported as supports for the sulfides [1–3]. The higher activity, selectivity and less coke formation provided by such supports are highly appreciated, although the mechanical strength and catalyst life are concerned.

As far as the hydrotreating configuration is concerned, the multi-stage treating has been examined because the hydrogenation and cracking as key steps of the hydrotreating carry their respective optimum conditions. For the second reaction, acidity may play a key role while its coking activity is moderated by the hydrogenation of the substrate prior to the acidic reaction.

In the present study, the catalytic activity of NiMo sulfide supported on carbons was extensively examined in the hydrodesulfurization (HDS) of 4,6-dimethyldibenzothiophene (4,6-DMDBT) to describe its kinetics and mechanism. The characteristics of carbon-supported NiMo catalyst were to be closed up in comparison with a commercial alumina-supported one.

## 2. Experimental

Carbons examined in the present study are listed in Table 1, which summarizes some properties of the carbon black of nanoparticles, granular active carbons of moderate and large surface areas and pitch-based activated carbon fibers (ACF-OG 20A) of large surface areas.

Nickel and molybdenum salts (nickel acetate and MoO<sub>2</sub>-acetylacetonate, respectively) were dissolved in aq. methanol to be impregnated by a simultaneous impregnation method according to a previous paper [4]. After the impregnation, the oxides on the carbon were presulfided at 360°C for 2 h just before the use.

A commercially available Ru/C (NE-Chem. Cat.) was used for the hydrogenation of 4,6-DMDBT after the presulfidation at 360°C for 2 h, to find its hydrogenation equilibrium.

4,6-DMDBT of above 99% purity was synthesized by a modified procedure of Gerdil and Lucken's method [5].

The catalytic reaction was performed in a 50-ml autoclave equipped with a sampling apparatus under hydrogen pressures of 3 to 15 MPa. The stirring was attempted at the maximum rotation around 1500 rpm to achieve better dispersion of the catalyst in the liquid reactant. The reaction time was counted after the temperature reached to the prescribed one.

The liquid products were sampled out and analyzed by GC-FID. The gaseous product was negligibly small under the present conditions.

## 3. Results

### 3.1. Effect of reaction temperatures on the HDS product distribution of 4,6-DMDBT

Figs. 1–3 illustrate the products from 4,6-DMDBT vs. conversion over NiMo/Maxsorb

Table 1  
Elemental analysis and physical properties of carbon supports

Carbon	C	H	N	(O + S)	Ash	Pore size (Å)	Surface area (m <sup>2</sup> /g)
	(wt.%, dry ash-free base)				(wt.%)		
Ketjen Black	99.3	0.3	0.1	0.3	0.6	30	1270
Diahope	94.9	0.5	0.1	4.5	2.4	12.5	1350
BP2000	92.6	0.4	0.1	6.9	1.2	15	1450
Max sorb 3060	89.9	0.6	0.2	9.3	0	9.9	3060
ACF(OG-5A)	89.6	1.1	0.7	8.3	0.3	–	480
ACF(OG-10A)	93.9	0.7	0.3	4.6	0.5	–	1060
ACF(OG-15A)	91.6	0.7	0.4	7.3	Trace	–	1500
ACF(OG-20A)	93.9	0.7	0.3	4.6	0.5	9.0	2150

