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Hydrotreating of residue oil over aluminum borate-supported CoMo and NiMo catalysts

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Abstract

A series of aluminum borates with various Al/B ratios were prepared by the precipitation method. These materials were used as the support of CoMo and NiMo catalysts. Hydrotreating of heavy Kuwait atmospheric residuum were carried out in a bench scale trickle bed reactor at 663 K and 7582 kPa. These catalysts were more active than the alumina-supported catalysts. An optimal boria content which gave the highest HDS and HDM activities was located around 4 wt% for both CoMo and NiMo catalysts. In addition, CoMo catalyst was always more active than NiMo catalyst provided the same boria content for both HDS and HDM reactions.

Keywords: Aluminum borate; Hydrodesulfurization; Hydrodemetalation; Hydrotreating; Molybdenum catalyst

1. Introduction

With sweet crudes in short supply and with increasing oil prices, hydrotreating of heavy residual oils becomes more attractive, resulting in even more stringent demands on the catalyst employed in the process [1]. Several authors [2,3] have reported that hydrotreating of heavy oils is generally carried out over alumina-supported catalysts containing combinations of cobalt and molybdenum salts or nickel and molybdenum salts where cobalt and nickel play an important role in promoting the active sites of molybdenum-based sulfide catalysts. Changing the nature of the carrier is an interesting line of research to achieve more thorough hydrotreating reactions. A detailed review of support effects on hydrotreating catalysts have been published [4]. Mixed oxides, particularly alumina-based binary oxides, are well suited catalytic materials [5]. However, less attention has been devoted to aluminum borate (AB). In the previous studies [6–8], aluminum borate was reported to be a good support material for HDS reactions. The aim of this study was on hydrotreating reactions of heavy residue oils over CoMo and NiMo/AB catalysts. Conventional CoMo/Al_2O_3 and NiMo/Al_2O_3 catalysts were included for comparison. The chemical and physical properties of these catalysts were characterized to obtain the correlation with their catalytic properties. This study mainly focused on the effects of boria content and the Co and Ni promoter.

2. Experimental

Aluminum borate supports were prepared from the common solution of aluminum nitrate and boric acid, using an ammonium hydroxide solution (pH 10) as a

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precipitant. By altering the relative amount of aluminum nitrate and boric acid, a desired AB composite could be obtained. After calcination, dry clump AB was well grinded, and then extruded to 15.8 mm cylindrical extrudates. The wet extrusion was dried in air at room temperature, dried at 393 K overnight, and calcined at 773 K for 6 h. CoMo/AB and NiMo/AB catalysts were prepared by incipient wetness impregnation of supports in the form of extrusion with the solutions of $(NH_4)Mo_7O_{24}\cdot 4H_2O$ and $Co(NO_3)_2\cdot 6H_2O$ or $Ni(NO_3)_2\cdot 6H_2O$, respectively, in distilled water. Mo was added first, and catalyst was dried and calcined before addition of Co or Ni. The first impregnation (Mo) was dried at atmospheric pressure and room temperature overnight and at 393 K for 6 h, and then calcined at 773 K for 6 h. The second impregnation (Co or Ni) was dried and calcined in the same way. The MoO_3 content was 12 wt% and Co/Mo or Ni/Mo atomic ratio was 0.6. The sample was then sulfided with dimethyl disulfide in the diesel oil. For convenience, we denote CoMo/aluminum borate and NiMo/aluminum borate as CoMo/AB*x* and NiMo/AB*x*, respectively, where *x* represents the Al/B atomic ratio.

Hydrotreating of Kuwait residue oil was conducted in a stainless steel cocurrent downflow trickle bed reactor. The feedstock used was Kuwait atmospheric tower bottom (ATB) residue oil. The characteristics of oil is presented in Table 1. The feed was passed through the reactor (0.5 ml/min) at 663 K, 7.6 MPa, and WHSV=1.5. The hydrogen flow rate was 300 ml (STP)/min, which is high enough to prevent readsorption of H_2S in oil and to prevent inhibition effect of H_2S on hydrotreating reactions.

In order to promote the activity of catalyst, presulfiding treatment was necessary. The diesel oil feedstock, which was doped to 1 wt% sulfur by addition of dimethyl disulfide, was passed through the reactor with the following temperature program: heated from room temperature to 448 K and kept for 2 h; then increased to 523 K and held for 4 h; after that, increased to 598 K and retained until sulfiding completely. The weigh hourly space velocity (WHSV) of diesel oil was 2.4. The hydrogen flow rate was 300 ml (STP)/min and the pressure was maintained at 2757 kPa. The sulfur content of the liquid product was measured by a X-ray fluorescence spectrometer (Oxford, Lab-X2000), and the metal (vanadium and nickel) contents were measured by ICP-AES (Jarrell-Ash Model 1100). The detailed experimental procedure has been reported in the previous reports [6–8].

