Korean J. of Chem. Eng., **11**(2), 111-118 (1994)

CHARACTERISTICS OF BIMETALLIC COBALT AND MOLYBDENUM CATALYSTS SUPPORTED ON ACTIVATED CARBON OR ALUMINA IN HYDRODESULFURIZATION

Sang-Jin Moon* and Son-Ki Ihm**

Department of Chemical Engineering, Korea Advanced Institute of Science and Technology, Taejon 305-304, Korea

(Received 18 July 1993 • accepted 28 October 1993)

Abstract—A series of bimetallic cobalt (Co) and molybdenum (Mo) catalysts supported on activated carbon or alumina were prepared, and their activities in thiophene hydrodesulfurization and ethylene hydrogenation were compared. The nitric oxide (NO) chemisorption and temperature programmed desorption (TPD) were used to characterize the nature of the synergistic active sites. Carbon supported catalysts also demonstrated the synergism in activity, which is well known for alumina supported catalysts. The specific activity and the adsorption stoichiometry of each site were interpreted from NO chemisorption. The possibility of NO as a probe molecule for sulfide catalysts was provided by the present work.

INTRODUCTION

Among the much effort to develop more effective hydrotreating catalysts, some laboratory studies were reported, in which carbon supported Co/Mo catalysts showed higher hydrodesulfurization (HDS) activities compared to conventional alumina supported catalysts [1, 2]. Moreover, in connection with a relatively weaker interaction of carbon support with active metal phases [3], it was also expected that the carbon supported Co/Mo catalytic system might be helpful in elucidating the nature of the synergistic active sites which arised from a kind of contact of Co and Mo atoms [4].

In our recent studies [5, 6] where Co or Mo was loaded as a single component on alumina or carbon, the carbon supported catalysts showed higher hydrogenation (HYD) activities as well as higher HDS activities. Temperature programmed reduction studies on a microbalance reactor indicated that Co or Mo oxide phases seemed to have less and more homogeneous interaction with the carbon support [5]. It was also thought that their sulfide phases had higher active site densities and higher specific activities per site on the carbon support when based on the nitric oxide (NO) titration [6]. Since NO could be used with other spectroscopic methods such as IR [7] and ESR [8, 9], it seemed to be more effective probe molecule than O_2 [10, 11].

In the present work as an extension of the previous study on the monometallic catalytic system [6], the catalytic nature of bimetallic Co and Mo catalysts supported on activated carbon or alumina was comparatively investigated using thiophene HDS and ethylene HYD reactions, and NO chemisorption and TPD techniques.

EXPERIMENTAL

1. Preparation of Catalysts

Two series of both Co and Mo containing catalysts supported on either a γ-alumina or an activated carbon were prepared by the incipient wetness technique. The pore volume and the surface area of the γ-alumina (Strem Chem. 13-2500) were 0.25 cm^3/g and 220 m^2/g (BET, N_2), respectively, and those of the activated carbon (Darco G-60) were 0.82 cm^3/g and 581 m^2/g, respectively.

The total number of Co plus Mo atoms loaded on the series I catalysts was nearly constant with the variation of the relative atomic ratio, $r = Co/(Co+Mo)$, from zero to one. The total atomic loadings for alumina supported catalysts and carbon supported catalysts were $(4.13 \pm 0.03) \times 10^{20}$ atom/gcat. and $(4.28 \pm 0.04) \times 10^{20}$ atom/gcat., respectively. They corresponded to

---

*Present Address: Division of Chemical Engineering, Korea Research Institute of Chemical Technology, Taejon 305-606, Korea

**To whom all correspondences should be addressed.

about 7 wt% based on pure Mo loading.

The series II catalysts were prepared by increasing the Co loading gradually from 0.3 to 4.2 wt% with a constant Mo loading, about 7 wt%. Most of the catalysts were manufactured by a simultaneous impregnation of both components, except for the catalysts prepared to investigate the effect of impregnation order. After impregnation, each catalyst was dried in an air-circulating oven at 110℃ for 24 hrs, and then kept in a desiccator. Calcination was carried out in the reactor in-situ under a nitrogen atmosphere before each reaction or chemisorption experiment.