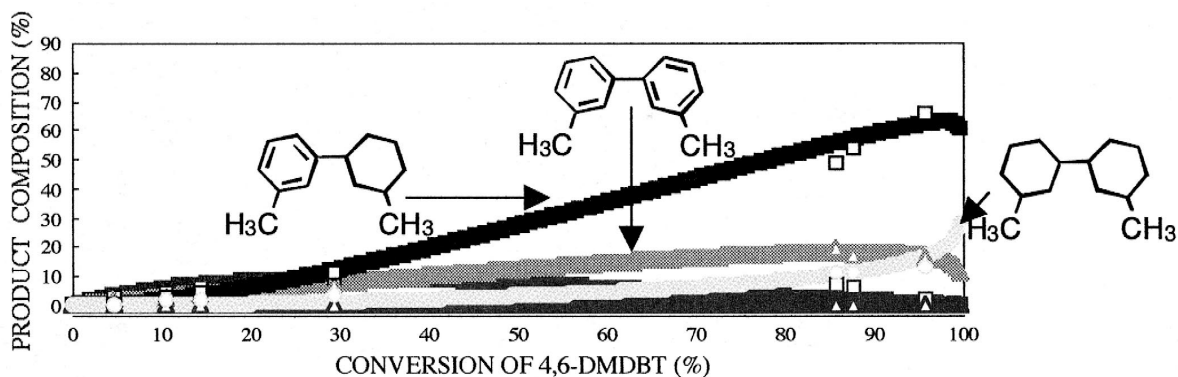


Fig. 1. Product selectivity for hydrodesulfurization of 4,6-DMDBT over NiMo/Max sorb at 300°C.

catalyst at 300°C, 340°C, and 380°C, respectively. At the lowest temperature of 300°C, 3,3'-dimethylbiphenyl (DMBP) was the principal product below 30% of the conversion. The higher conversion above 30% increased rapidly the selectivity of 3-(3'-methylcyclohexyl)toluene (MCHT) to be the principal product, while the selectivity of DMBP stayed at almost the same value. 3,3'-Dimethylbicyclohexyl (DMBCH) increased slowly up to the conversion of 95%, above which its selectivity increased sharply at the sacrifices of both MCHT and DMBP. The selectivity for 1,2,3,4-tetrahydro-4,6-dimethyl-dibenzothiophene (4H-DMDBT) stayed low, although the conversion showed the maximum selectivity of 10% at the conversion of 55%. The major product of MCHT is supposed to be produced through the successive desulfurization

of 4H-DMDBT and the successive hydrogenation of DMBP, although their contribution cannot be determined unless the kinetic analysis is applied.

Higher temperature of 340°C changed the product distribution drastically. DMBP became the major product up to the conversion of 85%, where the MCHT became the major product. The successive hydrogenation of DMDP reduced markedly its selectivity, increasing sharply both MCHT and DMBCH. 4H-DMDBT was found in the products at this temperature, although its largest selectivity was lower than that at 300°.

At 380°C, DMBP was the major product in all the range of the conversion. MCHT was the second major product. Composition of both products increased proportionally with the con-

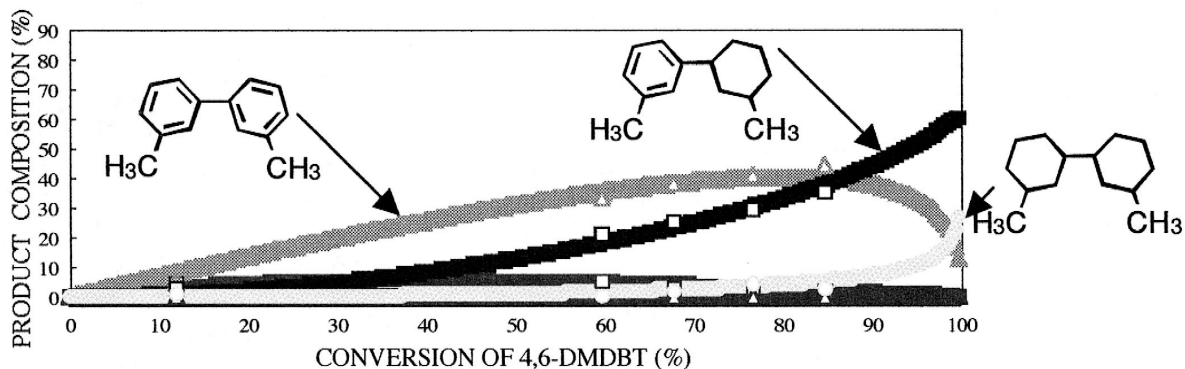


Fig. 2. Product selectivity for hydrodesulfurization of 4,6-DMDBT over NiMo/Max sorb at 340°C.

