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A ROLE OF MOLYBDENUM AND SHAPE SELECTIVITY OF CATALYSTS IN SIMULTANEOUS REACTIONS OF HYDROCRACKING AND HYDRODESULFURIZATION

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Abstract—The hydrocracking and hydrodesulfurization (HDS) of n-heptane containing 0.2 mole% dibenzothiophene (DBT) were performed simultaneously using NiPtMo catalysts supported on HZSM-5, LaY and γ-Al_2O_3 in a high pressure fixed bed reactor. Molybdenum played an important role in both hydrocracking and hydrodesulfurization (HDS). We found that the sulfur compound, dibenzothiophene (DBT), in the reactant was adsorbed on a molybdenum site and converted to hydrogen sulfide so that the active sites of the catalysts for hydrocracking were less poisoned by DBT and the conversion of n-heptane over molybdenum impregnated catalyst was higher than that over molybdenum-free catalyst. The crystal structures of the molybdenum supported on the zeolite and γ-Al_2O_3 were mainly $MoO_{2.5}(OH)_{0.5}$[021] and MoO_3[210] respectively as shown by XRD analysis. The structure of $MoO_{2.5}(OH)_{0.5}$ was easily reduced to MoS_2[003] during the reaction. After the reaction of 100 hours over the catalyst supported on γ-Al_2O_3, the crystal structure of MoO_3[210] partially changed to MoO_3[300] and the structure of MoS_2[003] was not observed. Because of the reactant shape selectivity of zeolite, the acid and the metal sites in the intracrystalline of the catalysts supported on zeolites were less poisoned by DBT. Therefore, both hydrocracking and HDS using n-heptane containing 0.2 mole% of DBT were successfully demonstrated over the prepared catalysts.

Key words: *Molybdenum, Shape-selectivity, Zeolite, Hydrocracking, Hydrodesulfurization*

INTRODUCTION

Recently, the consumption of petroleum has increased in light oil due to the development of automobile and aviation industry, but decreased in heavy oil. Hydrocracking process is one of the important process in petroleum industry and is used in order to solve the unequal balance of supply and demand in oil grades.

The hydrocracking process for petroleum refinery is classified as the following: First, the quality of hydrogenation products of unsaturated hydrocarbons is increased and Ni, Pd and Pt are used as catalysts. Second, the production of light oil by cracking of C-C bond. Cracking reactions of saturated hydrocarbons have been observed to be accompanied by the formation of molecular hydrogen both for reactions in liquid super acid media [Kirchen et al., 1986; Olah et al., 1971] and for reactions on solid acid catalysts at elevated temperatures [Abbot, 1980, 1988]. Finally, the removal of sulfur and nitrogen compounds in crude oil. There are many kinds of sulfur compounds in crude oil. They are generally the compounds of mercaptane, sulfide and thiophene compounds [Cerveny, 1986; Hilfman, 1979; O'hara et al., 1979]. If these sulfur compounds were released in the atmosphere by combustion, they would cause serious air pollution. The sulfur compounds in crude oil also poison the noble metals used for hydrocracking process. Therefore, hydrodesulfurization (HDS) process is employed as a pretreatment stage of hydrocracking process in order to remove these sulfur compounds. On the basis of this knowledge, HDS reaction has been studied over CoMo/γ-Al_2O_3 and NiMo/γ-Al_2O_3 [Fahrentört et al., 1982; Imlik et al., 1982]. CoMo and NiMo catalysts are used extensively for the hydrodesulfurization (HDS) of different oil fractions under high H_2 pressure. The improvement of this family of catalysts or their replacement by more active new catalysts requires time-consuming and very expensive tests on the pilot plant scale. Because most of the literature denies the possibility of using laboratory scale reactors under atmospheric pressure and thiophene as a probe molecule to simulate the activity of reaction.

HDS and hydrocracking reactions has been studied separately so far. However in this study, HDS and hydrocracking reactions were accomplished simultaneously. Molybdenum was used as a metal catalyst in order to perform simultaneous HDS and hydrocracking reactions by offering the active and the adsorption sites of dibenzothiophene (DBT). We used platinum as a metal to obtain high cracking activity and synergy effect between the metal and the acid sites of support and nickel was used as a promotor. Hydrocracking and HDS activities were studied over the prepared catalyst. Various reaction variables, roles of molybdenum and the shape selectivity of support were also discussed.

