

Hydrotreating Activity of Co-Mo/Al₂O₃ Promoted with Boron and Phosphorous

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Co-Mo/Al₂O₃ commercial catalytic used wetness impregnation method to prepare Co-Mo B/Al₂O₃ and Co-Mo P/Al₂O₃. We study the characterization of this catalyst which contains 12.0 wt. % Mo and 4.0 wt. % Co in γ -Al₂O₃ and gave the higher surface area of 192 m²/g.

The effects of boron and phosphores addition on the HDS and HDA of heavy gas oil over CoMo/g-Al₂O₃ catalysts have been studied. The addition of boron slightly improves the acidity of the acid sites, Thus, the catalytic hydroprocessing activities of heavy gas oil over the CoMo/g-Al₂O₃ catalysts may be related to the acidity and metal dispersion of the catalysts. Furthermore, the addition of phosphorus improves the dispersion of Co and Mo species, which also enhance the catalytic performance. Also, the addition of phosphorus caused the formation of acid centers.

Introduction

Environmental regulation to cleaner fuels researcher and refineries have been forced to develop incentives for performance which is much higher for hydrodesulfurization [1,2]. Molybdenum or tungsten supported sulfides have promoted by Co or Ni catalytic active components in industrial catalysts [3].

As Gandubert et al. [4] suggested, the promoted active sites catalysts are the so called Co(Ni)-Mo-S, where Co(Ni) atoms located on edges of MoS₂ particles [5]. Adding phosphorus to Co(Ni)- Mo(W) Al₂O₃ catalysts in an effort to increase the performance of HDS catalysts [6,7]. It was found that there is a small amount of phosphorus in the sulfided Co(Ni)-Mo/Al₂O₃ catalysts have positive effect on the performance of HSD catalysts [8]. Meanwhile, Sundaramurthy et al. [9], reported that the addition of phosphorus does not change the HDS rendering of catalysts Co- Mo/Al₂O₃. Many group [10] indicate that the addition of phosphorus promotes solubility of molybdate due to the formation of complexes phosphomolybdate, which simulates the preparation of the catalyst. Garcia-Vila et al. [11] and Li et al. [12] indicated that the addition of phosphorus improves the surface Al₂O₃ which consumes OH groups of Al₂O₃.

Effect of phosphorus addition on the performance of HDS catalysts approaching of

boron addition point in the surface of the catalyst supports modification [13,14]. The effect of boron addition to essential activity of the Co-Mo-S structure supported on Al₂O₃, we have shown [15,16] that the addition of an appropriate amount of boron (about 0.6 wt% B) weakens the interactions between the surface of oxides molybdenum and alumina [17].

The present study focuses on the effect of boron addition and that of the additives on Co-Mo/Al₂O₃ catalysts.

Experimental

Apparatus

The experimental were conducted in high-pressure reactor system [13] includes a tube reactor of 100 cm³ effective size free of back mixing, as well as laboratory instrument applied in hydrotreating stations (separator, pumps, heat exchangers, pressure, temperature and gas flow regulators). The experiments were carried out in a stable catalyst activity and stable condition. Periodically, it has been confirmed that the activity of a catalyst on a trial runs with comparable content of sulfur and aromatic compounds from the products that can be obtained in the same process conditions

Materials

Catalyst

The use of commercial CoMo/Al₂O₃ catalyst promoted with boron and phosphorous, which has the Co/ (Co+Mo) atomic ratio 0.25 (4% Co, 12%

Mo), 192 m²/g surface area and 0.657 cm³/g pore volume.

Reaction conditions

Applied parameters were as follows: temperature 300-380°C, liquid hourly space velocity (LHSV) of 1.0-3.0 h⁻¹ at fixed total pressure 55 bar and hydrogen to hydrocarbon ratio LL⁻¹.

Catalyst preparation

Catalysts CoMoB/Al₂O₃ were prepared by impregnation of a suitable solution of boric acid to a commercial CoMo/Al₂O₃ catalyst. It has been maintaining the pH of the solution in 7.0. Modified catalyst is emerging and then dried at 120 °C for 12 hr and finally catalysts calcined at 500 °C for 4 hr.