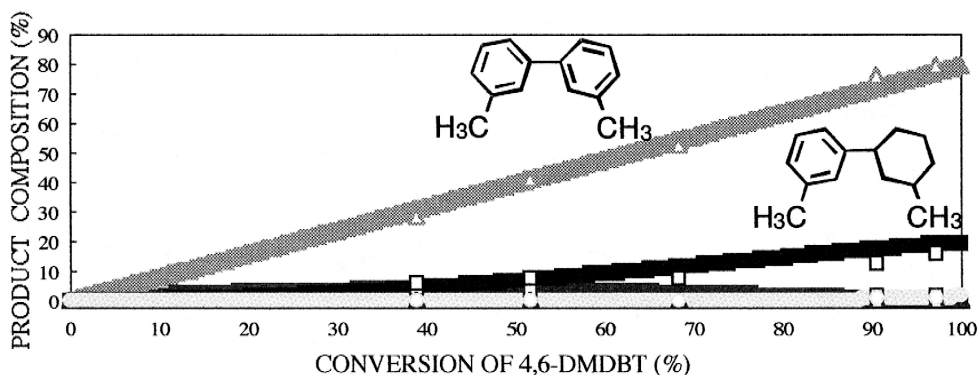


Fig. 3. Product selectivity for hydrodesulfurization of 4,6-DMDBT over NiMo/Max sorb at 380°C.

version. The selectivity of DMBCH was always low. 4H-DMDBT was still observed, although its maximum yield was much lower than those at 300°C and 340°C.

Such product distribution suggests the three routes of direct desulfurization, hydrogenative desulfurization, and successive hydrogenation. Their contribution can be kinetically solved by analyzing the reaction network.

### 3.2. Reactivity of 4,6-DMDBT over sulfided Ru/C under $H_2$ pressure

Figs. 4–6 illustrate the product composition of 4,6-DMDBT over sulfided Ru/C catalyst under 3 MPa of 5 vol.%  $H_2S$ /95 vol.%  $H_2$  pressure at 300°C, 340°C, and 380°C, respec-

tively. The reaction at 300°C provided 4H-DMDBT as the major product up to the conversion of 70%, while the increasing product of desulfurized MCHT took over 4H-DMDBT. MBCH became significant beyond the conversion 60%. DMBP of the direct desulfurization product was always minor at this temperature. Exclusive hydrogenation of 4,6-DMDBT was expected over Ru/C; however, the successive desulfurization was not ruled out. The maximum yield of 4H-DMDBT was about 30%, suggesting the hydrogenation equilibrium between 4,6-DMDBT and 4H-DMDBT.

A higher temperature of 340°C increased markedly DMBP as the major product, suggesting significant direct desulfurization over Ru/C at this temperature. 4H-DMDBT was the second

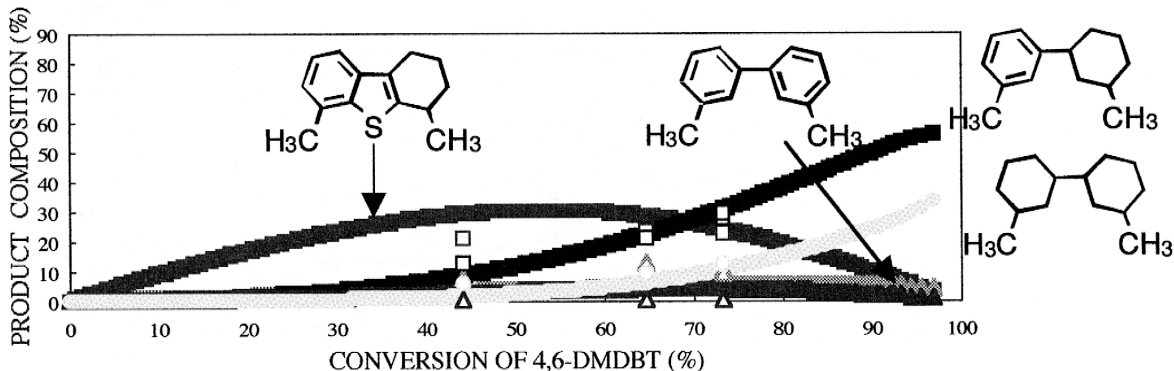


Fig. 4. Product selectivity for hydrodesulfurization of 4,6-DMDBT over Ru/C at 300°C.