EXPERIMENTAL

1. Materials

LaY (SiO_2 : Al_2O_3 : Na_2O : La_2O_3 = 65 : 22.7 : 1.6 : 10.7) was supplied by Strem chemicals Co., Ltd. HZSM-5 (Si/Al = 50) was prepared by a conventional catalyst synthesis method [Mikovsky et al., 1976]. γ-Al_2O_3 (0.16 cmϕ, pellet type) was supplied by Rhone Poulanc. ammonium molybdates [$NH_4Mo_7O_{24}\cdot 4H_2O$) and nickel

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Table 1. The symbols and amounts of impregnated metals on catalysts (wt %)

Symbols	Contents	Mo	Pt	Ni
NH	NiPtMo/HZSM-5	6.87	0.528	0.964
NY	NiPtMo/LaY	6.91	0.525	0.961
NA	NiPtMo/γ-Al_2O_3	6.89	0.534	0.963
NH*	NiPt/HZSM-5	-	0.531	0.958
NY*	NiPt/LaY	-	0.529	0.947
NA*	NiPt/γ-Al_2O_3	-	0.532	0.956

Table 2. Surface area of catalysts

Catalysts	B.E.T. surface area (m^2/g)	Pore volume (cm^3/g)
γ-Al_2O_3	212	0.89
LaY	550	0.64
ZSM-5	536	0.58
NA	162	0.71
NY	430	0.54
NH	396	0.50

nitrate [$Ni(NO_3)_2 \cdot 6H_2O$] was supplied by Sanyo Chem. and chloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$) was supplied by Inuishio Precious Metals Co.

2. Preparation of Catalysts

Ammonium molybdates ($NH_4Mo_7O_{24} \cdot 4H_2O$) was precipitated in the supports (LaY, γ-Al_2O_3, HZSM-5) dried at 110℃ for 24 hours. They were dried at 110℃ for 12 hours. Nickel nitrate [$Ni(NO_3)_2 \cdot 6H_2O$] and chloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$) were coprecipitated into these precursors and they were calcined at 500℃ for 4 hours. Finally NiPtMo catalysts supported on HZSM-5, LaY and γ-Al_2O_3 were obtained. The symbols and the amounts of impregnated metals on each catalyst are given in Table 1. Table 2 showed the surface area and pore volume of prepared catalysts and supports.

3. X-ray Diffractions

Fresh and aged catalysts were analyzed by XRD to examine the metal structure.

4. Reaction Experimental

The hydrocracking and hydrodesulfurization (HDS) of n-heptane containing 0.2 mole% of dibenzothiophene (DBT) were performed simultaneously over NiPtMo catalysts supported on HZSM-5, LaY and γ-Al_2O_3. The reaction was carried out in a high pres-

