THIOPHENE HYDRODESULFURIZATION OVER COBALT OXIDE LOADED SMECTITE CLAY MINERALS

Eiji Iwamatsu[1]*, Syed A. Ali[1], Mohammad E. Biswas[1], Shakeel Ahmed[1]
Halim Hamid[1], Yuzo Sanada[1] and Toshikazu Yoneda[2]

1) Research Institute, King Fahd University of Petroleum & Minerals,
Dhahran 31261, Saudi Arabia
2) Petroleum Energy Center, Japan

* Corresponding author: Tel & Fax +966-3-860-3847, E-mail iwamatsu@kfupm.edu.sa

Key words: hydrodesulfurization, cobalt, clay

ABSTRACT

Co oxide loaded smectite clay minerals catalysts showed high hydrodesulfurization (HDS) activity of thiophene used as a model compound. Among these catalysts, HDS activity of Co oxide loaded porous saponite was higher than $CoMo/Al_2O_3$ which is known to be a highly active catalyst for HDS. Further, HDS activity was increased by the calcination up to 600°C before Co oxide loading. MgO content was decreased and CoO content was increased with increasing calcination temperature up to 600°C before Co oxide loading. These catalysts were characterized by means of XRD and XPS. The correlation between the characteristics of catalysts and their activities were discussed. It can be concluded that (1) there are two types of Co oxide species : between the clay layers due to ion exchange with Na : and at the edge of the clay layer due to ion exchange with Mg, and (2) the latter type is highly active for thiophene HDS reaction.

INTRODUCTION

Generally, HDS catalyst applied in industry are derives from oxides of an element of Group VIB (Mo or W) and Group VIII (Co or Ni) supported on Al_2O_3. Catalytic activity is supposed to be connected with the presence of Group VIB elements while Group VIII elements are believed to act as promoters. However, it has been reported recently that only one metal, such as Co or Ni, oxide loaded on some supports shows higher HDS activity than $CoMo/Al_2O_3$ catalysts. Duchet et al. has reported the high HDS activity of carbon-supported Co sulfide[1]. In another report, Kloprogge et al. prepared Ni sulfide supported on Al oxide pillared montmorillonite catalysts with a high thiophene HDS activity[2]. Further, Sychev et al. has reported that sulfided Cr oxide pillared montmorillonite, showed high activity for thiophene HDS and the consecutive hydrogenation of butenes[3]. In the above references, montmorillonite is a well known clay used as catalyst support. However, other smectite clay minerals (saponite, hectorite, stevensite and so on) have not been used as a support of HDS catalyst in spite of their similar feature. Therefore, in this study, Co oxide loaded smectite clays were prepared and HDS activity was evaluated. Moreover, the active sites of Co oxide loaded porous saponite, which showed the highest HDS activity, was also discussed.

EXPERIMENTAL

Smectite clay minerals were supplied by Kunimine Kogyo Co. Ltd. Co oxide was loaded on various clay minerals by means of ion exchange. Ion exchange method is as follows. Co nitrate solution ($Co(NO_3)_2 \cdot 6H_2O$ 29.0 g and distilled water 500 ml) was aged at 80 °C for 2 h. Then 10 g of clay was added to the solution and stirred at 80 °C for 1.5 h. After that, the solution was filtered. The residue thus obtained was washed with water and ethanol, and dried at 120 °C for 12 h and calcined at 400 °C for 12 h.

Hydrodesulfurization experiments were carried out in a pulse flow reactor. Prior to the activity test, the catalyst (0.1 g) was sulfided at 400 °C by using a mixed gas of 5 % H_2S in H_2 (60 ml/min., 2 kg/cm^2) for 2 h. Then, the temperature and the gas flow rate were changed to the reaction condition (H_2 60 ml/min., 2 kg/cm^2). Thiophene (0.3 μl) was injected and its conversion was measured by an on-line gas chromatograph, after the pulse reaction results had been stabilized.

RESULTS AND DISCUSSION

Table 1 shows thiophene HDS activity of Co oxide loaded smectite catalysts. As shown in this table, the smectite-supported catalysts showed higher activity than the Al_2O_3-supported catalyst (Co/Al_2O_3). Further, Co oxide loaded porous saponite showed the highest

thiophene conversion in the Co oxide loaded other smectite series and its activity was higher than that of CoMo/Al$_2$O$_3$ which is known to be highly active catalyst for HDS reaction. Then, the modification of porous saponite was carried out in order to improve the activity, further. In this experiment, the precalcination at various temperatures up to 700 °C in the air for 24 h before Co oxide loading was carried out. Table 2 shows the results. As shown in this table, thiophene HDS activity was increased with increasing precalcination temperature up to 600 °C. It is noted that the HDS performance is remarkable as low as 225 °C.

