Transactions of the Materials Research Society of Japan 25 [1] 143-146 (2000)

Preparations of Binary Metal Sulfides for Hydrotreating Catalyst by Using the Mechanical Comminution

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Preparations and catalytic activities of unsuported mixture of CoS-MoS_2 and NiS-MoS_2 were investigated. One series of catalysts was prepared by mixing metal sulfides CoS or NiS to MoS_2 after the individual comminution, and the other was prepared by mixture comminution of CoS or NiS and MoS_2. The reaction activity of those catalysts was studied on hydrogenation of 1-methylnaphthalene(1-MN), hydrodesulfurization of dibenzothiophene (DBT) and coal liquefaction. The reaction rates using the mixed catalysts of individually comminuted metal sulfides increased proportional to the weight fraction of the constituents. On the other hand, those rates using the mixture-comminution of binary metal sulfides obviously improved. The active surfaces of each catalyst were contacted closely by mixture. It seems that new catalytic sites had been created on the surface of mixture-comminuted binary metal sulfides, which indicates the synergistic effect of comminution.

Key words: mechanical comminution, mixture comminution, binary metal sulfide, hydrotreating catalyst, synergistic effect

1. INTRODUCTION

It is important to produce the clean motive fuel by using high performance catalysts. Many researchers investigated to prepare highly active hydrotreating catalysts for industrial petroleum processes and coal liquefaction processes. Metal carbonyls as catalyst precursors [1] and bimetallic catalysts [2] were such examples. Mechanical comminution is another trial to obtain high performance coal liquefaction catalysts. In a 150 t/d NEDOL process, which is the well-known coal liquefaction process in Japan, a natural pyrite comminuted through a two-stage pulverization system provided an excellent catalytic activity [3].

We have showed the improved catalytic activity of comminuted metal sulfides (MoS_2, CoS and NiS) in the previous paper [4]. In this report, we comminuted the binary metal sulfides CoS-MoS_2 and NiS-MoS_2, and compared their catalytic activities on hydrogenation of 1-MN, hydrodesulfurization of DBT and liquefaction of Tanito Harum Indonesian coal to those of comminuted individual metal sulfides.

2. EXPERIMENTAL

2.1 Comminution of metal sulfide particles

Commercially available MoS_2, CoS and NiS particles were used without further purification. These particles were comminuted in a media-agitation mill with zirconia vessels (100 cm^3). The detail of comminution was described in the previous report [5]. As for comminuting the binary metal sulfides, CoS or NiS as hard materials was comminuted for 50 hours, then MoS_2 was mixed, and continued comminution for 50 hours.

Particle size distribution was measured by a centrifugal sedimentation photo-extinction method (Shimadzu SA-CP3). Specific surface area was obtained by a nitrogen adsorption BET method (Micromeritics Flowsorb II). Particles were observed with a transmission electron microscope (TEM, JEOL JEM-2000 FXII).

2.2 Catalytic activity

All the experiment of catalytic activities was conducted with a stainless steel micro-autoclave (50 cm^3). In case of hydrotreating reaction, 5g feedstock was put in the reactor and hydrogenated at 573K and 623K for 60 min. In case of coal liquefaction, 3g coal (particle size < 100 mesh) was dispersed in 4.5g tetralin as a solvent and reacted at 723K for 60min. The initial H_2 pressure was 7.9 MPa at room temperature for all the runs. The catalyst amount was shown in Tables II-III and Figures 2-4. After reaction and venting gases, the gaseous products were analyzed with GC-TCD. The liquid products were analyzed by using GC-MS and GC-FID (HP5890).

The liquid products of the coal liquefaction were extracted into tetrahydrofuran (THF) and n-hexane. Conversion of coal was determined as THF soluble fraction (THFs) and yield of oil (included water and gases) as the fraction (Hs) soluble to n-hexane on a daf-coal basis.