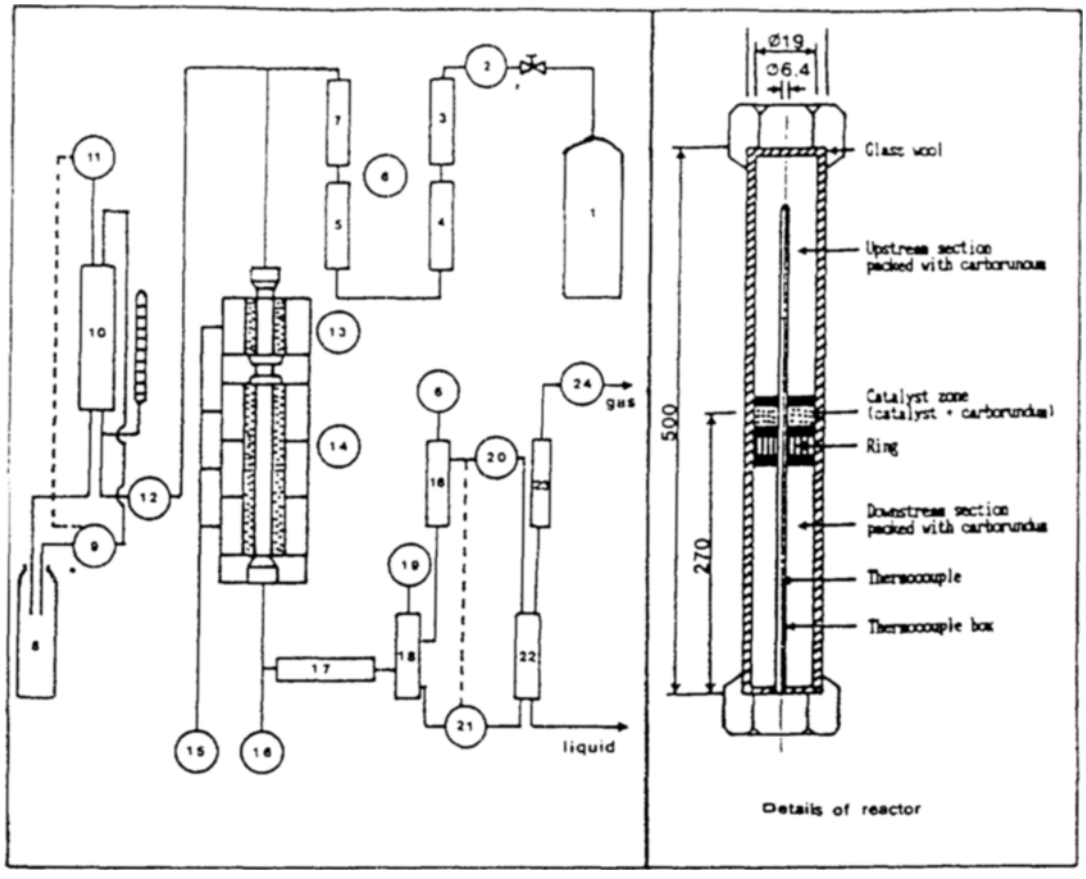

Fig. 1. Schematic diagram of experimental apparatus.

1. H_2 gas tank
2. Pressure regulator
3. Deoxo unit
4. Drying column
5. Gas mass flowmeter
6. Pressure gauges
7. Capillary tube
8. Supply tank
9. Supply pump
10. Feed tank
11. Feed tank level controller
12. Metering pump
13. Preheater
14. Stainless steel reactor
15. Temperature regulator
16. Temperature recorder
17. Condenser
18. H.P. separator
19. H.P. sep. level controller
20. Back pressure regulator
21. Level control electrovalve
22. L.P. separator
23. Gas sampler
24. Wet gas meter

Table 3. Operation ranges and standard conditions

Reaction variables	Operation ranges	Standard conditions
1. Catalysts		
*Loading weight	2-20 g	4 g
*Particle size	30-100 mesh	80 mesh
2. Reaction		
*Temperature	250-500℃	450℃
*Pressure	1×10^5-50×10^5 Pa	30×10^5 Pa
*Contact time (W/F)	5-50 g-cat.hr/mol	20 g-cat.hr/mol
*H_2/H.C. mole ratio	2-10	4
*DBT mole %	0.05-1 mole %	0.2 mole %

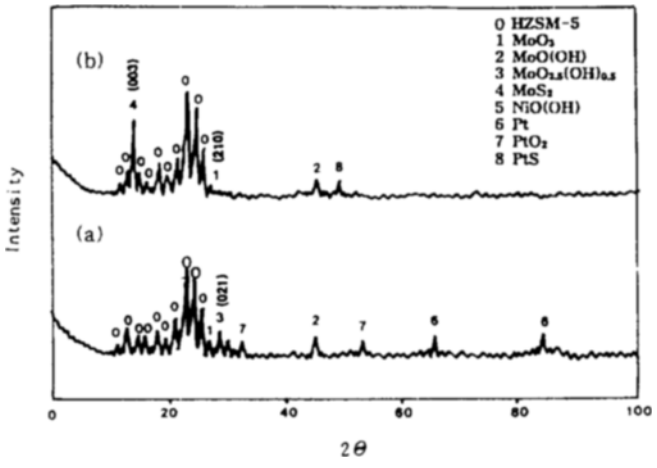

Fig. 2. XRD patterns of NH catalysts.
(a) fresh catalyst, (b) aged catalyst.

sure fixed bed reactor (Catatest Unit model C), at the using conditions as shown in Fig. 1 and Table 3, respectively.