As well, the CoMo/Al₂O₃ catalyst was prepared using the method of wetness impregnation. In this way, impregnated with a solution containing the required amount of phosphoric acid (H₃PO₄) in the water on a commercial CoMo/Al₂O₃ catalyst, and the pH of the solution was 3.5. This was followed by saturation of support by drying for 12 hr at 120 °C and calcined at 500 °C for 4 hr [18].

After that, catalysts were sulfided using light gas oil and mixed feed stock with dimethyl disulfide (DMDS) and passed through the reactor (3ml/min) at 320 °C and pressure of 3.0 MPa for 12 hr [7].

Also, we can determine the total sulfur and aromatic contents in the feed stocks with ASTM D-4294 and D-2549, respectively.

Catalysts characterization

BET surface area, pore volume and pore size measurement

Measuring BET surface area, pore volume and pore size distribution of calcined catalysts using Quantachrome equipment adsorption (Nova-3200, Quantachrome, USA) in 78k using liquid N₂. Before analysis, it has been evacuated sample catalyst in 300°C for 4hr in vacuum of 5×10⁻⁴ atm to remove all moisture from the surface of the catalyst.

Temperature programmed reduction (TPR)

The temperature-programmed reduction with hydrogen for various samples of catalyst by Quantachrome instrument (Chem BET model 3000, Quantachrome, FL, USA). The sample was put in U tube and heated from 0-1000 °C with the flow rate 20 ml/min in the gas reduced from 5% H₂/N₂ in the electric furnace.

Result and Discussion

Catalyst

BET surface area, pore volume and pore size measurement

The surface area for Co-Mo/Al₂O₃ commercial incentive for change with adding 2.0 wt.% p and 1.7 wt.% B from 225 to 190 and 162, respectively (Table 1). This is due to clogged pores, bulk crystalline formation of P₂O₅ and B₂O₃ in boron and phosphorus loading, respectively. Size of the pore diameter and pore volume of Co-MoP/Al₂O₃ and Co-MoB/Al₂O₃ varied between 94-83 and 0.43 – 0.40 cm³/g, respectively.

TABLE 1. Surface area, pore volume and pore diameter of catalysts.

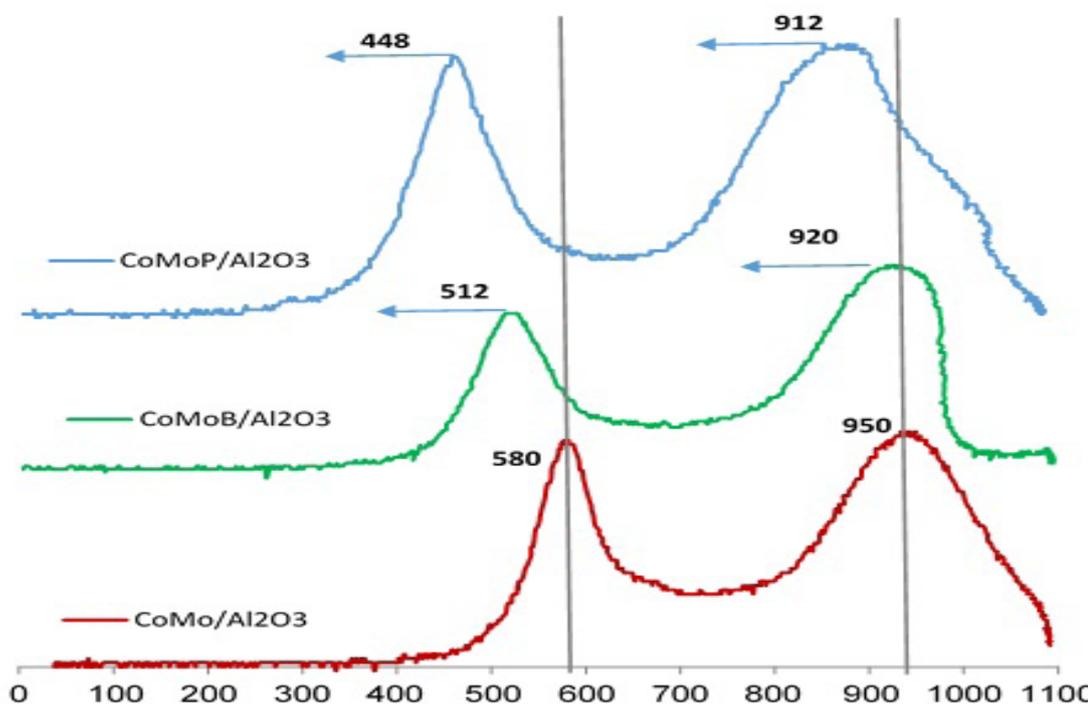
catalyst	BET (m ² /g)	Pore volume (cm ³ /g)	Pore volume Å
Co-Mo/Al ₂ O ₃	192	0.657	110
Co-MoP/Al ₂ O ₃	180	0.43	94
Co-MoB/Al ₂ O ₃	160	0.40	83