The composition of these catalysts were estimated by atomic absorption spectroscopy. The surface area of each catalyst was measured using a conventional BET apparatus and a special in-situ quartz cell after the standard presulfiding step described below.

2. Activity Measurements

The activities of catalysts were measured in a stainless steel flow microreactor operating at atmospheric pressure. Before starting the reactions, each catalyst was presulfided at 400℃ in-situ by a 90% H_2/H_2S mixture.

Hydrodesulfurization of thiophene (Aldrich 99%+) was performed at 350℃ with the molar ratio of hydrogen to thiophene at 16. Reaction products were analyzed using a gas chromatograph equipped with a flame ionization detector and two columns packed with OV-101 and n-octane on Porasil C.

Hydrogenation of ethylene (Matheson CP grade) was carried out at 350℃ with the molar ratio of hydrogen to ethylene at 9. Reaction products were analyzed by a gas chromatograph using a column of Chromosorb 102.

3. NO Adsorption and TPD Measurements

NO chemisorption and NO TPD experiments were performed by a dynamic method in an once-through flow apparatus equipped with a thermal conductivity detector. First, each catalyst was presulfided in-situ just as in the cases of reaction experiments above and then purged with helium at 400℃ for 2 hrs. Pulses of NO gas were introduced at 30℃ from a 6-port valve with a loop volume of 0.13 cm^3 till the catalyst was saturated fully. If further NO adsorption does not take place, TPD experiment was carried out subsequently by monitoring NO desorption peak from this catalyst saturated with NO. The heating rate was 10℃/min over 30℃ to 400℃. Other details of experiments are shown in the literature [6].

RESULTS AND DISCUSSION

1. Activity Measurements

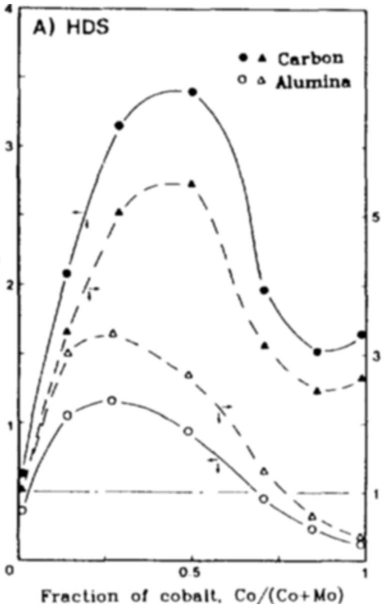

Fig. 1(A). Variation of HDS activity with the relative atomic ratio, r=Co/(Co+Mo).

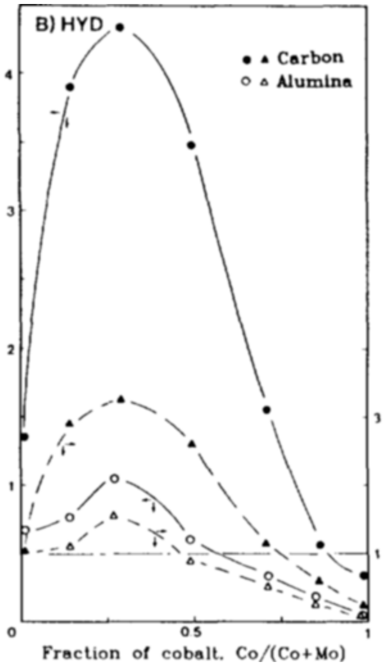

Fig. 1(B). Variation of HYD activity with the relative atomic ratio, r=Co/(Co+Mo).