It was found that the conversions of n-heptane and DBT over each catalyst were stabilized after the reaction run of thirty hours. All reactions were carried out by varying the reaction variables after the stabilization period of 30 hours.

RESULTS AND DISCUSSION

1. The Structure of Metals

Fresh and aged catalysts were analyzed by XRD to examine the metal structure.

Fig. 2 and Fig. 3 showed that molybdenum was mainly impregnated as a structure of $MoO_{2.5}(OH)_{0.5}$[021] and the structure of $MoO(OH)_2$ which resulted from binding of hydroxyl group in zeolite supports, and the structure of MoO_3 existed as well. This structure of the molybdenum cluster of $MoO_{2.5}(OH)_{0.5}$[021] was very unstable and easy to change. During the reaction molybdenum cluster of $MoO_{2.5}(OH)_{0.5}$[021] combined with sulfur compound, dibenzothiophene (DBT), was reduced to the structure of MoS_2[003]. The structure of $MoO(OH)_2$ and MoO_3 remained constant even after the reaction of one hundred hours.

The structure of molybdenum in the catalyst supported on γ-Al_2O_3, exhibited as MoO_3[210] as shown in Fig. 4. After the reaction of 100 hours those of the crystal structure of MoO_3[210] remained constant and some of MoO_3[210] was changed to MoO_3 [300] while the structure of MoS_2[003] was not observed. So the crystal structure of MoO_3 was more stable against sulfur compound (DBT) than that of $MoO_{2.5}(OH)_{0.5}$[021].

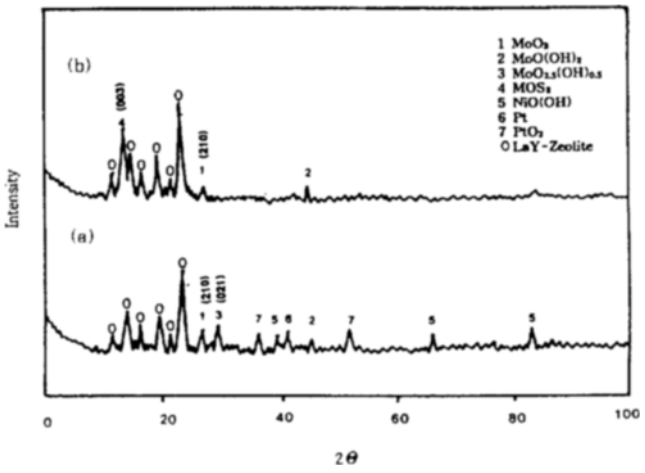

Fig. 3. XRD patterns of NY catalysts.
(a) fresh catalyst, (b) aged catalyst.

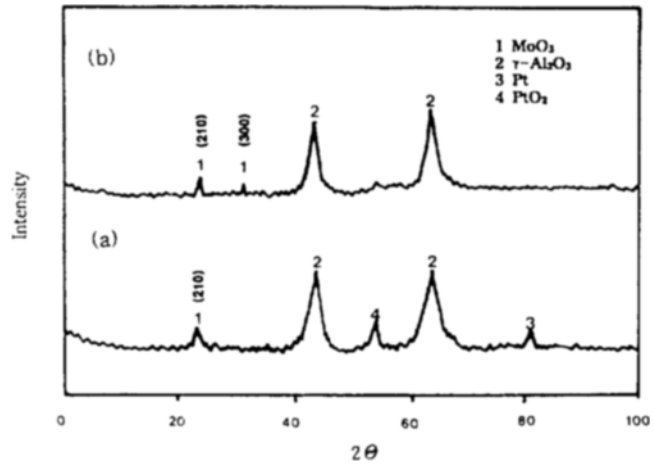

Fig. 4. XRD patterns of NA catalysts.
(a) fresh catalyst, (b) aged catalyst.

