TUNGSTEN INCORPORATED CoMo/γ-Al_2O_3 HYDRODESULFURIZATION CATALYST

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ABSTRACT

The promotional effect of tungsten in the CoMo / γ- Al_2O_3 *catalyst was studied for series on tungsten incorporated CoMo /* γ- Al_2O_3 *catalysts with different content of tungsten. Two series of the catalysts were prepared by changing the impregnation order of cobalt and tungsten onto a base Mo /* γ- Al_2O_3 *catalyst. Impregnation of tungsten was achieved under the condition that the pH of an aqueous impregnation solution of tungsten anion was controlled to 9.5. The hydrodesulfurization (HDS) activity of the studied catalysts were evaluated by thiophene HDS reaction. The dependence of catalytic activities on tungsten content showed initially an increase and subsequent decrease with increasing tungsten content. The maximum promotion of HDS activity occurred at low content of tungsten corresponding to 0.5 wt% regardless of the impregnation order of tungsten and cobalt. In general, the catalysts prepared by impregnating tungsten onto the CoMo /* γ- Al_2O_3 *catalyst showed higher activities than the catalysts prepared by impregnation tungsten onto Mo /* γ- Al_2O_3 *catalyst prior to impregnation of cobalt.*

INTRODUCTION

Alumina-supported Co (Ni)- Mo (W) sulfide pairs are the most widely employed catalysts in petroleum oil hydrotreating processes. However, there have been various attempts to improve the performance of the conventional catalysts by applying novel preparation methods, replacing the conventional promoters with other metals, adding a third element to the catalysts, or adopting a new support material instead of γ- Al_2O_3.

A number of studies on the use of some transition metals like Ti(1-3), Ni (4-6), Ru (7,8), Zn (1,2,9) and Fe (1,10-12) as promoters or additives to Al_2O_3 supported Mo or CoMo catalysts have been carried out in an attempt to developed new catalytic systems with improved hydrotreating performance.

Recently, Lee D.K. et al (13,14) reported that the introduction of a small amount of tungsten into a commercial catalyst CoMo / γ- Al_2O_3 brought about beneficial effects on the catalyst performance for hydrodesulfurization, asphaltene conversion and conversion of heavier to lighter oil fractions during the high pressure hyrdotreatment of an atmospheric residual oil feed. The tungsten added to the CoMo / γ- Al_2O_3 was expected to play a certain role in promoting the catalytic activities of the catalyst.

In this paper, we reported the effect of the amount of tungsten incorporation and the impregnation order of tungsten on the catalytic activities of the tri-metallic catalysts and suggest an optimum tungsten content.

EXPERIMENTAL

Preparation of catalysts

Six base γ-Al_2O_3 supported catalysts of compositions Mo (15 wt%), Co (4.6 wt%) Mo (15 wt%) were first prepared by incipient wetness impregnation of γ-Al_2O_3 with solutions of ammonium hepta-molybdate tetrahydrate (Fluka, $(NH_4)6Mo_7O_{24}.4H_2O$, 99+%), ammonium metatungstate (Fluka, $(NH_4)6H_2W_{12}O_{40}$, 97+%) and cobalt nitrate hexahydrate (Fluka, $Co\ (NO_3)2.6H_2O$) as required.

The γ-Al_2O_3 used as a support whose physical properties are as follows: surface area, 280 m2/g; pore volume, 0.55 cm3/g and mean pore diameter, 167Å.

To prepare CoMo or W Mo catalysts, molybdenum or tungsten was first impregnated. After the impregnation of each metal precursor, the catalyst was dried at 110° C for 12 h and then calcined in dry air at 500° C for 6 h as a routine preparation procedure.

Two series of γ-Al_2O_3 supported tri-metallic catalysts with different contents of tungsten (0.25, 0.5, 1,and 2 wt%) were prepared varying the order of tungsten impregnation. Series of catalysts denoted as CWM were prepared by impregnating tungsten onto the base catalyst Mo (15-wt%) before impregnation of cobalt. The other series of catalyst denoted as WCM were obtained by impregnation of tungsten onto Co (4.6 wt%) Mo (15 wt%).