The HDS and HYD activities for the series I catalysts are shown in Fig. 1 (A) and (B). The relative activity ratio on the right y-axis of these figures represents the relative value based on the activity of pure Mo catalyst (namely, the activity of each catalyst/the activity of pure Mo catalyst with $r=Co/(Co+Mo)=0$). It was apparent that coexistence of Co and Mo species on the same support had brought about some synergistic activities for both HDS and HYD reactions. The degree of the synergy was more prominent for the HDS reaction. This synergistic phenomenon on CoMo/Al_2O_3 catalysts is well known and has become the main issue of those many studies for this catalytic system [12-14]. The present result showed that the synergistic effect was conserved for the carbon supported catalysts also and furthermore the effect was more remarkable.

In the case of HDS reaction, the optimum atomic ratio for the CoMo/Al_2O_3 catalysts was located in the range, $0.15<r<0.4$, whereas that for the CoMo/C catalysts $0.3<r<0.6$. The Co/C catalysts showed the highest HDS activity but lower HYD activity among the monometallic Co or Mo catalysts supported on alumina or carbon in the previous study [6]. However, even when the relative activity ratio was based on the straight line connecting the two points, $r=0$ and $r=1$ assuming a simple mechanical mixture of pure Mo and pure Co, these optimum ranges did not shift much, i.e., only to $0.3<r<0.5$ for CoMo/C and $0.15<r<0.45$ for CoMo/Al_2O_3. Meanwhile, it was seen that the optimum ratio for the HYD reaction in CoMo/C catalysts was in the Mo-richer side ($0.15<r<0.45$) compared to the case of HDS reaction, and that the synergistic HYD effect for CoMo/Al_2O_3 catalysts was more or less poor. This kind of trend was sometimes reported for CoMo/Al_2O_3 catalysts and regarded as an evidence that the active sites for HDS reaction and HYD reaction were not identical [15, 16].

It was also noted that the synergistic HYD activity of CoMo/C catalysts was fairly on a high level and that the HDS activity of Co/C catalysts and the HYD activity of Mo/C catalysts could be maintained by a comparable or even higher level of the corresponding optimum synergistic activities of CoMo/Al_2O_3 catalysts. Recently, Topsoe et al. [4] proposed a "secondary support" concept, which described the MoS_2 crystallites as the secondary supports for better accommodation of Co atoms being the origin of the synergistic activity. Thus they suggested that more active synergistic sites could be developed on an another type of MoS_2 crystallite formed under such a high presulfiding temperature as about 1000℃ [17], which was thought to keep a weaker interaction with alumina. In this respect, it was thought that the carbon might act as an another

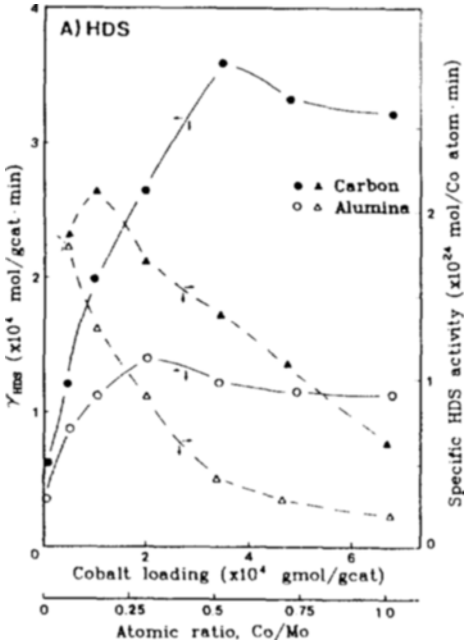

Fig. 2(A). Variation of HDS activity with the increase of cobalt loading.