Table 4. Structures of supported metals

Supports / Metals	γ-Al_2O_3	LaY	HZSM-5
Ni	NiO	NiO(OH)	NiO(OH)
Pt	Pt, PtO_2	Pt, PtO_2	Pt, PtO_2
Mo	MoO_3	$MoO_{2.5}(OH)_{0.5}$	$MoO_{2.5}(OH)_{0.5}$
		$MoO(OH)_2$	$MoO(OH)_2$
		MoO_3	MoO_3

Table 4 showed various structures of supported metals. Nickel was impregnated as a form of NiO on NA catalyst and NiO(OH) on NH and NY catalyst. Platinum was observed as the structures of Pt and PtO_2 on all catalysts.

2. The Role of Molybdenum

Initial conversions of n-heptane over each catalyst dropped rapidly after the time of thirty hours and were stabilized as shown in Fig. 5. Hydrocracking reactions of saturated hydrocarbons were observed to be accompanied by formation of olefin media [Heinemann et al., 1953]. Fig. 6 showed that n-heptane were converted

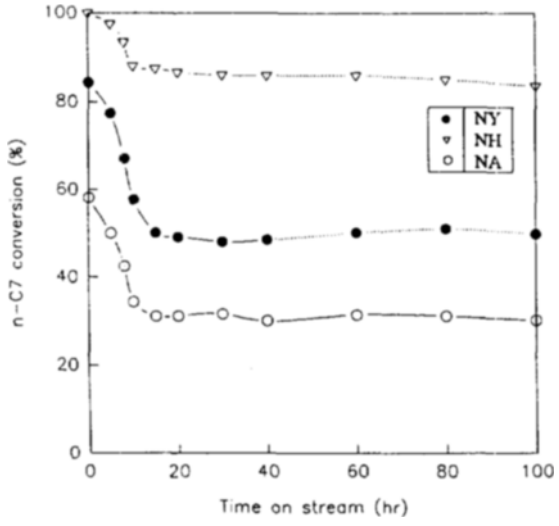

Fig. 5. Stabilization of catalysts for hydrocracking reaction.
T=450℃, P=3 MPa, W/F=20 g-cat.hr/mol, H_2/H.C.=4.

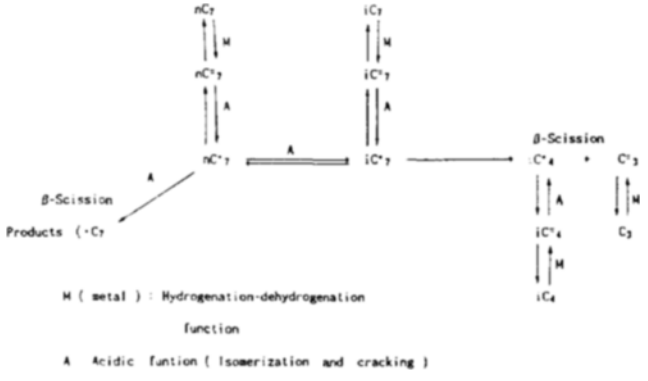

Fig. 6. Transformation of n-heptane on bifunctional catalysts.

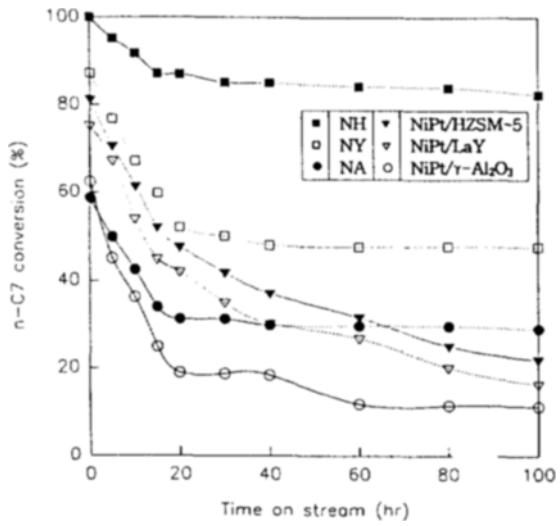

Fig. 7. Effect of molybdenum as a promotor.

