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Effect of preparation methods and content of phosphorus on hydrotreating activity

S.K. Maity *, G.A. Flores, J. Ancheyta, Mohan S. Rana

Instituto Mexicano del Petróleo, Eje Central Lázaro Cárdenas Norte 152, Col. San Bartolo Atepehuacan, México, D.F. 07730, Mexico

Abstract

The effect of phosphorus content and preparation methods is studied in this present investigation. Three different methods are employed for preparation of catalysts. The catalysts are characterized by pore size distribution, X-ray diffractogram and temperature programmed reduction. Thiophene hydrodesulfurization (HDS), cumene hydrocracking (HC), gas oil HDS and Maya heavy crude HDS and hydrodemetallization (HDM) activities are performed. It is found that specific surface area gradually decreases with P loading. The addition of phosphorus increases the formation of polymolybdate species which are more active for hydrotreating reaction. It is also observed that reducibility of these species also increases with P loading. However, at higher P loading the crystalline MoO_3 is formed at the expense of these multilayer polymeric molybdates. The increment in the activity is more in the catalyst prepared by co-impregnation method. The activity increases with P loading up to 1 wt% P content. At higher loading the activity decreases. It is also noted that P inhibits coke formation on the catalyst during hydrotreating of heavy crude oil. Phosphorus can also modify the Brønsted acidity of the catalyst and hence cumene hydrocracking activity slightly increases.

Keywords: Phosphorus; HDS; HC; HDM; TPR; Maya heavy crude

1. Introduction

The sulfur specifications in the gasoline and diesel all over the world are becoming very stringent in every year. For this reason, very high active and stable catalyst is necessary to cope-up with the coming problems. To increase activity, impregnation of additives is one of the options. Among all elements, phosphorous is mostly used as a third element in hydrotreating catalysts.

Thiophene HDS activity on P containing catalysts is compared with P free catalyst by several researchers [1–4]. HDS activity increases with P content and it reaches maximum at 2–3 wt% P. With further increase in P content, HDS activity decreases. It is explained that at lower P content the polymerization of Mo–S bonding in Mo/Al-P is less than that in Mo/Al. It may be the reason to show higher HDS activity. At higher P content, molybdenum agglomerate and hence HDS activity decreases [1]. Lewis et al. [2] found that thiophene HDS activity increases with P concentration into the catalyst and it reached maximum at 1 wt% P loading. However, the increment in activity depends on the catalysts preparation method. If P is impregnated first and then metals (Mo and Ni), the increment in activity is higher than that of the catalyst prepared by co-impregnation method. It is proposed that phosphate may block direct interaction of nickel with alumina support and hence reduced the formation of inactive nickel aluminate. The effect of phosphorus content and preparation method on NiW/Al_2O_3 catalyst is investigated by Atanasova et al. [3]. The thiophene HDS activity of catalyst prepared by step impregnation is higher than that for catalyst prepared by co-impregnation. The maximum activity is found at 2–3 wt% P_2O_5 concentration. At higher P content the activity decreases rapidly and it is more pronounce in the case of the catalyst prepared by co-impregnation. Author pointed out that P containing catalyst is very complex in nature, several factors like dispersion of active metals, nickel coordination, type of bonding, and degree of polymerization of W, etc. play a role some in synergic way and others are in opposite way. It has been concluded that the introduction of phosphorus in the first impregnation step inhibits the strong interaction of metals with support and hence reduces the formation of hardly sulfidable $NiAl_2O_4$ and $Al_2(WO_4)_3$ type of species. Very slight increment

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* Corresponding author. Fax: +52 55 91758429.
E-mail address: skumar@imp.mx (S.K. Maity).

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in thiophene HDS activity was found by Spojakina et al. [4], suggesting that P does not lead to the formation of new sites rather it modified existing sites.