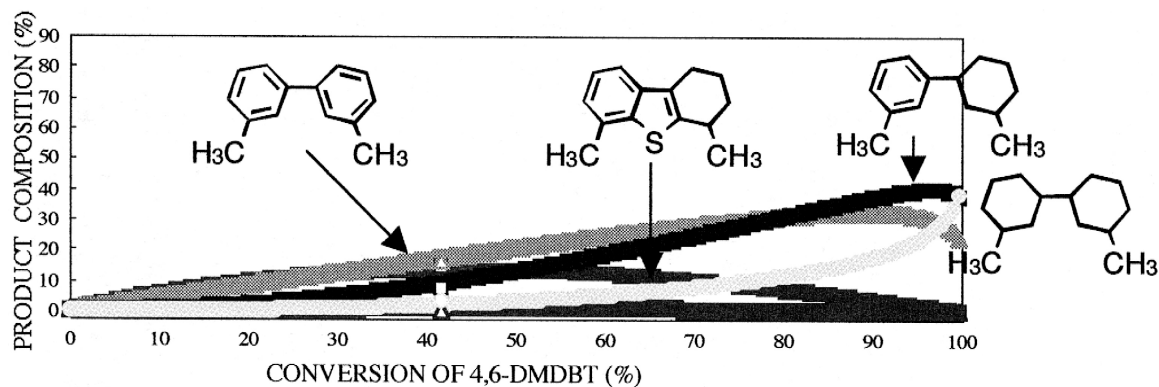


Fig. 5. Product selectivity for hydrodesulfurization of 4,6-DMDBT over Ru/C at 340°C.

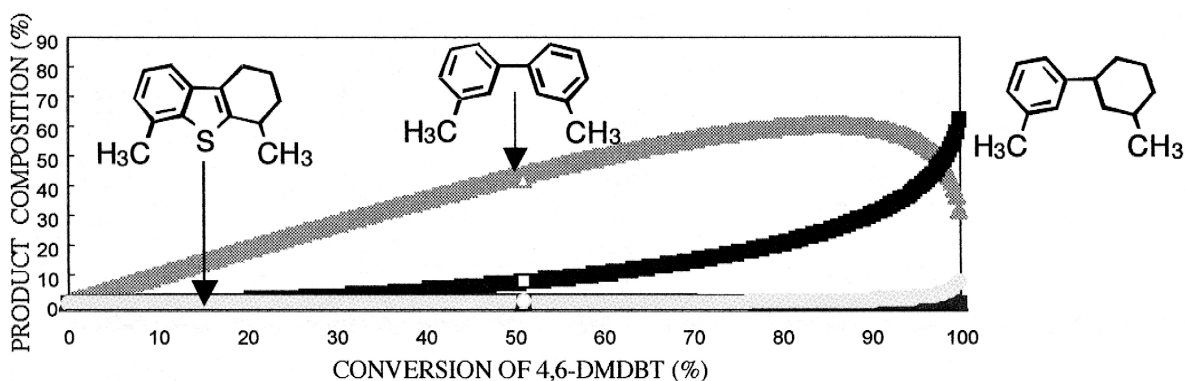


Fig. 6. Product selectivity for hydrodesulfurization of 4,6-DMDBT over Ru/C at 380°C.

major product, but its successive desulfurization took place at the same time to take over at 50% conversion. The maximum yield of 4H-DMDBT was around 15%, suggesting the hydrogen equilibrium. It is interesting that significant amount of DMBCH was produced above 70% conver-

sion. The hydrogenation equilibrium of DMBP was fairly high.