Temperature programmed reduction

There has been a reduction temperature programmed (TPR) analysis to determine the nature of the different types present on the surface of the oxide catalyst calcined to study the catalyst reducibility. TPR has been shown to be sensitive to a technical study on the reducibility [7].

The TPR data for CoMo/Al₂O₃ catalyst showed the major peaks located at about 580° and 950° C. Figure 1 shows that the low temperature at 580 °C is expected to the result in a partial reduction of similar types polymolybdate dispersed well, and high temperature at 950°C represents a full reduction of polymolybdate addition to the reduction of molybdate coordinated set in a tetrahedral (Mo⁶⁺→ Mo⁴⁺ and Mo⁴⁺→ Mo⁰⁺) [19].

Figure 1 shows the effects of B concentration on TPR profile which; the addition of B led to decrease the reducibility of the CoMo/Al₂O₃ catalyst. Where, the addition of 1.7 wt. % boron concentration decreased the reduction temperature of polymolybdate from 580 to 512 °C and 950 to 920 °C. Adding boron varied molybdenum oxide structure and caused less reducibility in the formation of molybdenum borate [20].



.Fig. 1.TPR profiles of CoMo/ γ - Al₂O₃ catalysts with boria and phosphor concentration.

Also, the addition of 2.0 wt. % phosphorus to CoMo/Al₂O₃ catalyst caused a decrease in the reduction temperature of polymolybdate and tetramolybdate from 580° to 448 °C and 950 to 858 °C (Fig. 1). The reducible catalyst was due to the strong interaction between cobalt with aluminum phase, and because of the formation of AlPO₄ on the surface of support [21].

Entanglement of the characterization results on hds and hda activities

The reducibility of oxide catalysts preferred by their changes to sulfided state is an important aspect for the activities of HDS and HDA. Numerous efforts have been made to link the reducibility of catalyst oxides hydrotreating activity to their sulfided state [22]. Where, molybdenum on the B or P/Al₂O₃ support, mainly that bonded to B-OH or P-OH groups, is more simply sulfided / reduced matched to that on Al₂O₃ support [19].

Though, excess B₂O₃ content led to the strong interaction between MoO₃ and the support, the MoO₃ came to be more difficult to sulfide / reduce and consequently the activity decreased. So, we can say that the reducibility of CoMo oxide can affect the characteristics of their sulfided

compound. When B₂O₃ content is larger than 2 wt. %, the interaction among alumina boria support and MoO₃ become too strong, thus reduces the covalent character of the bonds Mo-S and affects the decrease of the anion vacancy. The Mo anion vacancies respond the active sites of HDS reaction; so, the interaction strong support hinder led to formation of sulfide active phase and gave weak HDS activity. So the suitable concentration of boria addition to CoMo/ γ - Al₂O₃ was about 2.0 wt. % [20].