Cruz et al. [5] extensively studied the effect of P on gas oil HDS activity. It is found that the P catalysts have a higher activity than the corresponding P free catalysts. The increment in HDS activity of P containing catalysts is more prominent at lower pH of preparation. Authors concluded that the increment in gas oil HDS activity may depend on the increase in sulfidability of P catalyst and on other factors like dispersion of metals and morphology of WS_2 like slab. They proposed that phosphorus incorporation can change distribution of the active sites, either increasing the number of active sites or creating new sites with a high intrinsic activity for HDS.

The HDS and HDM activities of Kuwait atmospheric residue were studied on P impregnated catalyst. It is found that with increasing P loading those activities increase and these reach maximum at 0.5–1 wt% P [6]. It is also observed that these activities are high on the catalyst prepared by co-impregnation method than that of catalyst P-CoMo. Kushiyama et al. [7,8] reported that an appropriate concentration of P improved catalytic activity of heavy oil; however, an excess amount of it decreases activity. The authors assumed that P might interact strongly with the vanadium compound in the heavy feed, and it prevented to deactivate the active Mo species. In resent years, Maity el al. [9,10] has stated the research work on the effect of P on the hydrotreating activities of Maya heavy crude.

Although there are several studies of phosphorus effect on catalysts for the hydrotreating of model compounds and of light fraction, there are very few studies of it on heavy oils. Therefore, in this work, a systematic approach is adapted to investigate the effect of P content and preparation method on the model compound, gas oil as well as heavy crude oil. In this regards, three different preparation methods are employed to prepare catalysts having 0.3–3 wt% P loading.

2. Experimental

2.1. Preparation of catalysts

Several catalysts having different concentration of phosphorus were prepared by wetness impregnation method. In this method appropriate amounts of salts were dissolved into the predetermined distilled water. The prepared solution was impregnated into the dry support. Ammonium heptamolybdate (AHM), cobalt nitrate and phosphoric acid were used for impregnation of molybdenum, cobalt and phosphorus, respectively. Three different methods were employed for impregnation of phosphorus. In 1st method, phosphorus was impregnated first into the support and then the impregnated samples were dried at 393 K for 7 h and calcined at 723 K for 5 h. Active metal molybdenum and promoter, cobalt were then impregnated into the dry sample by co-impregnation. This series of catalysts is assigned as *X*P-CoMo; where *X* is wt% of P and '-' represents dry and calcination.

In 2nd method, solution of AHM, cobalt nitrate and phosphoric acid was impregnated into the dry support by co-impregnation (*X*PCoMo). In 3rd method, molybdenum and cobalt impregnated first and then phosphorus. In between two impregnations, samples were dried and calcined (CoMo-*X*P). A series of catalysts (*X*P) having 0.3–3 wt% of P were also prepared. This series do not contain active metal, Mo and promoter, Co. Finally all catalysts were calcined at 723 K for 5 h. All the catalysts contain a fixed amount of MoO_3, 10 wt% and CoO, 3 wt%, but P content is varied from 0.3 to 3 wt%. Gamma alumina was used as support material which has specific BET surface area 240 m^2/g, total pore volume 0.75 mL/g and mean pore diameter 124 Å.

2.2. Characterization of catalyst

Specific BET surface area, pore volume and pore size distribution of the catalysts were measured by nitrogen adsorption at 77 K (Quantachrome Nova 2000). X-ray diffractograms were recorded on a SIEMENS D-500 model using a Cu K∝ radiation. Temperature programmed reduction (TPR) apparatus consisted of a quartz reactor and a thermal conductivity detector (TCD). Heating was performed with tubular furnace regulated by a temperature controller. The reducing gas mixture having 10% H_2 in argon was purified by molecular sieves. For each TPR experiment, 0.1 g of catalyst weight was taken. Before each run, the baseline was stabilized at room temperature by passing a gas mixture at a flow rate of 25 mL/min. After stabilization the sample was heated at 10 K/min from room temperature to 1000 K.

The total metals in the feed and products were measured by atomic absorption (Thermoelectron model Solaar AA). Sulfur was analyzed by X-ray fluorescence (HORIBA model SLFA-2100).