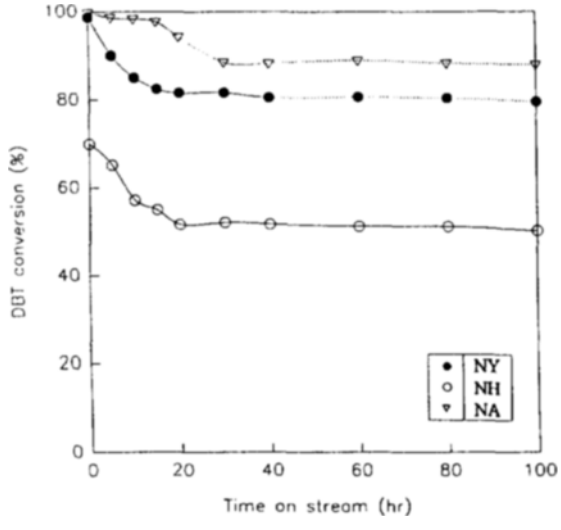

Fig. 8. Stabilization of catalysts for HDS reaction.
T=450℃, P=3 MPa, W/F=20 g-cat.hr/mol, H_2/H.C.=4.

to olefin by hydrogenation and dehydrogenation on the metallic site and the acid sites. Olefin was attacked by hydrogen cation and converted to carbon cation (n-C_7^+). Then hydrocracking and isomerization reactions occur by means of cracking and rearrangement of carbon cation [Sinfelt, 1964].

The order of hydrocracking activity of each catalyst was NH >NY>NA as shown in Fig. 5. It was considered, to be due to the fact that NH catalyst had strong acid site on HZSM-5 (Si/Al=50) support. It was found that zeolites (HZSM-5, LaY) played roles of both catalyst and support simultaneously with their acid site. The order of hydrocracking activity might be explained by this fact.

Compared Fig. 5 with Fig. 7, hydrocracking activities of molybdenum impregnated catalysts were stabilized after the reaction of 30 hours and maintained for 100 hours. However molybdenum-free catalysts were deactivated rapidly and lost hydrocracking activity shortly. In this hydrocracking reaction, it was considered that molybdenum played a very important role in offering the adsorption and active sites for DBT in the n-heptane feed so that the metal and acid sites of the molybdenum impregnated catalysts were less poisoned by DBT than those of molybdenum-free catalysts.

Fig. 8 showed hydrodesulfurization (HDS) of DBT in the n-heptane feed. The order of HDS activity for each catalyst was NA >NY>NH. In general, DBT conversion over the catalyst with medium acid strength is higher than that of with strong or very weak acidity. Therefore, DBT conversion of NA catalyst was higher than that of NH and NY catalysts because of their strong acidity due to zeolite supports.

On the other hand, the conversion over NA catalyst for hydrocracking was lower than that of NH and NY catalysts. NY catalyst showed high activities in both hydrocracking and HDS. Therefore, both hydrocracking and HDS using n-heptane containing 0.2 mole percentage of DBT were successfully demonstrated over these molybdenum impregnated catalysts.

3. Shape Selectivity of Zeolite

Shape selective catalysis means the variation of selectivity and/or product distribution of catalytic reaction due to the geometrical shape of catalyst pore [Cscsery, 1974]. Reactant shape selectivity, for example, is removal of linear hydrocarbon by selective cracking in gasoline. In other words, reactant shape selectiv-

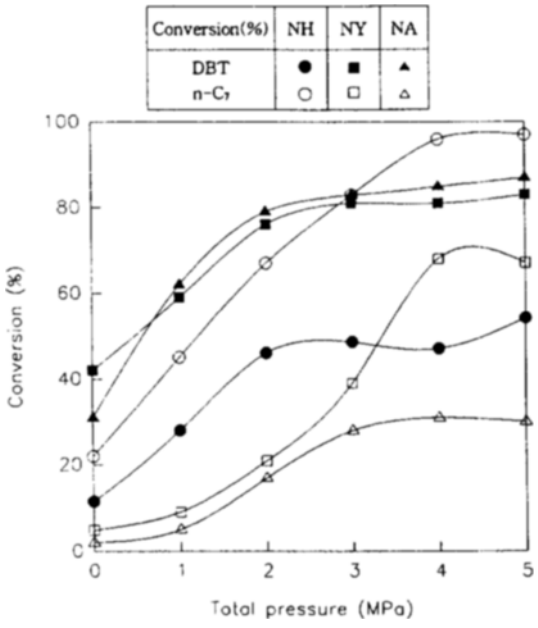

Fig. 9. Effect of pressure over NH, NY and NA catalysts.
T=450℃, W/F=20 g-cat.hr/mol, H_2/H.C.=4.