The reaction temperature of 380°C produced DMBP as the major product upto the very high conversion above 95%, when the selectivity of MCHT took over. 4H-DMDBT was always very

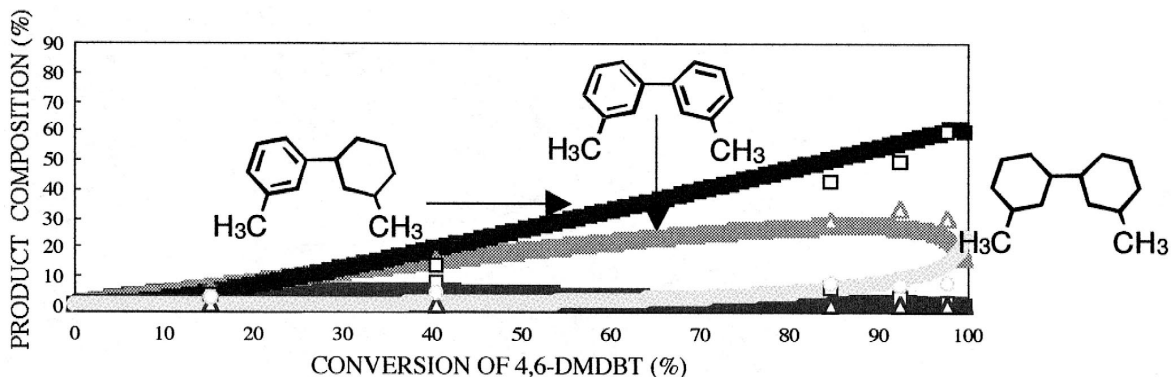


Fig. 7. Product selectivity for hydrodesulfurization of 4,6-DMDBT over NiMoMax sorb at 300°C with Cu.

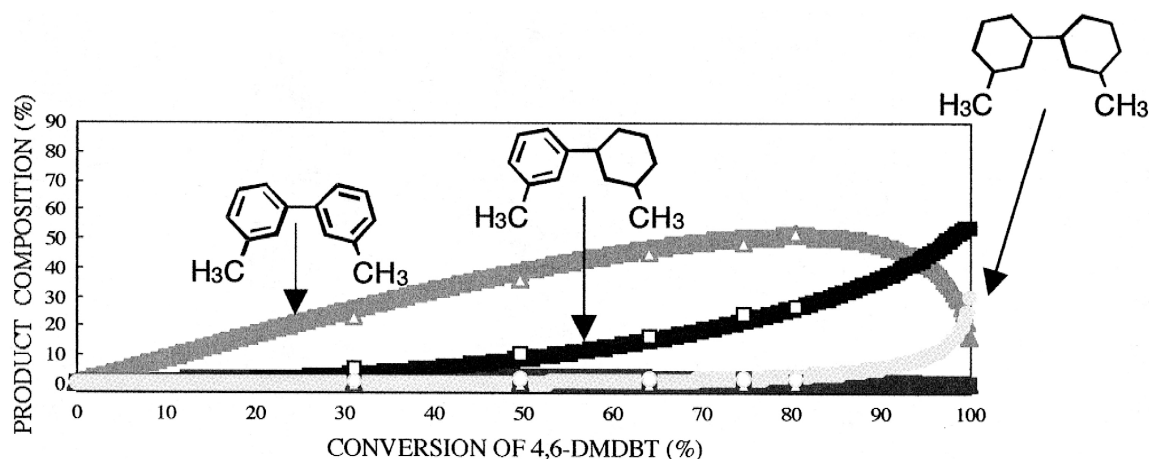


Fig. 8. Product selectivity for hydrodesulfurization of 4,6-DMDBT over NiMo/Max sorb at 340°C with Cu.

minor, its maximum yield being as low as 5%. DMBCH was also minor all through the conversion.

### 3.3. Effect of $H_2S$ capture on the HDS of 4,6-DMDBT

Figs. 7–9 illustrate the HDS product composition of 4,6-DMDBT over NiMo/Maxsorb catalyst with the addition of Cu as a  $H_2S$  scavenger at 300°C, 340°C, and 380°C, respectively. In comparison with the results of Figs. 1–3, where the self-produced HS remained in the reaction system, the selectivity for DMBP was markedly increased by the addition of Cu, where  $H_2S$  produced due to HDS was always cap-

tured.  $H_2S$  is suggested to inhibit significantly the direct HDS route. It is noted that the yield of MCHT produced through the hydrogenative HDS route decreased by the addition of Cu, indicating that carbon-supported NiMo catalyst may require a certain amount of  $H_2S$  to maximize the hydrogenation activity.