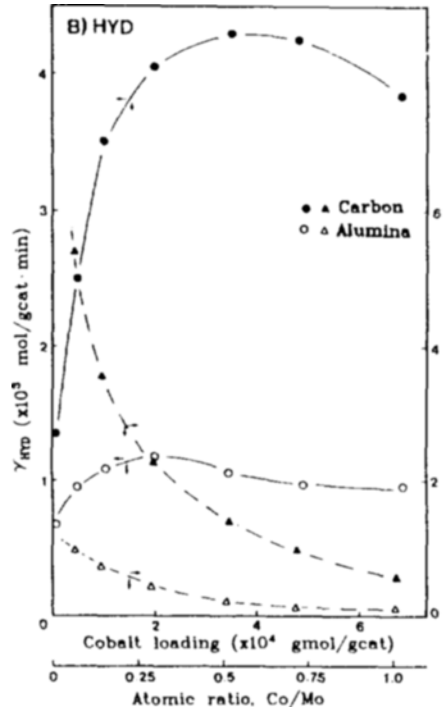

Fig. 2(B). Variation of HYD activity with the increase of cobalt loading.

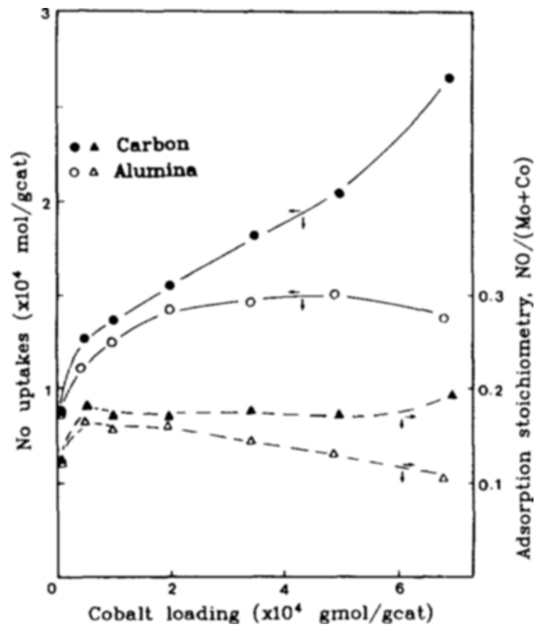

Fig. 3. Variation of NO uptakes and adsorption stoichiometry with the increase of cobalt loading.

type of support to tender better opportunities for higher activity to the MoS_2 crystallite or Co atom than alumina.

In order to investigate the effect of Co on the synergistic activity more closely, Co loading was increased in a progressive manner into the respective Mo/Al_2O_3 catalyst and Mo/C catalyst with a constant Mo loading, about 7.0 wt% (series II). The results are shown in Fig. 2 (A) and (B). The dotted lines (the right y-axis) represent average increases of activity per Co atom added when based on the respective pure Mo catalyst: (activity of each CoMo catalyst minus activity of Mo catalyst)/total number of Co atoms added. Apparent activities increased sharply at an initial small Co addition (All the active sites formed by interaction or coexistence of Co and Mo atoms and then contributing to the development of synergistic activities were called "synergistic sites".). Fig. 2 showed that the initially added Co atoms acted most effectively for formation of the synergistic sites for HDS and HYD reactions. It was however shown that more Co loading was needed for a full development of the synergistic sites for HDS reaction in CoMo/C catalysts. This observation seemed to imply that all the initially added Co atoms might not participate in formation of the synergistic sites for HDS reaction possibly due to lower Mo surface loading on carbon and thus another anchoring sites were available for Co species. The average Mo surface loading for the carbon supported catalysts was (1.082± 0.008) atom/nm^2 and that for the alumina supported catalysts was (2.493± 0.018) atom/nm^2. It was suggested that the synergistic sites showed different reactivity to each HDS reaction and HYD reaction, or different synergistic sites were effective for each reaction.