Mohamed, et al. [19], indicated that increasing the concentration of B to 1.7 wt. % resulted in a substantial reduction in the surface area. According to the literature, it was detected that the high HDS and HAD activities were relevant to a reduction in surface area. Martínez-Juárez et al. [23] described a decrease in the surface area and increase in the activities of HDS and HAD with the addition of B (1.7 wt. %). Also, Chouzier et al. [24] described a decrease in the surface area and increase in the HAD and HDS activities with adding 2.0 wt. % P to CoMo/ Al₂O₃. Though, it is difficult to link the activities of HDS and HAD with surface area, meanwhile the activities of HDS and HAD do not depend only on the surface area but also on other physical properties of the catalyst.

The effects of phosphate can be explained by the formation of new phosphate-containing active phase. The addition of phosphate led to formation of AlPO_4 on the Al_2O_3 support which decrease the surface area and pore volume of the support [21]. Phosphate is as AlPO_4 strongly bound to the Al_2O_3 surface and thereby changes also the concentration of the acid sites and their acid strength, an important parameter with respect to the cracking and hydrogenation activity, as well as to the coke formation. But this acidity effect might be independent from the effect of phosphate on the HDS and HDA activities of the catalysts. So, the high activity for HDS and HAD was also related to a rise in the amount of acid centers of weak and middle strength [25].

On other hand, it is recognized that adding P to the $\text{CoMo}/\text{Al}_2\text{O}_3$ has ordered effect, such as an increase in the number of piles. When using H_3PO_4 , AlPO_4 were formed by partial solubility of the Al cations, when the amount of molybdenum increases in the formula of breakages sulfidable easily, such as many-layered molybdate or MoO_3 . Compounds containing large nitrogen, such as heavy gas oil molecules have better organization of active sites in the top stacks of MoS_2 what's near to surface of Al_2O_3 . Therefore, it can be expected that the activities HDS and HAD from B and P containing catalysts $\text{CoMo}/\text{Al}_2\text{O}_3$ activities will give the highest HDS and HAD of heavy gas oil devoid of B and P (Figs. 2,3).

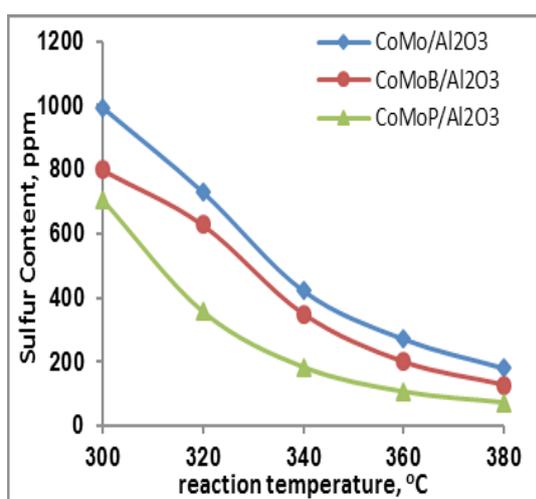


Fig. 2. Effect of reaction temperature on the sulfur removal of hydrotreated product for different catalysts.

Hydrodesulfurization of vacuum gas

Hydrodesulfurization of heavy gas oil in the fixed bed catalyst reactor is a complicated process and many variables affect the degree of sulfur removal. Key variables are the pressure, temperature, LHSV and hydrogen to oil ratio. Meanwhile in this study, the pressure of hydrogen and hydrogen to oil ratio remain constant. Results revealed that the removal of sulfur from hydrotreated increases as the temperature increases and LHSV decreases as shown in Fig. 2&3. The results obtained agreed with other HDS studies [26]. Increasing sulfur removal in the high reaction temperature can be ascribed to many causes. First, the most properly unreactive sulfur compounds appropriate to thiophene derivatives became activated sufficiently to react with hydrogen. Second, these degrade aromatic compounds and a smaller one that can be more easily spread in micro and mesopore catalysts and access to internal active sites where desulfurization interaction occurs mainly. Thus, the value of the high temperature is limited because of side reactions such as unwanted thermal cracking and the thermal cracking reactions which take place at high temperature. Contact time among the reaction liquid and catalyst reductions with the rise LHSV this leads to a decline in the extent of sulfur removal. The percentage of sulfur in hydrotreated portions reduced with decreasing LHSV used in temperature (380°C). Several categories of interactions occur at one time in the HDS process, take account of hydrocracking, hydrogenation, hydrodeoxygenation (HDO) and hydrodenitrogenation [27].