Table 3 shows properties of Co oxide loaded porous saponite catalysts. As shown in this table, the amount of MgO was decreased and that of CoO was increased with increasing precalcination temperature up to 600 °C. Therefore, it is supposed that the ion exchange of Na with Co takes place at first, then, ion exchange of Mg with Co takes place. It seems that the increase of Co oxide amount loaded on porous saponite by precalcination up to 600 °C is one of the reasons for HDS activity improvement. Phase transition from saponite to enstatite between 600 and 700 °C was observed by means of XRD. The drastic change of specific surface area by the precalcination at 700 °C may be due to this phase transition. It seems that the decrease of thiophene HDS activity at 700 °C is caused by the decrease of CoO amount due to this phase transition which was observed by the substancial reduction in specific surface area and XRD.

Table 1.   HDS activity of Co-smectite catalysts

Support	Loaded metal as oxide (wt%)	Thiophene conversion (%)		
		300°C	350°C	400°C
Montmorillonite	3.1	25.7	50.7	69.6
Saponite	5.0	73.1	78.5	86.2
Porous saponite	7.7	92.7	96.0	97.9
Hectorite	7.8	67.0	80.0	88.5
Stevensite	8.6	57.5	71.9	81.1
Al$_2$O$_3$	4.0	7.4	14.7	22.0
-	100[a]	7.2	11.5	17.2
Al$_2$O$_3$	Co 4wt% + Mo 15wt%	85.0	97.0	98.3

a) CoO was used as catalyst

Table 2.   HDS activity of Co-porous saponite catalysts

Sample	Precalcination Temperature (°C)	CoO (wt.%)	Thiophene conversion (%)			
			225	250	275	300°C
Porous saponite*	-	-	0.0	0.0	0.0	0.0
Co-porous saponite	-	7.7	28.2	73.5	81.8	92.7
	200	7.9	36.9	79.7	83.0	92.0
	300	8.6	33.5	85.5	90.7	94.6
	400	10.5	47.4	90.3	91.4	94.1
	500	13.5	56.4	92.2	92.8	95.1
	600	18.0	69.6	92.5	93.0	94.4
	700	9.3	10.7	25.1	40.0	52.1

* as received

Table 3   Properties of Co-porous saponite catalysts

Support	Precalcination Temperature (°C)	Composition (wt.%)					Surface Area (m^2/g)
		SiO$_2$	MgO	Al$_2$O$_3$	Na$_2$O	CoO	
Porous saponite*	-	49.2	29.2	4.5	3.0	-	514
Co-porous saponite	-	50.5	27.3	4.7	0.04	7.7	510
	200	46.9	24.9	4.5	0.05	7.9	415
	300	47.5	24.6	4.5	0.05	8.6	467
	400	46.9	22.9	4.5	0.05	10.5	402
	500	48.2	21.6	4.5	0.11	13.5	378
	600	44.9	16.9	4.3	0.08	18.0	342
	700	50.7	27.4	4.7	0.75	9.3	121

* as received

X 10^{-21}

[ln (1/1-x)] · atom-Co^{-1}
x : Conversion at 225°C

14
12
10
8
6
4
2
0

0   200   400   600   800

Precalcination temp. / °C
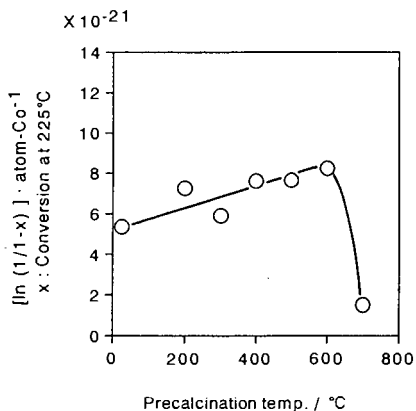
Fig. 1   [ln(1/1-x)] · atom-Co^{-1} as a function of precalcination
temperature of porous saponite

1.5

ln (1/1-x)
x : Conversion at 225°C

1

0.5

0

0   5   10   15   20

CoO / wt%
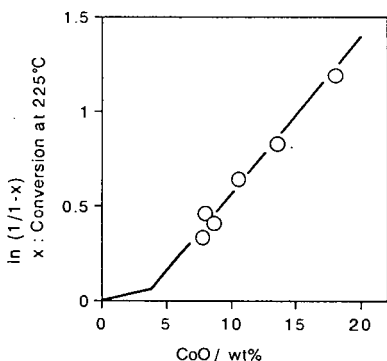
Fig. 2   ln(1/1-x) as a function of CoO content over porous
saponite