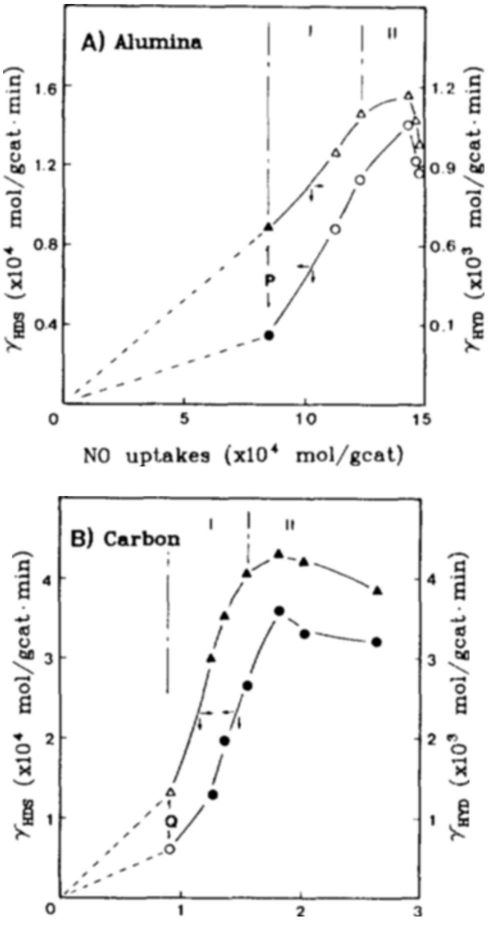

Fig. 4. Correlation of HDS and HYD activities with NO uptakes for (A) $CoMo/Al_2O_3$ catalysts and (B) CoMo/C catalysts.

2. Correlation of NO Uptakes and Catalytic Activities

Fig. 3 shows the variation of total NO uptakes at 30℃ and the adsorption stoichiometry, [NO/(Mo+Co)] with increasing Co content for each series of $CoMo/Al_2O_3$ and CoMo/C catalysts with a constant Mo content (series II). The HDS and HYD activities of

Table 1. Adsorption stoichiometries and specific HDS and HYD activities for each series of catalysts

Catalyst	Range or reference	NO/metal atom	r_{HDS}/NO (min^{-1})	r_{HYD}/NO ($\times 10^{-1} min^{-1}$)
Mo/Al_2O_3 (6.6 wt%)	point P of Fig. 4 (A)	0.11	0.41	0.79
Co/Al_2O_3 (0.3-4.1 wt%)	Table 1 of Ref. 6	0.32-0.05	0.12-0.32	0.04-0.09
CoMo/Al_2O_3 (series II)	Fig. 4 (A),	*	*	*
	Range I	0.16	0.98	0.88
	II	0.10	0.82	0.70
Mo/C (6.8 wt%)	point Q of Fig. 4 (B)	0.12	0.68	1.49
Co/C (0.3-4.2 wt%)	Table 1 of Ref. 6	0.75-0.33	1.01-0.69	0.24-0.14
CoMo/C (series II)	Fig. 4 (B),	*	*	*
	Range I	0.17	1.98	2.63
	II	0.19	1.22	1.46

*The figures represent the maximum attainable values in the corresponding ranges.

Table 2. Effects of presulfiding temperature and impregnation order on adsorption stoichiometry and specific HDS activity

Catalyst	Presulfiding temperature (℃)	r_{HDS} ($\times 10^4$ mol/gcat. min)	NO uptake ($\times 10^4$ mol/gcat.)	NO/metal atom	r_{HDS}/NO (min^{-1})
CoMo/Al_2O_3	300	0.89	1.02	0.15	0.87
	400	0.94	0.94	0.14	0.99
	500	0.95	0.91	0.13	1.05
CoMo/C	300	3.87	2.16	0.31	1.79
	400	3.40	2.10	0.30	1.62
	500	2.05	1.72	0.25	1.19
Co(Mo)/Al_2O_3	400	0.78	0.89	0.12	0.88
(Co)Mo/Al_2O_3	400	1.05	0.92	0.13	1.14
Co(Mo)/C	400	3.94	2.46	0.35	1.60
(Co)Mo/C	400	2.00	1.13	0.16	1.77

( ) The components in the parentheses indicate first-impregnated ones.