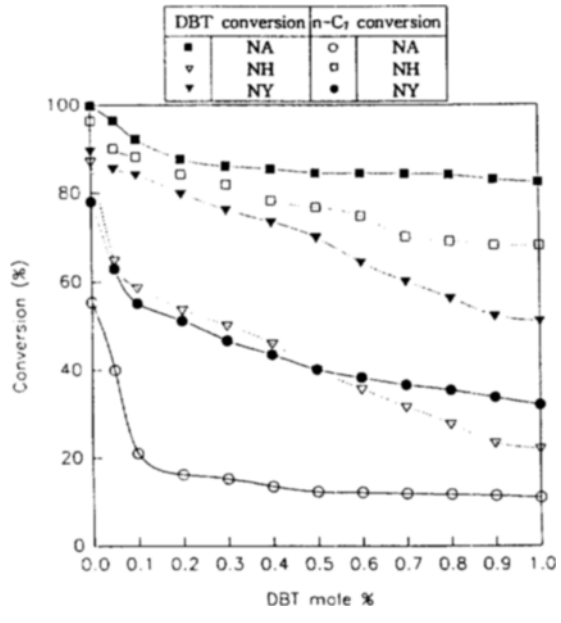

Fig. 10. Effect of DBT mole %.

ity is to react only on special material or without using size difference between reactant and the pore of a catalyst.

Fig. 9 showed the n-heptane conversion increased rapidly with increasing pressure. However, DBT conversion initially increased up to 2MPa and above that pressure increased very slowly over NH catalyst. It was considered that the acid sites inside the zeolite pore were inhibited from poisoning by DBT and n-heptane and also had a better chance to reach the acid sites inside the ZSM-5 pore than DBT when increasing the pressure. Because the size of n-heptane (2.15×11.4 Å) was more slim than that of DBT (4.94 ×8.22 Å). So it was easy for n-heptane to pass into the inner space of HZSM-5 pore of which pore size was 5.4×5.6 Å.

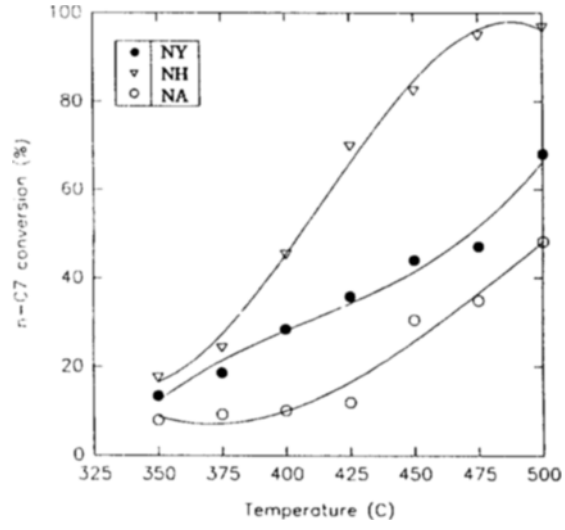

Fig. 11. Effect of temperature on hydrocracking.
P_T=3 MPa, W/F=20 g-cat.hr/mol, H_2/H.C.=4.

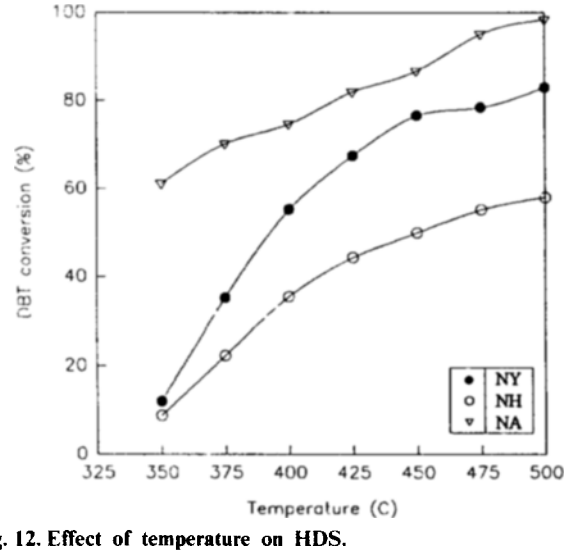

Fig. 12. Effect of temperature on HDS.
P_T=3 MPa, W/F=20 g-cat.hr/mol, H_2/H.C.=4.