3. RESULTS AND DISCUSSION

3.1 Property of the comminuted metal sulfide

Table I shows the median diameter and specific surface area of the comminuted metal sulfide, together with the comminution conditions. Excepting the comminuted NiS, the median diameters of the individually comminuted MoS_2 and CoS were smaller than 0.1 μm. Comminuted CoS-MoS_2 and NiS-MoS_2 mixtures had also the median diameter smaller than 0.1 μm. The specific surface area of NiS-MoS_2 mixture was slightly larger than that of CoS-MoS_2.

Every X-ray diffraction patterns of the comminuted catalysts consisted of broad peaks characteristic of a poorly crystalline material. However, the TEM image of the mixture-comminuted NiS-MoS_2 in Figure 1 showed the ultrafine particles of NiS and MoS_2. The layered structure of MoS_2 seems to be contacted closely with the fine granular of NiS. Similar image was obtained for mixture-comminuted CoS-MoS_2 catalyst.

3.2 Hydrogenation of 1- methylnaphthalene

Raw (as-received) metal sulfides had rather low 1-MN conversion as shown in Table II. Among the three metal sulfides, CoS had the highest activity, but the conversion was only 10%. The conversions of individually comminuted metal sulfides were much higher than those of raw materials. Increased number of catalytic sites by means of mechanical comminution has been demonstrated in the previous paper [5].

The conversions of 1-MN using comminuted CoS-MoS_2 and NiS-MoS_2 were higher than expectations from the conversions using the mixed catalysts of individually comminuted metal sulfides. For example, 1-MN conversion of the mixture-comminuted catalyst NiS-MoS_2 was higher as 95.5% exceeding that of the mixed catalyst, 63.5%, for the similar weight fraction of the constituents.

The reaction activities of 1-MN by using the mixed catalyst of the individually comminuted NiS and MoS_2 and by using the mixture-comminuted catalyst NiS-MoS_2 for the weight fraction of those constituents were shown in Fig.2. The conversions using the mixed catalysts were increased proportionally to the weight fraction of MoS_2. Contrary, the conversion for the mixture-comminuted NiS-MoS_2 indicated obviously higher conversion beyond those of the mixed ones.

It was thought that the active surfaces of each catalyst were contacted closely by mixture-comminution, and new catalytic sites had been created on the contact surface.

The selectivity of 1-methyltetralin (1-MT) to 5-methyltetralin (5-MT) in the reaction products is shown in Table II. This ratio for NiS was rather low in contrast to that for MoS_2 and CoS. The ratio for the mixture-comminuted NiS-MoS_2 was lower than that of all the other mixed catalyst.

Considering the decreasing of selectivity (1-MT)/(5-MT) by mixture-comminuted catalyst, it was indicated that the structural change of those binary metal sulfide occurred on the surface of catalysts. Synergistic effect [6] was brought by comminuting binary metal sulfide.

Fig.1 TEM image of mixture-comminution NiS-MoS_2
mixed ratio of NiS/ MoS_2 : 1/2
shape of metal sulfide : NiS/granular, MoS_2/layer

Table I Preparation by media-agitating mill and physical properties of catalysts.

Catalyst	feed for comminution g	comminution time Hr	median diameter nm	specific S.A.[a] m^2/g
MoS_2	-	as-received	2600	5.8
CoS	-	as-received	5460	0.9
NiS	-	as-received	4980	0.8
com. MoS_2 [b]	5	50	40	119
com. CoS [b]	5	50	60	89
com. NiS [b]	5	50	150	52
mixture-com.(CoS-MoS_2) [c]	CoS:2, MoS_2:4	100	80	69
mixture-com.(NiS-MoS_2) [c]	NiS:2, MoS_2:4	100	60	86

a: specific surface area, b: individually comminuted metal sulfide,
c: mixture-comminuted binary metal sulfide

Table II Hydrogenation of 1-methylnaphthalene with 3 wt % of metal at 623 K for 60 min.