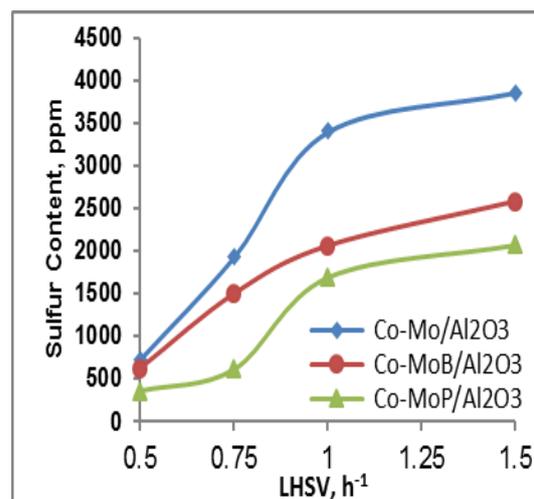


Fig. 3. Effect of LHSV on the sulfur removal of hydrotreated product for different catalysts.

As illustrated in Fig. 4&5, the increase in reaction temperature and decrease of LHSV lead to diminution of aromatic content of hydrotreated product as a result of the increasing of contact time and the rate of hydrogenation of aromatics [14].

The result of LHSV and hydrotreating temperature on aniline point for the treated product is illustrated in Fig. 6&7. Aniline point

increases with increasing temperature and decreasing LHSV as indication of increased rate of hydrogenation reaction. Depressing kinematic viscosity, specific gravity and increasing flash point with an increase in temperature and contact time (decrease LHSV) as shown in Fig. 8-13, so these properties decreasing due to the increase in hydrocracking and hydrogenation reactions [16].

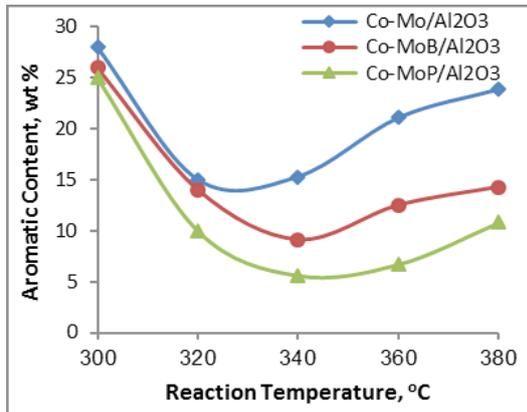


Fig. 4. Effect of reaction temperature on the aromatic content of hydrotreated product for different catalysts.

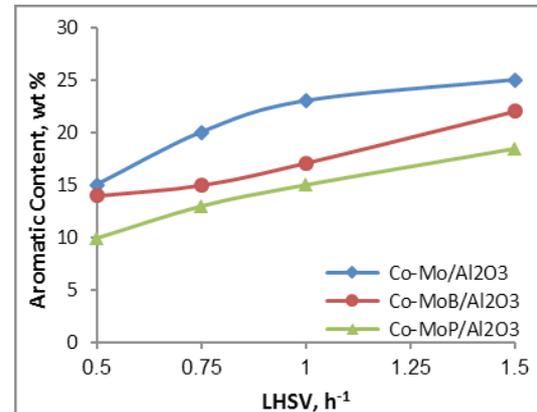


Fig. 5. Effect of LHSV on the aromatic content of hydrotreated product for different catalysts.

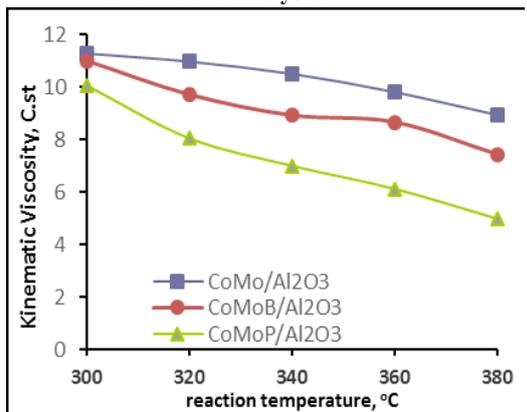


Fig. 6. Effect of reaction temperature on Aniline point of the hydrotreated product.