Table 1
Characteristics of Kuwait residue oil

O_{API}	16.8
Sulfur (wt%)	3.72
Nitrogen (wt%)	0.21
Conradson carbon residue (wt%)	10.1
Nickel (ppm)	14.0
Vanadium (ppm)	53.0
H/C ratio	0.146
ASTM distillation	
5%	554 K
10%	584 K
20%	633 K
30%	673 K
40%	704 K
50%	743 K
60%	794 K
65%	811 K

3. Results and discussion

3.1. Sulfur removal

Since all the catalysts tested were advanced HDS catalysts, under normally recommended operation conditions all samples gave greater than 90% conversion of the sulfur compounds to hydrogen sulfide. In order to magnify any difference in activity, the tests were carried out under condition that was less severe for the catalysts than those in commercial practice. Under the conditions used in this study, the different catalysts showed differences of conversions varying over the range 30–90%. In order to investigate the influence of boria content on HDS activity, all the correlations are plotted against B_2O_3 content. The percentages of sulfur removal at 60 h time on stream were arbitrary chosen for comparison. However, the same trends holds at other times on stream. Fig. 1 demonstrates HDS activities as a function of B_2O_3 contents of CoMo/AB and NiMo/AB catalysts. The results revealed that the aluminum borate-supported catalysts were more active than the alumina-supported (boron-free) catalysts and the optimum B_2O_3 content

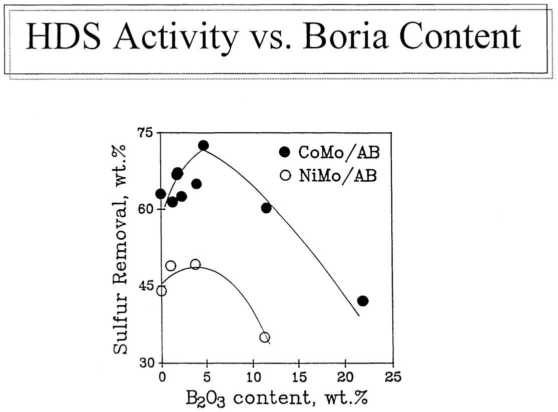

Fig. 1. The effect of boria content on HDS activity.

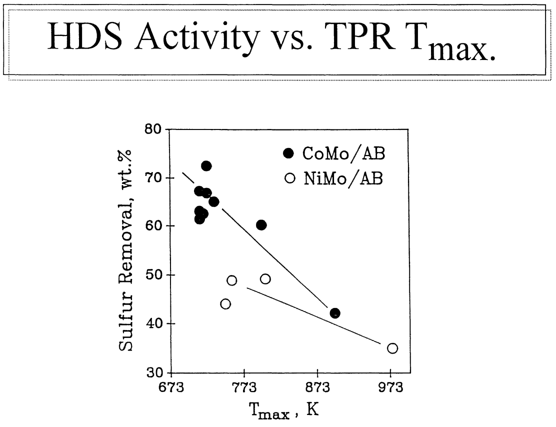

Fig. 2. HDS activity vs. TPR T_{max}.

is in the vicinity of 4 wt%. The high HDS activities of AB-supported catalysts can be ascribed to the presence of highly dispersed boron on the support surface. Several concurrent effects on these catalysts may facilitate their HDS activities: the carriers can actually enhance the cracking or hydrocracking abilities through their own high acidities than pure alumina; on the other hand, the carriers can increase the metal dispersions and hydrogenation abilities. Since the electronegativity of boron (2.0) is higher than that of aluminum (1.5), and thus, B–OH has a stronger acidic strength than the Al–OH on the surface of aluminum borate support. This infers that $Mo_7O_{24}^{-6}$ bonds with B^{3+} stronger than with Al^{3+}. Therefore, it is speculated that more Co–Mo–O or Ni–Mo–O groups existing on the surface of aluminum borate than on the surface of alumina. This would produce more HDS active sites, generate higher hydrogenation capability, and make higher HDS activity. The low HDS activities for high boron content catalysts are because of lower surface areas and higher reducibility surroundings. In addition, the overdose of boron would form bulk B_2O_3 which could be leached out in the presence of steam. The percentage of sulfur removal of CoMo/AB catalysts are always greater than those of NiMo/AB ones. This can be attributed to the stronger interactions between NiMo and supports than those of CoMo and supports. Molybdenum on the AB supports, particularly that bonded to B–OH groups, is more easily sulfided/reduced compared to that on Al_2O_3 support. However, due to the stronger interaction between MoO_3 and the support with excess B_2O_3 content, the MoO_3 would become more difficult to reduce/sulfide and results in the decrease of activity.