Fig. 2 have been correlated with these total NO uptakes to result in the relationship in Fig. 4. The specific activity per adsorption site (r_{HDS}/NO or r_{HYD}/NO) could be obtained from the slope of each point on Fig. 4. The adsorption stoichiometry which is the measure of the adsorption site density and the specific activity per adsorption site are summarized in Table 1. This scheme was rather satisfactory for the monometallic Co or Mo catalysts supported on alumina or carbon [6], which demonstrated that NO probe molecule might titrate various kinds of active sites including general anion vacancy sites and even the oxygen specific sites. If the synergistic sites were also titrated by NO probe molecule (this might be evidenced from the NO TPD profiles later), some informations regarding the synergistic sites were available from Table 1.

The highest apparent HDS and HYD activities of CoMo/Al_2O_3 catalysts have been about 4 times and 1.8 times higher than those of the 6.6 wt% Mo/Al_2O_3 catalyst, respectively as shown in Fig. 2. However the adsorption site density of these catalysts, which was assumed to be proportional to the active site density, increased to only about 1.5 times compared to that of 6.6 wt% Mo/Al_2O_3 catalyst as shown in Table 1. By addition of Co into the 6.6 wt% Mo/Al_2O_3 catalyst, the specific activities per site have increased to about 2.5 times for the HDS reaction and 1.1 times for the HYD reaction, respectively. This indicated that the synergistic sites for the HDS reaction did not play a role fully for the HYD reaction.

The overall trend for the CoMo/C catalysts was not so much different from that for the CoMo/Al_2O_3 catalysts. Both the number of active sites and the intrinsic activity per site increased with addition of Co, but the former to a less degree than the latter. The specific HDS and HYD activities have increased to about 2.9 times and 1.8 times of those for 6.8 wt% Mo/C catalyst, respectively. The synergistic sites developed on the carbon seemed to have higher specific HDS activity than on alumina, and showed a considerable activity for the HYD reaction also.

3. Effects of Presulfiding Temperature and Impregnation Order

In order to investigate the effects of preparation variables, the presulfiding temperature was changed and some sequentially impregnated catalysts were prepared. The HDS activities and the NO chemisorption amounts were measured with variation of these two variables and then correlated with each other to obtain the active site density and the specific activity per site as shown in Table 2. All these catalysts had nearly the same Mo and Co loadings as those catalysts with r=Co/(Co+Mo)=0.5 in Fig. 1. Sequentially impregnated catalysts were calcined intermittently at 400 ℃. The component which was impregnated first is shown in the parenthesis of the notation in Table 2.

The apparent HDS activity for CoMo/Al_2O_3 catalyst was not affected much by variation of the presulfiding temperature. However the variation trend was of the slight decrease in the active site density but a little increase in the specific activity per site with increasing temperature from 300℃ to 500℃. The CoMo/C catalyst indicated a rather thermal instability by showing a rapid decrease in activity with increasing presulfiding temperature from 400℃ to 500℃. This decrease mainly due to sintering resulted in decrease in both of active site density and specific activity per site, as in the case of Mo/C catalysts [6].

The Co-first impregnated catalyst showed higher activity than the Mo-first impregnated catalyst for alumina support, and vise versa was true for carbon support. It was thought that a considerable amount of Co might be still available on alumina support for formation of the synergistic sites with subsequently impregnated Mo even though a fraction would have been masked by alumina (possibly through $CoAl_2O_4$-like structure) [5]. It is shown from Table 2 that the difference of apparent activities of carbon supported catalysts with variation of impregnation order was mainly due to the difference in the active site densities with the following order, contrary to the results of alumina supported catalysts: Mo-first>simultaneous≫Co-first. This trend in carbon supported catalysts is in line with weaker interaction of carbon with metallic species than alumina support. The synergistic activity must be directly related to the effective use of Co.