2.3. Catalyst activity test

The activities of thiophene-hydrodesulfurization and cumene hydrocracking were tested in micro-plant. In this plant, 0.3–0.5 g of catalyst was sulfided *in situ* into a glass-tubular reactor at atmospheric pressure and 673 K temperature. For sulfidation, hydrogen was passed through a container having CS_2. The saturated mixture of CS_2 and hydrogen was passed through the reactor. Hydrogen flow was 40 mL/h and duration of sulfidation was 2 h. After sulfidation, the catalyst was flushed at this temperature by H_2 until no CS_2 could be detected in the effluent gas. Thiophene or cumene feed was introduced through the gas bubblers. H_2 flow rate was 50 mL/min. Reaction products were analyzed by an on-line gas chromatography using a FID.

Five grams of fresh catalyst was sulfided *ex situ* for each experiment to study hydrotreating activities of straight run gas oil (SRGO) and Maya crude. An atmospheric unit was used for sulfidation. In this unit, hydrogen was passing through a container having CS_2. The saturated mixture of CS_2 and hydrogen passed through the reactor. The sulfiding conditions for the sulfidation of catalyst were: temperature, 673 K; atmospheric pressure; duration of sulfidation, 3 h; hydrogen flow, 40 mL/min.

Table 1
Reaction conditions for different feeds

	Micro-plant		Batch	
	Thiophene	Cumene	SRGO	Maya
Catalyst weight (g)	0.3	0.5	5	5
Feed weight (g)	–	–	300	200
Temperature (K)	673	673	633	653
Pressure (MPa)	0.1	0.1	5.9	9.8
Duration (h)	4	4	6	6

The catalytic activities of diesel and Maya heavy crude were studied in a batch reactor. An appropriate amount of feed (SRGO or Maya heavy crude) was taken into the reactor vessel (1 L capacity). The sulfided catalyst was transferred into the reactor in nitrogen atmosphere very quickly so that catalyst would not contact with air for long time. The reactor vessel was tight properly and checked for leakage. The reactor vessel was then purged two/three times with hydrogen gas so that there was no air left inside the reactor. Heating was started from room temperature to the required temperature at the rate of 3 K/min. Stirring was started when temperature reached the set point (reaction temperature) and the time was noted as the beginning of the reaction at this point. Hydrotreated products of SRGO were collected every hour and its sulfur content was analyzed. However, for hydrotreating of Maya crude, only one product was collected at end of the reaction. Products were separated from catalyst after reaction and metals and sulfur contents of the products were analyzed. The experimental conditions for micro-plant and batch reactor are given in Table 1. In Table 2, the properties of SRGO and Maya heavy crude are presented.

3. Results and discussion

3.1. Textural properties of catalyst

Specific BET surface area of P containing catalysts is measured and change in it with P loading is presented in Fig. 1. It shows that with increasing P content, surface area gradually decreases. In this figure only results of *X*P (without Mo and Co) and *X*PCoMo catalysts are presented. However, trends are similar for the other series (*X*P-CoMo) and (CoMo-*X*P) catalysts. In Fig. 2, distribution of surface area with pore diameter of the catalyst is presented. This figure clearly demonstrates that the surface area contributed from micropores decreases with increasing concentration of P. It indicates that phosphorus ions are deposited on the pore mouth particularly on the pore diameter below 200 Å and it causes loss of total surface area. This is in agreement with the findings by others [2,3,11] that surface area decreases with P impregnation.

Table 2
Properties of straight run gas oil (SRGO) and Maya heavy crude

Properties	SRGO	Maya
API gravity	29.99	20.99
Sulfur (wt%)	1.46	3.42
Nitrogen (wppm)	585	3006
Ramsbottom carbon (wt%)		11.01
Asphaltenes (in C_7) (wt%)		12.26
Ni (wppm)		52
V (wppm)		270

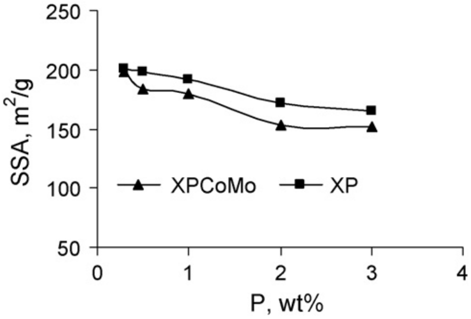

Fig. 1. Effect of phosphorus loading on surface area.