## 4. Discussion

### 4.1. Kinetic analyses of 4,6-DMDBT desulfurization and estimation of its hydrogenation equilibrium

The desulfurization of 4,6-DMDBT is believed to take place through the consecutive as

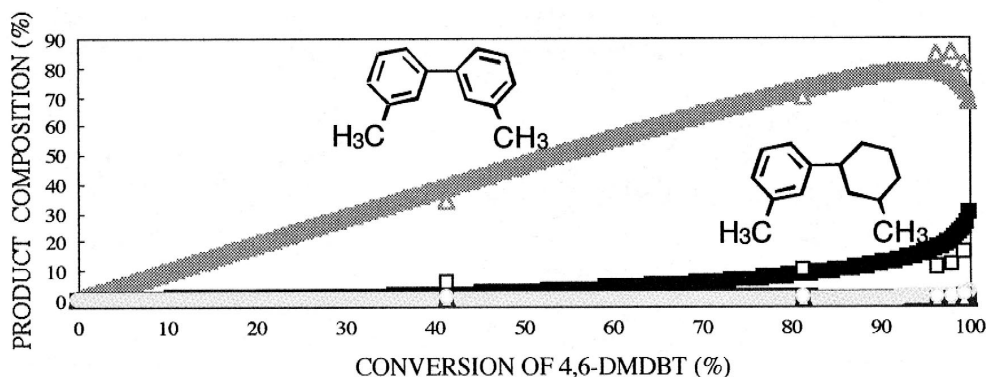


Fig. 9. Product selectivity for hydrodesulfurization of 4,6-DMDBT over NiMo/Max sorb at 380°C with Cu.

well as successive routes as illustrated in Fig. 10. The rate constants of every step are calculated according to the computer curve fitting of yield vs. time plots. There is a problem to determine all values of rate constants, because the consecutive route becomes significant only at the very high conversion. However, more accurate estimation is possible, since when the hydrogenation equilibrium of 4,6-DMDBT was obtained under the reaction conditions, the ratio of  $k_1/k_{-1}$  must be equal to the equilibrium constant. The reaction of 4,6-DMDBT over Ru/C gives us its approximate hydrogenation equilibrium values at least at lower reaction temperatures of 300°C and 340°C when HDS is limited. HDS became very marked at 380°C even over Ru/C in the presence of  $H_2S$ . We can only guess the equilibrium constants. The values are summarized in Table 2.

The hydrogenation equilibrium constant can be calculated according to MOPAC molecular orbital and molecular dynamics theories. The calculated values are also included in Table 2. It is worthwhile to point out that hydrogenation is found favorable up to 340°C, being sharply unfavorable between 340°C and 380°C. The values obtained experimentally are certainly larger than those expected by the calculation.

It is also of value at this stage to point out that Ru/C showed significant activity for desulfurization of 4,6-DMDBT at 380°C, which is almost comparable to that of NiMo/C catalysts. Some applications of such activity can be attempted.

Using the hydrogenation equilibrium constants of 4,6-DMDBT, the rate constants of each step in Fig. 10 are calculated and summarized in

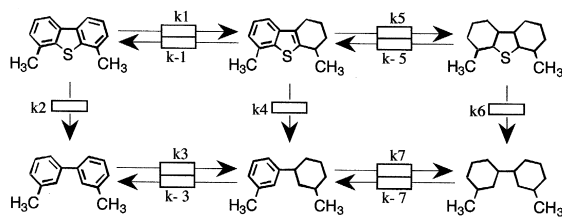


Fig. 10. HDS reaction network of 4,6-DMDBT.