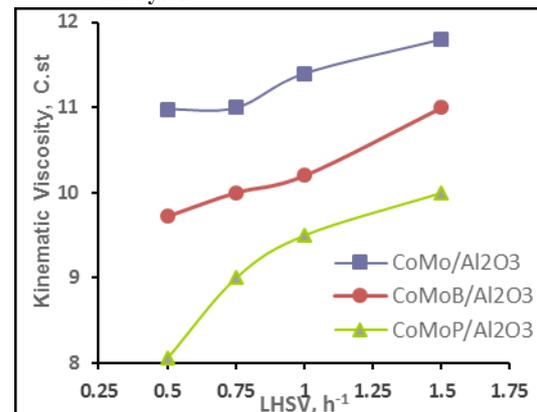


Fig. 7. Effect of LHSV on Aniline point of the hydrotreated product.

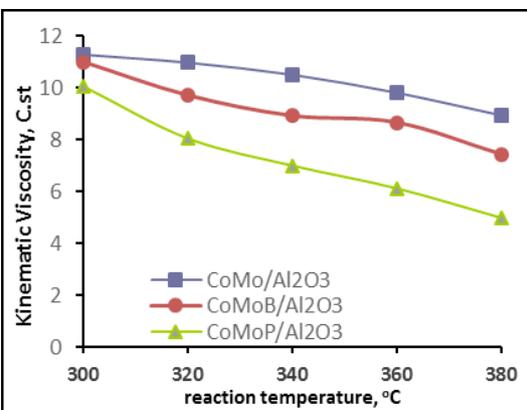


Fig. 8. Effect of reaction temperature on kinematic viscosity of the hydrotreated product.

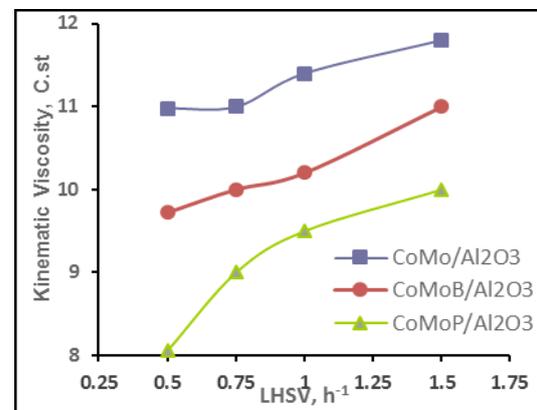


Fig. 9. Effect of LHSV on kinematic viscosity of the hydrotreated product.

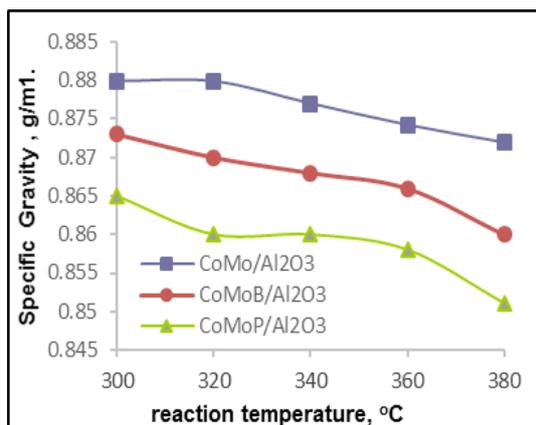


Fig. 10. Effect of reaction temperature on specific gravity of the hydrotreated product.