4. TPD Profiles of CoMo/Al_2O_3 and CoMo/C Catalysts

4-1. CoMo/Al_2O_3

Fig. 5 (A) shows the variation of NO TPD profiles with increasing Co content on the 6.6 wt% Mo/Al_2O_3

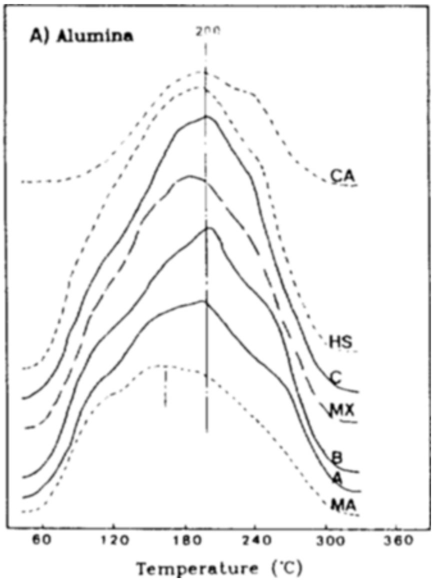

Fig. 5(A). Variation of NO TPD profiles with the increase of cobalt loading in CoMo/Al_2O_3 catalysts.
MA (6.6 wt% Mo/Al_2O_3), CA (4.1 wt% Co/Al_2O_3), A (Co 0.57 wt%), B (Co 2.0 wt%), C (Co 4.0 wt%), MX (mixture of 6.6 wt% Mo/Al_2O_3 and 2.0 wt% Co/Al_2O_3), HS (Harshaw HT-400E)

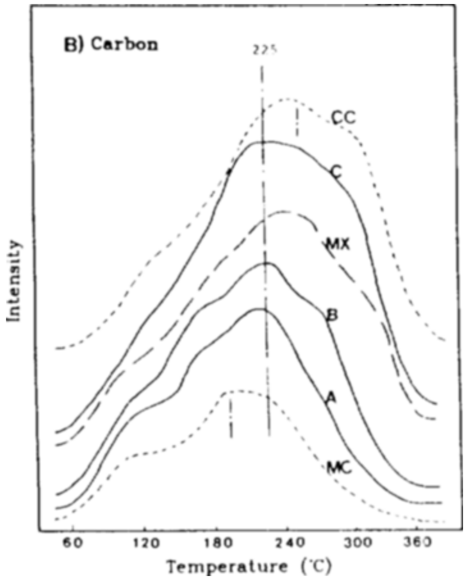

Fig. 5(B). Variation of NO TPD profiles with the increase of cobalt loading in CoMo/C catalysts.
MC (6.8 wt% Mo/C), CC (4.2 wt% Co/C), A (Co 0.6 wt%), B (Co 2.1 wt%), C (Co 4.1 wt%), MX (mixture of 6.8 wt% Mo/C and 2.1 wt% Co/C)

catalyst (series II). When Co was added by a small amount, a rapid increase of HDS activity was observed [Fig. 2 (A)] and a rather sharp peak developed around 200℃ (profile A). This peak increased more sharply with further Co addition (profile B). There still existed the characteristic shoulders (at about 120℃, 165℃) of the Mo/Al_2O_3 catalyst in these cases, but their relative intensities decreased with Co addition. Furthermore, the shape and the position of this peak around 200℃ on the profile B were apparently different from those of the profile MX which was obtained from a mechanical mixture of 6.6 wt% Mo/Al_2O_3 catalyst and 2.0 wt% Co/Al_2O_3 catalyst with the same Mo and Co contents as the catalyst for the profile B. Therefore this sharp peak developing around 200℃ on the profile A and B was thought to be a new kind of peak resulting from the interaction between Co and Mo, and assigned to the synergistic site. As the Co loading was further increased (profile C), the peak became much broad and the characteristic shape for Co/Al_2O_3 catalyst (profile CA) was introduced into the profile. It was noted here that the profile C was more or less similar to the profile HS for the commercial catalyst [Harshaw HT-400E, CoMo (2.7/10 wt%)/Al_2O_3].