catalyst	atomic ratio of metal -	conversion %	1-MT %	5-MT %	selectivity (1-MT)/(5-MT) -
MoS_2	-	3.5	1.6	1.8	0.889
CoS	-	10.0	4.7	5.1	0.910
NiS	-	2.1	0.7	1.3	0.561
com. MoS_2	-	85.3	38.4	43.8	0.876
com. CoS	-	89.5	42.3	40.3	1.049
com. NiS	-	19.2	8.1	10.0	0.809
mixed (com. CoS and com. MoS_2) [a]	Co/Mo=35.5/64.5	85.9	39.8	40.3	0.988
mixed (com. NiS and com. MoS_2) [a]	Ni/Mo=34.6/65.4	63.5	28.8	32.1	0.898
mixture-com.(CoS-MoS_2)	Co/Mo=35.1/64.9	92.3	32.9	49.7	0.663
mixture-com.(NiS-MoS_2)	Ni/Mo=35/65	95.5	27.7	56.8	0.488

a: mixed of individually comminuted metal sulfide

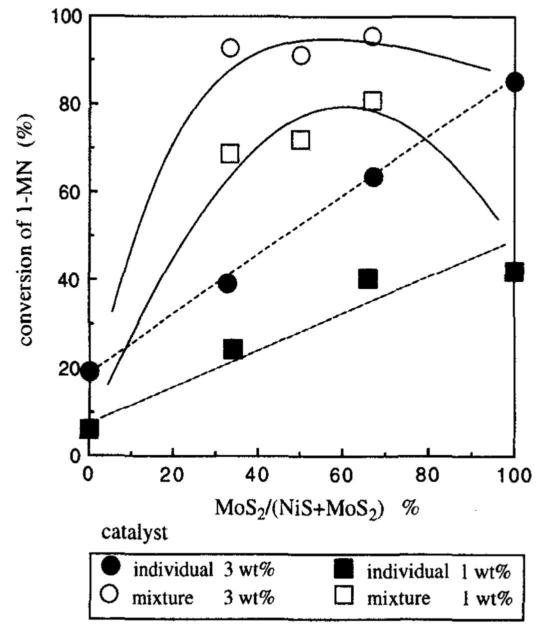
3.3 Hydrodesulfurization of dibenzothiophene

The feedstock for the hydrodesulfurization was 5 % of DBT in n-hexadecane. In the reaction of DBT, three kinds of hydrogenated sulfides (tetrahydrodibenzothiophene, hexahydrodibenzothiophenes and perhydrodibenzothiophenes) and several desulfurised compounds (biphenyl, cyclohexylbenzenes, bicyclohexyl, benzene, etc.) were produced. When the conversion of DBT was higher, the yield of the hydrogenated sulfides decreased, and the yield of the desulfurized compounds increased.

Fig. 3 shows the conversions of DBT by using the mixed catalyst of individual comminuted CoS and MoS_2 and by using the mixture-comminuted catalyst CoS-MoS_2 for the weight fraction of those constituents. The catalytic activity of the mixture-comminuted catalysts was improved remarkably. The catalytic ability similar to that of CoS-MoS_2 was obtained for NiS-MoS_2. The synergistic effect of the mixture-comminution was appeared also in this reaction.

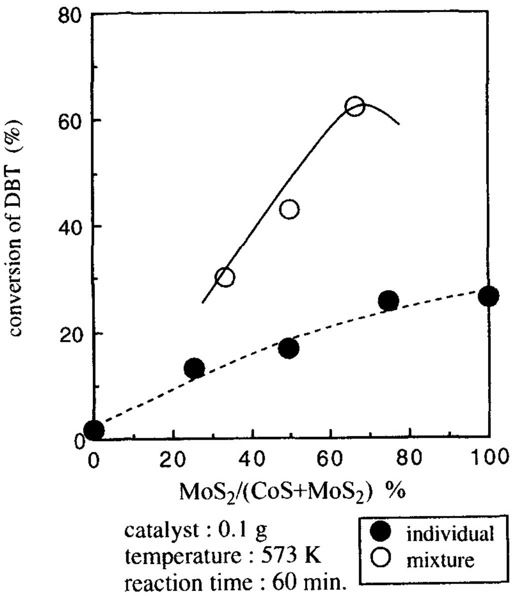
3.4 Coal liquefaction

Table III shows the result of coal liquefaction by using tetralin as a solvent. The comminuted NiS did not indicate the improved reaction ability from non-catalytic reactions. However, the conversions THFs and



temperature : 623, reaction time : 60 min.