The conversion of n-heptane increased rapidly with increasing pressure but DBT conversion increased very slowly above 2 MPa over NY catalyst supported on LaY whose pore diameter was 7.4 Å.

Compared with NH, NY and NA catalysts, n-heptane conversion increased rapidly with increasing pressure over NH and NY catalysts. But n-heptane conversion increased slowly to 3 MPa and remained constant above that pressure, over NA catalyst which had an irregular pore shape.

This result was due to not only the acid sites and strength of supports but also the reactant shape selectivity of each support. It is considered the latter was more persuasive in the high pressure reaction than the former one.

4. Performance of Reactions

With increasing DBT mole% in the n-heptane feed, the DBT conversion over catalysts supported on zeolites decreased linearly with the exception of the NA catalyst supported on γ-Al_2O_3 as shown in Fig. 10. NA catalyst had good activity of hydrodesulfuri-

zation and deactivated a little with increasing sulfur compound in this range of DBT mole% (0-1.0).

Fig. 11 showed that n-heptane conversion increased with increasing temperature up to 450℃, because of the enhancement of molecular motion of n-heptane by increment of temperature. n-Heptane had a better chance to contact with the acid and the metal sites of catalysts with a little pyrolysis. The DBT conversion over each catalyst increased with increasing temperature.

At low temperature below 400℃, the DBT conversion of NA catalyst was much higher than that of NH and NY catalysts as shown in Fig. 12. At high temperature above 475℃, most of the DBT in the feed was converted over NA catalyst. NH catalyst had more hydrocracking activity than that of NY catalyst with increasing temperature but the activity of HDS was opposite. It is considered that NH catalyst supported on HZSM-5 had more inhibiting effect on the deactivation of hydrocracking activity by DBT than NY catalyst supported on LaY zeolite which had supercage. On the other hand, NY catalyst had higher HDS activity than NH catalyst. It is considered that the molybdenum site in the intracrystalline of NY catalyst played a role of by offering the active site of DBT because the more DBT penetrated the supercage with increasing temperature.

CONCLUSIONS

This study demonstrated the hydrocracking and HDS reaction of n-heptane containing sulfur compound (DBT) simultaneously over molybdenum impregnated catalysts. As conclusions, the following statements are proposed and some of which may require further clarification:

1. Over the catalyst supported on γ-Al_2O_3, molybdenum was impregnated as the crystal structure of MoO_3[210]. However we could not find the crystal structure of MoS_2[003] after the reaction. In the catalyst supported on zeolites, molybdenum was impregnated mainly as the structure of $MoO_{2.5}(OH)_{0.5}$[021]. This structure readily reduced to MoS_2[003] during the reaction.

2. Molybdenum played a role to offer the adsorption and the HDS active sites of DBT, so the metal and the acid sites of the catalysts were less poisoned by DBT. Therefore, both hydrocracking and HDS using n-heptane containing 0.2 mole percentage of DBT were successfully demonstrated over these molybdenum impregnated catalysts.

3. Over the prepared catalysts supported on highly shape selective zeolites, the acid and metal sites in the intracrystalline of these catalysts were inhibited to the deactivation of the hydrocracking reaction due to DBT.

4. NY catalyst had good activities in both hydrocracking and HDS reactions at these experimental conditions. NA catalyst had good activity in HDS but had poor activity of hydrocracking. This result was opposite over NH catalyst.

ACKNOWLEDGEMENT

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NOMENCLATURE

F : feed rate [mol/hr]
H.C. : hydrocarbon (n-heptane)
H_2/H.C. : hydrogen to n-heptane mol ratio [mol/mol]
MPa : mega pascal (pressure)
P : products
Pa : pascal in pressure unit
P_T : total pressure
W : catalyst weight [g]
W/F : contact [g-cat.hr/mol]
X : conversion

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