The tungsten content of the impregnation solutions was simply increased with respect to the fixed amount of Mo or CoMo. When preparing tungsten-incorporated catalysts, the pH of the solution of ammonium metatungstate was adjusted to 9.5 by adding a diluted NH_4OH solution. However, the pH of the impregnating solution of cobalt nitrate or ammonium molybdate was not adjusted. The pH control of tungsten solution was based on reports that the monomeric species of tungsten anion WO_4^- predominated in alkaline solution of pH around 9.5 and that a more flat impregnation profile of tungsten across the alumina support was achieved from high pH solutions. (15)

Presulfiding of the Catalyst

The fresh catalyst was charged in the HDS reactor after drying at 383 K for 2 h. catalyst presulfiding was accomplished by a solution of 1.2 vol% of thiophene in one liter of gasoil. The first 4 hours of presulfiding was carried out at 21 bar, 204° C and LHSV of 3 h^{-1}. The next step in the catalyst activation was continued for 16 hours using the following operating conditions; temperature of 300° C, LHSV of 1 h^{-1}, pressure of 21 bar and hydrogen to oil ratio of 200 l/l.

Hydrodesulfurization Experiments

The hydrodesulfurization experiments were performed in a laboratory continuous high-pressure unit. The unit consists of feed pump, reactor, separator and cooler.

Hydrodesulfurization of gasoil (supplied by Baiji Refinery) was carried out using prepared CWM and WCM catalyst. The temperature range varied from 573 to 648 K over liquid hourly space velocity from 1 to 4 h^{-1}. The pressure and hydrogen feed ratio was kept constant at 25 bar and 200 l/l, respectively. The properties of gasoil are given in table below.

Table 1, Properties of straight run gasoil supplied from Baiji-Refinery

Test	Value
Specific gravity at 15.6° C/15.6° C	0.8
Sulfur content, wt%	1.00
Pour point, ° C	-10
Flash point, ° C	65
ASTM distillation, 20% distilled at ° C	340

Test Methods

Sulfur contents of both feedstock and hydrodesulfurized products were determined using standard test methods IP 63/55.

RESULTS AND DISCUSSIONS

Effect of Tungsten on the Catalyst Activity

As shown in figure 1, HDS activity of both CWM and WCM series catalysts increase sharply with lower loading of tungsten but decrease with further increase in tungsten content. The maximum increases in the HDS activity are observed at 0.5 wt%. It is observed that the increase in HDS activity is higher for the WCM catalysts than for the CWM catalysts.

These results show that the HDS activity of the W-incorporated catalysts increased or decreased depending on their tungsten composition. This plays a role of promoter. The enhancement in catalytic activities by the tungsten incorporation is projected by the increase in the frequency factor without significant changes in the activation energy. It is strongly suggesting that the promotion by tungsten incorporation results mainly from an increase in the number of active sites rather than a change in the nature of active sites.

It is found from figure 1 that WCM series catalysts result in higher activity in HDS than CWM series catalysts at the same condition. According to the "Co-Mo-S" model proposed by Topsoe et al (16,17), the active metal sulfide phases in the two catalysts of CoMo / γ-Al_2O_3 and CoW / γ-Al_2O_3 would be Co-Mo-S and Co-W-S, respectively. The thiophene HDS activity of CoMo / γ-Al_2O_3 were higher than those of CoW / γ-Al_2O_3 are in agreement with our results.

Effect of Operating Conditions on Catalyst Activity

The effect of LHSV at different temperatures on the percentage of sulfur removal from gasoil using prepared W-CoMo / γ-Al_2O_3 catalyst of composition W (0.5 wt%), Co (4.6 wt%), Mo (15 wt%) are shown in figure 2. The desulfurization increases with increasing temperature and decreasing LHSV. These results are in agreement with other studied on the hydrodesulfurization of gasoil. (18,19)

The HDS reaction is a function of space-time. Therefore, increasing LHSV will shorten the space-time leading to decrease in the extent of sulfur removal. The increasing of sulfur removal at higher reaction temperatures may be due to the fact that at high reaction temperatures, molecules are decomposed to smaller molecules, which can more easily diffuse to the catalyst micro-pores and reach the active sites where the desulfurization reaction mainly occurs. But the upper temperature level is limited by the undesirable side reaction such as cracking reactions.