It has been reported that the reducibility of CoMo oxide or NiMo oxide can influence the characteristics of their sulfided compound. Therefore, it is meaningful to find a possible correlation between T_{max} of the TPR spectra and HDS activity of the catalyst. The TPR spectra have been reported in the previous reports. The HDS activity versus TPR T_{max} is presented in Fig. 2. The results showed that HDS activity is strongly influenced by the TPR T_{max}. The higher the T_{max} is, the lower is the HDS activity. The TPR patterns showed that when B_2O_3 content is greater than 10 wt%, the interaction between MoO_3 and AB support becomes very strong. A strong interaction decreases the covalent character of the Mo–S bond and results in the reduction of anion vacancy. The anion vacancies on Mo are the active sites for HDS reaction; in other words, the strong support interaction hinders the formation of active sulfide phase and results in poor HDS activity.

To further investigate the effect of Mo on HDS activity, the surface coverage of Mo on the support was used for comparison and the result was presented in Fig. 3. The definition of surface coverage is the number of Mo atoms over the catalyst surface area. Although it is important to know the fraction of transition metal atoms present as surface or bulk compounds, the exact number of active sites are not known for the CoMo/AB and NiMo/AB catalysts, and some monolayer Mo is not on effective active sites. It is assumed that all Mo ions are active on the catalysts.

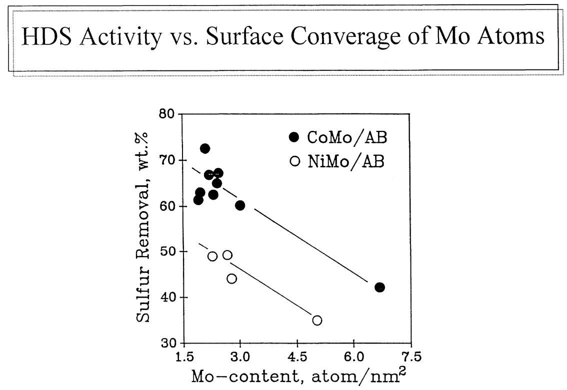

Fig. 3. HDS activity vs. surface coverage of Mo atoms.

Since Co or Ni was generally recognized as a promoter, the quantity of Co or Ni was not counted for active metals; i.e., the calculated surface coverage only included Mo atoms. Fig. 3 shows that the HDS activities of CoMo and NiMo/AB increased with decreasing the surface coverage of Mo on the support. This implies that the greater surface area possesses more opportunity to provide better dispersion of active sulfide phase and results in a higher HDS activity.

One interesting feature of Fig. 3 is that the obtained result is more similar to Mo/SiO_2 than to Al_2O_3 [9,10]. This can be interpreted on the basis of support effect: probably the incorporated boron, whether the amount of boron was much or less, transferred the characteristics alumina and resulted in the characteristics of aluminum borate rather similar to silica ones.

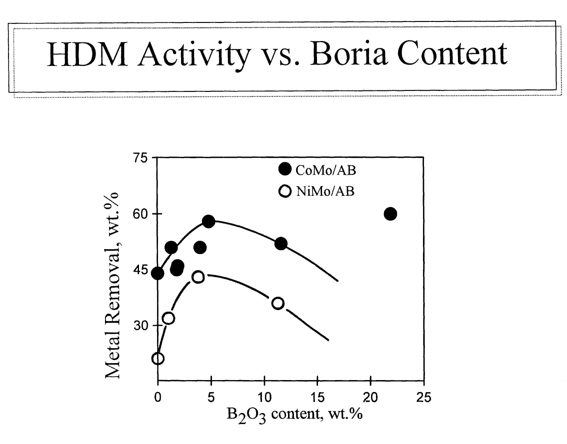

Fig. 4. The effect of boria content on HDM activity.

3.2. Metal removal

Fig. 4 shows that the boria content of the catalyst could affect the HDM activity. The aluminum borate-supported catalysts were more active than the alumina-supported (boron-free) ones. In addition, the HDM activities of CoMo/AB catalysts were always greater than those of NiMo/AB, proving the same boria content. It should be noted that the sulfur contents are in wt%, but the metal contents (Ni and V) are in ppm. The highest HDM activity is also located around 4 wt% B_2O_3 content.

4. Conclusions

The hydrotreating results revealed that the AB-supported CoMo and NiMo catalysts were more active than those of Al_2O_3-supported ones. This can be rationalized by the presence of boron. Several concurrent effects in AB-supported catalysts may facilitate their hydrotreating activities: enhance the dispersion of active sulfide phase; increase the hydrogenation ability and the amount of active site. All are beneficial for hydrotreating. In addition, CoMo catalysts were more active than NiMo catalysts for both HDS and HDM reactions. The hydrotreating activities of CoMo/AB and NiMo/AB are a function of boria content. An optimum B_2O_3 content which gave the highest activity was observed around 4 wt%.

Acknowledgements

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