Fig. 2 Hydrogenation of 1-MN by using the catalyst of NiS and MoS_2



catalyst : 0.1 g
temperature : 573 K
reaction time : 60 min.

Fig. 3 Hydrodesulfurization of DBT by using the catalyst of CoS and MoS_2

Hs of mixed NiS and MoS_2 had increased. Moreover, those conversions had been increased by the use of the mixture-comminuted NiS-MoS_2 especially for Hs. It was shown in Fig.4 that THFs and Hs of mixture-comminuted NiS-MoS_2 were larger than expectations from those ground MoS_2 and NiS for the weight fraction of the constituents. In this reaction, the catalytic effect of mixture-comminution catalyst was admitted though it was much different from the hydrotreating of 1-MN and DBT.

4. CONCLUSION

Preparations and catalytic activities of unsuported mixture of CoS-MoS_2 and NiS-MoS_2 were investigated. One series of catalysts was prepared by mixing metal sulfides CoS or NiS to MoS_2 after the individual comminution, and the other was prepared by mixture-comminution of CoS or NiS and MoS_2. The reaction activity of those catalysts was studied on hydrotreating of 1-MN and DBT and coal liquefaction. The reaction rates using the mixed catalysts of individually comminuted metal sulfides increased proportional to the weight fraction of the constituents. Contrary, the conversion for the mixture-comminuted catalyst indicated obviously higher conversion beyond those of the mixed ones. On the other hand, those rates using the mixture-comminution of binary metal sulfides obviously improved. The active surfaces of each catalyst were contacted closely by mechanical comminution. We thought that new catalytic sites had been created on the surface of mixture-comminuted binary metal sulfides, which indicates the synergistic effect of comminution. The relation between the structural change as synergistic effect and catalytic activity of binary metal sulfides by mechanical comminution will be examined in detail.

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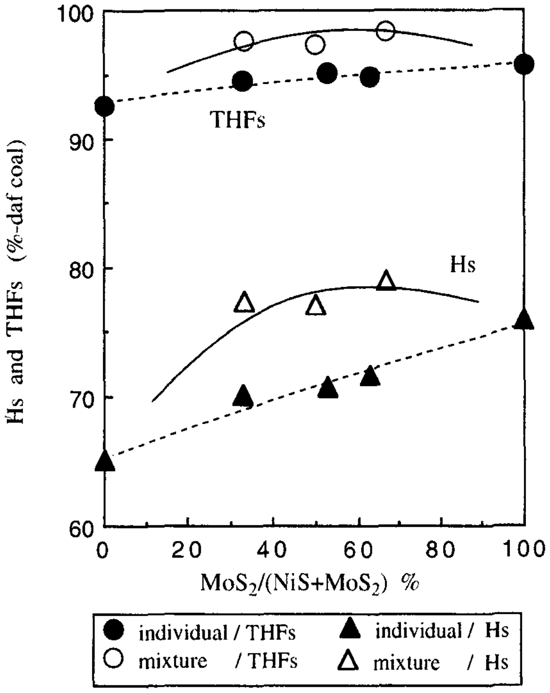

catalyst : 1.2 wt%

temperature : 723 K reaction time : 60 min.

Fig. 4 Coal liquefaction by using the catalyst of NiS and MoS_2

Table III Liquefaction of Tanito Harum coal in tetralin with 1.2 wt % of metal at 723 K for 60 min

% daf-coal

catalyst [a]	THFs	Hs	gas	H_2 consumption
no	91.4	65.3	12.1	1.3
com. MoS_2	95.7	75.9	11.2	2.8
com. CoS	97.6	75.0	11.6	3.2
com. NiS	92.6	65.1	11.9	2.0
mixed (com. CoS and com. MoS_2)	97.1	76.9	10.6	2.7
mixed (com. NiS and com. MoS_2)	94.9	71.6	11.4	2.2
mixture-com.(CoS-MoS_2)	98.3	79.9	11.0	3.1
mixture-com.(NiS-MoS_2)	98.4	78.9	9.4	4.0

a: see Table II

(Received December 17,1999 ; Accepted February 15,2000)