Co 2p$_{3/2}$

782.4

a)

782.9

b)

795 790 785 780 775
Binding Energy (eV)
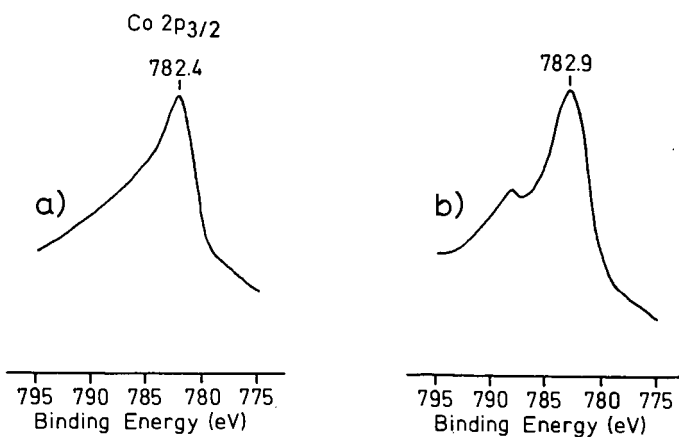
795 790 785 780 775
Binding Energy (eV)

Fig. 3   XPS spectra of Co-poropus saponite
a) Co-porous saponite (non calcined before Co oxide loading)
b) Co-porous saponite (calcined at 600°C before Co oxide loading)

545

On the basis of the assumption that thiophene HDS is first-order reaction, the relation between $[\ln(1/1-x)] \cdot$ atom-Co^{-1} and precalcination temperature of Co oxide loaded porous saponite was investigated. The HDS activity at 225 °C was used as x, because of the low conversion values. Fig.1 shows the results. The vertical axis means the activity index per Co atom. This value was increased with increasing precalcination temperature up to 600 °C. Therefore, it seems that the increase of activity with increasing precalcination temperature is not due to the increase of the equivalent Co species.

Assuming that ion exchange of Na with Co takes place at first, then, ion exchange of Mg with Co takes place, as mentioned before, the amount of CoO just after the ion exchange of all Na with Co was 3.9 wt% in case of Co oxide loaded porous saponite. Hence, good relation between the activity and CoO amount was obtained by using this point (3.9 wt%) as an inflection point (Fig.2). The slope after this inflection point was larger than before 3.9 wt.%. Therefore, it seems that Co species which is exchanged with Mg is more active than that which is exchanged with Na.

Fig.3 shows XPS spectra of Co oxide loaded porous saponite. XPS spectra pattern of Co oxide loaded porous saponite, which was non-calcined before Co oxide loading, was similar with Co_3O_4 type, and that of Co oxide loaded porous saponite, which was precalcined at 600 °C before Co oxide loading was similar with CoO type[4,5]. Therefore, Co species exchanged with Na, which were located between the clay layers, seem to be mainly Co_3O_4 type. On the other hand, Co species exchanged with Mg, inside the clay layer, seem to be mainly CoO type. It seems that the part of Mg which exist at the edge of the clay is easier to exchange with Co than with Mg located inside the bulk. Consequently, this CoO type species at the edge of the clay seems to show higher HDS activity than Co_3O_4 type species between the clay layers.

CONCLUSIONS

Co oxide loaded smectite catalysts showed high HDS activity of thiophene. Among these catalysts, HDS activity of Co oxide loaded porous saponite was higher than CoMo/Al_2O_3 which is known to be a highly active catalyst for HDS. Further, HDS activity is increased by the calcination before cobalt oxide loading. MgO content was decreased and CoO content was increased with increasing calcination temperature before Co oxide loading. It can be concluded that (1) there are two types of Co oxide species : between the clay layers due to ion exchange with Na : and at the edge of the clay layer due to ion exchange with Mg, and (2) the latter type is highly active for thiophene HDS reaction.

ACKNOWLEDGEMENTS

REFERENCES

1.   J. C. Duchet, E. M. van Oers, V. H. J. de Beer and R. Prins, J. Catal., **80**, 386 (1983).
2.   J. T. Kloprogge, W. J. J. Welters, E. Booy, V. H. J. de Beer, R. A. van Santen, J. W. Geus and J. B. H. Jansen, Appl. Catal., **97**, 77 (1993).
3.   M. Sychev, V. H. J. de Beer, R. A. van Santen, R. Prihod o a nd V. Goncharuk, Stud. Surf. Sci. Catal., **84**, 267 (1994).
4.   R. L. Chin and D. M. Hercules, J. Phys. Chem., **86**, 3079 (1982).
5.   Y. Okamoto, T. Imanaka and S. Teranishi, J. Catal., **65**, 448 (1980).