4-2. CoMo/C

Fig. 5 (B) shows the variation of NO TPD profiles as Co is added on the 6.8 wt% Mo/C catalyst (series II). A new peak developed around 225℃ with increasing Co content (profile A and B), which was neither the characteristic peak for Mo/C catalyst (profile MC) nor that for Co/C catalyst (profile CC). Also the shape of the profile B was different from the profile MX which was obtained from the mixture of 6.8 wt% Mo/C catalyst and 2.1 wt% Co/C catalyst with the same metal contents as the catalyst with the profile B. This new peak around 225℃ could be assigned to the synergistic site formed by interaction of Co and Mo species on carbon as in the case of alumina. With further increase of Co, a broad shape with the characteristic profile of the Co/C catalysts developed (profile C).

It should be noted that the peak position of the synergistic site formed on carbon (around 225℃), which showed the highest specific HDS activity, was located between that for the synergistic site on alumina (around 200℃) and that for the Co site on the Co/C catalyst (around 250℃). Whatever the exact nature of the synergistic sites [18], these sites were shown to be titrated by the NO probe molecule.

CONCLUSION

The major conclusions found or suggested by the present study are as follows:

1. New synergistic active sites were developed on the carbon supported Co/Mo catalysts due to the interaction between Co and Mo. These synergistic sites showed different reactivities in each of thiophene HDS reaction and ethylene HYD reaction.
2. The specific activities and the site densities based on the NO titration were much higher on carbon than on alumina.
3. The role of cobalt was mainly to increase the specific HDS activity, and each cobalt-related site seemed to be titrated by the NO probe molecule.

REFERENCES

1. Duchet, J. C., Van Oers, E. M., de Beer, V. H. J. and Prins, R.: *J. Catal.*, **80**, 386 (1983).
2. de Beer, V. H. J., Duchet, J. C. and Prins, R.: *J. Catal.*, **72**, 369 (1981).
3. Ledoux, M. J., Michaux, O. and Agostini, G.: *J. Catal.*, **102**, 275 (1986).
4. Topsoe, H., Clausen, B. S., Topsoe, N. Y. and Pederson, E.: *Ind. Eng. Chem. Fundam.*, **25**, 25 (1986).
5. Moon, S. J., Jeon, G. S. and Ihm, S. K.: *Hwahak Konghak*, **26**(6), 617 (1988).
6. Moon, S. J. and Ihm, S. K.: *Appl. Catal.*, **42**, 307 (1988).
7. Topsoe, N. Y. and Topsoe, H.: *J. Catal.*, **84**, 182 (1983).
8. Moon, S. J.: Ph.D. Dissertation, KAIST, Seoul, Korea (1988).
9. Derouance, E. G., Pederson, E., Clausen, B. S., Gabelica, Z. and Topsoe, H.: *J. Catal.*, **107**, 587 (1987).
10. Bachelier, J., Duchet, J. C. and Cornet, D.: *Bull. Soc. Chim. Belg.*, **90**, 1301 (1981).
11. Vissers, J. P. R., Bachelier, J., ten Doeschate, H. J. M., Duchet, J. C., de Beer, V. H. J. and Prins, R.: Proc. 8th Int. Congress on Catal., vol. 2, p. 387, Berlin, West Germany (1984).
12. Schuit, G. C. A. and Gates, B. C.: *AIChE J.*, **19**, 417 (1973).
13. Hagenbach, G., Courty, P. H. and Delmon, B.: *J. Catal.*, **31**, 264 (1973).
14. Farragher, A. L. and Cosse, P.: Proc. 5th Int. Congress on Catal., p. 1301, Miami Beach, U. S. A. (1972).
15. Hargreaves, A. E. and Ross, R. H.: Proc. 6th Int. Congress on Catal., p. 937, London, U. K. (1976).

16. Lopetz, R.: *Collec. Czecho. Chem. Commun.*, **48**, 2269 (1983).
17. Candia, R., Sorensen, O., Villadsen, J., Topsoe, N. Y., Clausen, B. S. and Topsoe, H.: *Bull. Soc. Chim. Belg.*, **93**, 763 (1984).
18. Clausen, B. S., Niemann, W., Zeuthen, P. and Topsoe, H.: ACS Meeting, p. 208, Boston, U. S. A. (1990).