Kinetic of Hydrodesulfurization Process

Second order kinetic model used to fit the data obtained. Plotting $1/CSout - 1/C_{Sin}$ vs. 1/LHSV at different temperatures gives straight lines with slopes equal to the rates constant as shown in figure 3.

CONCLUSIONS

HDS activity of the W-incorporated CoMo / γ-Al_2O_3 catalyst was promoted or suppressed depending on the amount of tungsten. The promotional effect was observed for the catalysts containing a relatively low content of tungsten whereas the catalysts containing a higher content of tungsten showed an inhibition effect.

The maximum activity promotion occurred at a low content of tungsten corresponding to 0.5 wt%. The catalysts WCM prepared by impregnating tungsten onto CoMo / γ-Al_2O_3 resulted in higher activities than did the catalysts CWM prepared by impregnation tungsten onto Mo/γ-Al_2O_3 followed by impregnation of cobalt.

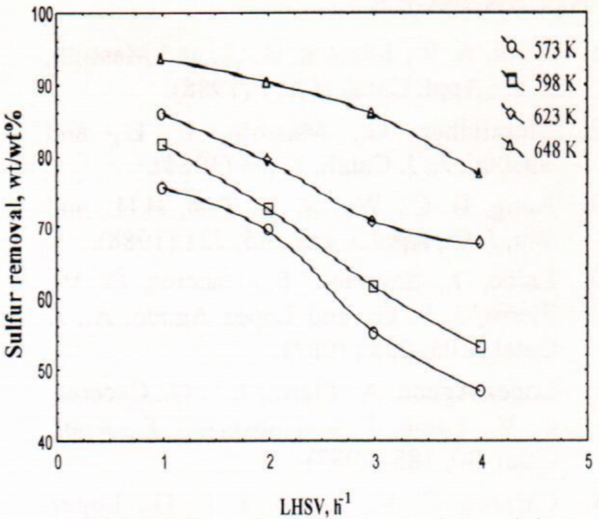

Fig. 1, Effect of tungsten on catalyst activity

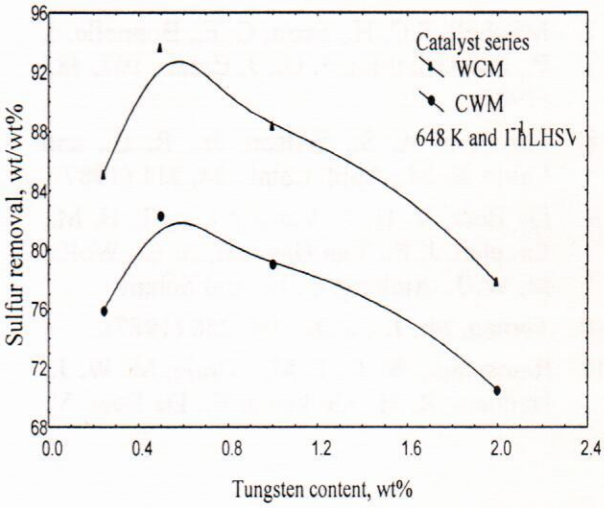

Fig. 2, Effect of LHSV on sulfur removal from gasoil at different temperatures

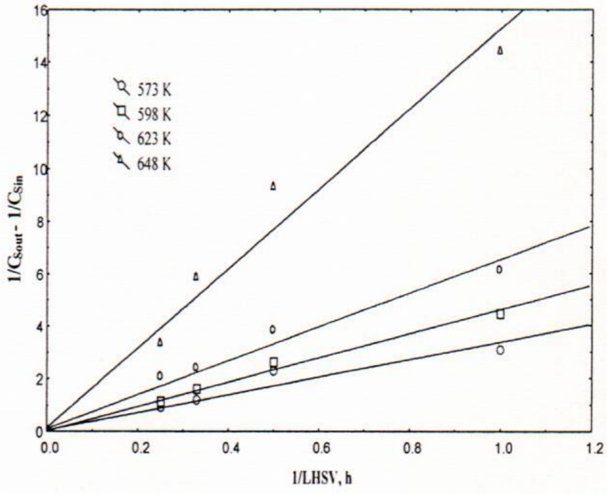

Fig. 3, Second order kinetic model for HDS of gasoil using W-CoMo / γ-Al_2O_3 catalyst.

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