Table 2  
Hydrogenation equilibrium constants

	Temperature (°C)		
	300	340	380
Observed	45	20	10
MOPAC	20	4	1

Table 3. According to the rate constants, the two reaction routes are kinetically compared. First of all, the direct desulfurization and hydrogenation of 4,6-DMDBT are competitive, since the successive desulfurization of 4H-DMDBT is always very rapid. The successive hydrogenation of DMBP is limited at lower conversions; hence, MCHT is principally produced through the hydrogenative desulfurization. Higher temperature enhanced very much the direct desulfurization, while hydrogenation is much less enhanced and even deactivated partly due to the equilibrium limit by higher temperature, leading to the major route of direct desulfurization. Nevertheless, successive hydrogenations of DMBP and MCHT take place to satisfy the equilibrium.

#### 4.2. Comparative HDS kinetics of NiMo/alumina and NiMo/carbon catalysts

Figs. 11–13 compares the HDS rate constants of NiMo catalysts supported on alumina and various carbons at the reaction temperatures of 300°C, 340°C, and 380°C, respectively. At the lowest temperature of 300°C, NiMo supported on Ketjen Black exhibited the highest activity due to its largest  $k_1$  value. A commer-

Table 3  
Rate constants of each step in HDS network of 4,6-DMDBT over NiMo/Maxsorb

	Temperature (°C)		
	300	340	380
$k_1$	52.5	67.6	131.1
$k_1$ with Cu	47.4	22.3	30.6
$k_2$	17.5	154.5	476.9
$k_2$ with Cu	29.6	161.0	611.2

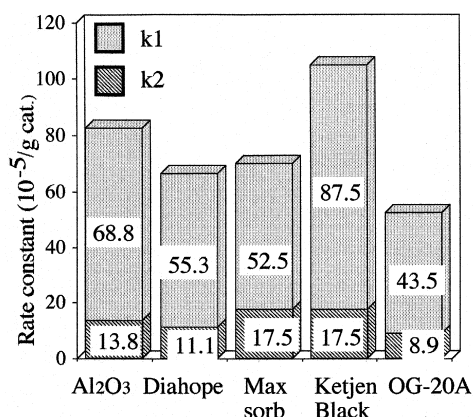


Fig. 11. Overall rate constants of 4,6-DMDBT over NiMo catalysts at 300°C.

cial NiMo/alumina catalyst gave the second largest  $k_1$  rate constant, although the difference in the catalytic activities was not significant at 300°C. The hydrogenative HDS route was dominant at 300°C, where the hydrogenation takes place rapidly, and the desulfurization rate ( $k_4$ ) of the tetrahydro-4,6-DMDBT was much larger than that of nonhydrogenated 4,6-DMDBT. Although such a tendency was also observed with alumina-supported NiMo catalysts [6], the contribution of the hydrogenative HDS route was larger with NiMo/carbon catalysts due to the higher hydrogenation activity.

At higher temperatures of 340°C and 380°C, the HDS rate increased as the direct HDS route

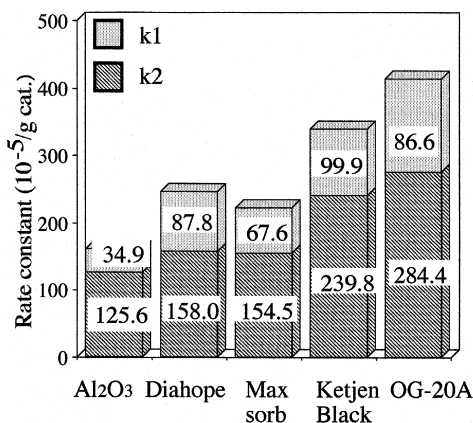


Fig. 12. Overall rate constants of 4,6-DMDBT over NiMo catalysts at 340°C.