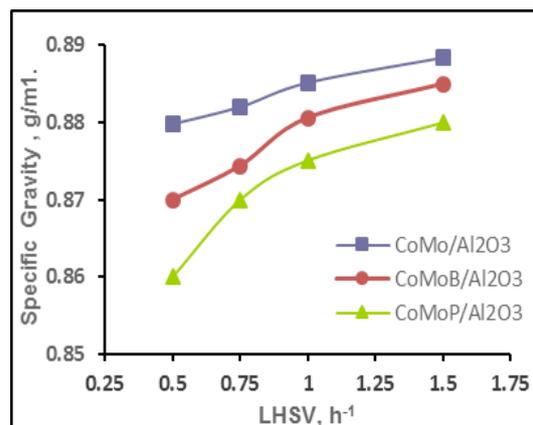


Fig. 11. Effect of LHSV on specific gravity of the hydrotreated product.

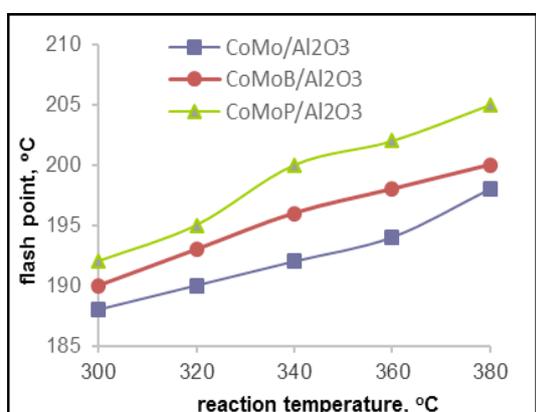


Fig. 12. Effect of reaction temperature on flash point of the hydrotreated product.

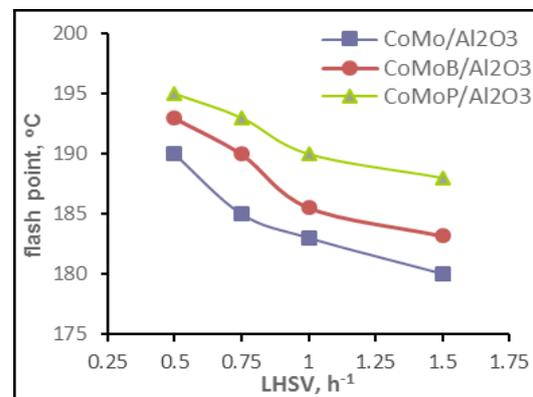


Fig. 13. Effect of LHSV on flash point of the hydrotreated product.

Conclusions

The hydrotreating results showed that the CoMoP/Al₂O₃ catalyst has higher activity than those of CoMoB/Al₂O₃ ones. This can be efficient by the existence of boron or phosphor. Numerous coexisting properties in boron or phosphor supported catalysts may simplify their hydrotreating activities, increase the dispersal of active sulfide phase and rise the sum of active site.

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المعالجة الهيدروجينية لحفاز الكوبلت موليبدنم على ألومينا المنشط مع البورون والفوسفور

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نستخدم طريقة التشريب للحفاز التجاري كوبلت موليبدنم على ألومينا لتحضير كوبلت-موليبدنم-بورون على ألومينا و كوبلت-موليبدنم- فوسفور على ألومينا. ندرس تتميز هذه المحفزات التي تحتوي على ١٢,٠٪ بالوزن موليبدنم و ٤,٠٪ بالوزن كوبلت على ألومينا وهو يعطي مساحة سطح ١٩٢ م^٢/جم .

وقد تم دراسة الآثار المترتبة على إضافة البورون والفوسفور إلى حفاز كوبلت موليبدنم على ألومينا ومدى تأثيره على عمليتي إزالة الكبريت والمركبات العضوية من زيت الغاز الثقيل. و إضافة البورون إلى حفاز كوبلت موليبدنم على ألومينا يؤدي إلى زيادة الحموضة للحفاز. وبالتالي فإن زيادة كفاءة الحافز عند إضافة البورون في عملية المعالجة الهيدروجينية يرجع أيضا إلى انتشار المعادن على سطح الحفاز. وعلاوة على ذلك، فإن إضافة الفوسفور يحسن أيضا من الانتشار المعادن على سطح الحفاز مما يعزز أداء الحفاز. أيضا، إضافة الفوسفور تسببت في تشكيل مراكز الحمضية.