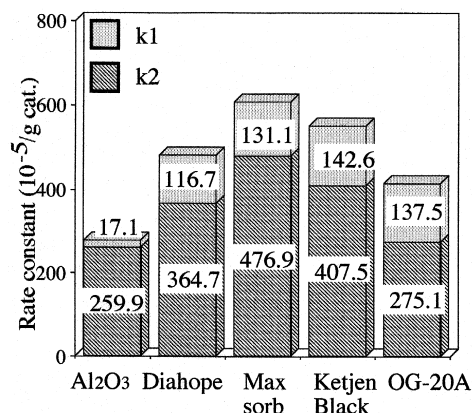


Fig. 13. Overall rate constants of 4,6-DMDBT over NiMo catalysts at 380°C.

became dominant, the carbon-supported NiMo catalysts exhibiting the higher HDS rate constants ( $k_2$ ) than that of alumina-supported one regardless of the carbon support species. Especially, OG-20A and Maxsorb supports gave the highest activity at 340°C and 380°C, respectively. It is worthwhile to point out that the hydrogenative HDS route significantly contributed to the HDS rate constants over the carbon-supported NiMo catalysts compared to the alumina-supported one at the higher reaction temperatures even where the direct HDS route was predominant.

Fig. 14 illustrates the effects of Cu addition on the HDS rate constant over NiMo/Maxsorb

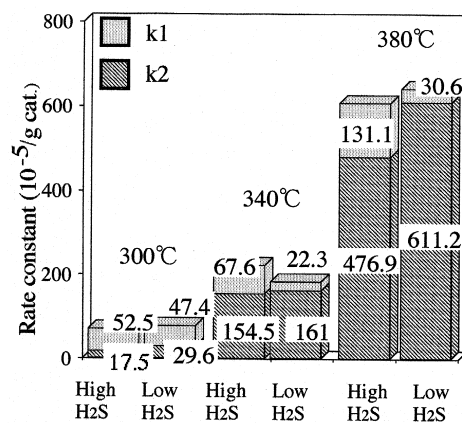


Fig. 14. Overall rate constants of 4,6-DMDBT over NiMo/Maxsorb catalyst.



at 300°C to 380°C, where high and low H<sub>2</sub>S concentrations are without and with Cu addition, respectively. At a lowest temperature of 300°C, the hydrogenation rate constant of  $k_1$  was always much higher than that of the direct desulfurization rate constant of  $k_2$  regardless of the H<sub>2</sub>S concentration, although the ratio of hydrogenative HDS to direct HDS route was much higher without Cu addition, because  $k_2$  increased but  $k_1$  decreased by lowering H<sub>2</sub>S concentration. Lowering H<sub>2</sub>S concentration increases the S elimination reactivity but decreases slightly the hydrogenation activity.

At a temperature of 340°C, lower H<sub>2</sub>S concentration provided a slightly lower activity, because the direct desulfurization is accelerated but the reduced activity of hydrogenative desulfurization was more marked. The highest temperature of 380°C increased very markedly the direct desulfurization, which is enhanced very much by lower H<sub>2</sub>S, giving the superior activity to that without Cu. Although lower H<sub>2</sub>S provided higher activity, reduced hydrogenation activity may bring about a problem of color which is believed to be caused by lack of hydrogenation or aromatics condensation [7–9].

#### 4.3. Active sites on NiMoS / C

Active sites of NiMoS have been discussed very extensively. The present study observed the very contrast responses of the direct desulfurization and hydrogenation to H<sub>2</sub>S concentration which was controlled by added Cu. Different active sites for such reactions are suggested.

The desulfurization site may be occupied by S at one of its coordinatively unsaturated vacancies to lose desulfurization active site. According to the desulfurization by coordinated compounds, two vacancies are required to remove S in the substrate to one vacancy while the other

keeps the substrate. In contrast, the hydrogenation site requires one vacancy and one SH site, which coordinates to and transfers to the substrate, respectively.

The influences of H<sub>2</sub>S concentration on the desulfurization have been extensively studied in the past. In many cases, more H<sub>2</sub>S is added to that produced by the desulfurization. Hence, the influence of HS at lower concentration may be overlooked.

H<sub>2</sub>S is often added continuously in the commercial desulfurization. This operation may be attempted to keep sulfide state constant for stable activity against unexpected oxygenated substrate or H<sub>2</sub>O.

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