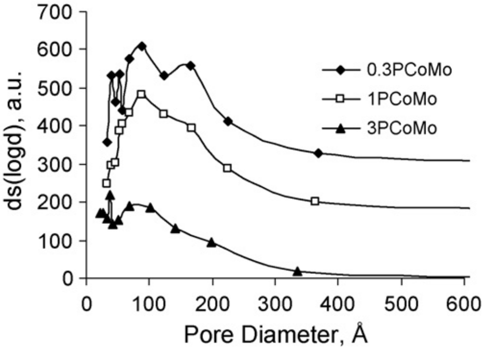

Fig. 2. Surface area distribution at different pore diameter.

3.2. X-ray diffraction (XRD)

X-ray diffractograms of phosphorus free and *X*PCoMo catalysts are presented in Fig. 3. The XRD diffractogram shows that the support used in this study is gamma alumina and molybdenum phases are well dispersed up to 1 wt% P loading. However, at 3 wt% P loading two small peaks appear at $2\theta = 25–27^\circ$ which corresponds to the presence of crystalline MoO_3. The XRD diffractograms of the P containing catalysts

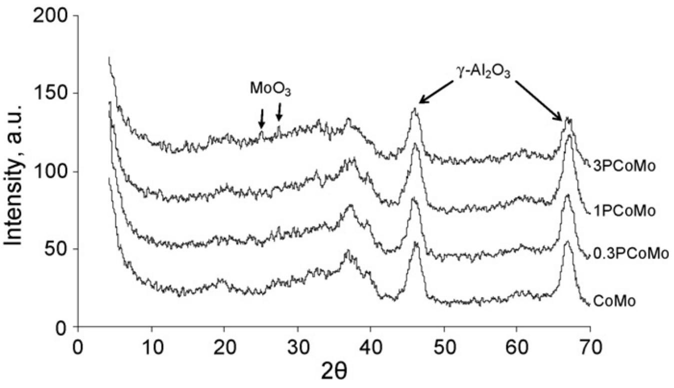

Fig. 3. XRD diffractograms of CoMo and *X*PCoMo catalysts.

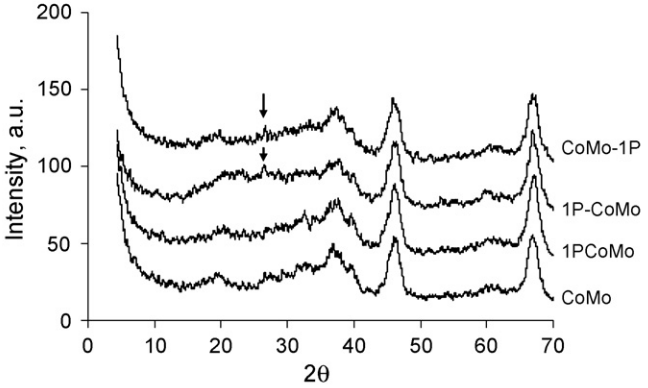

Fig. 4. XRD diffractograms of CoMo and catalysts prepared by different methods.

prepared by different methods are compared with P free catalyst in Fig. 4. This figure shows that a very small peak appears at $2\theta = 26.3^\circ$ (indicated by arrow in the figure) for 1P-CoMo and CoMo-1P catalysts. This peak may be due to the presence of crystalline MoO_3.

During impregnation of molybdenum, molybdenum anions remain at equilibrium in Mo solution as: $7MoO_4^{2-} + 8H^+ = Mo_7O_{24}^{6-} + 4H_2O$. At low pH, i.e. at higher H^+ concentration this equilibrium is more favorable in the right direction. It means at low pH molybdenum anions are in the polymeric forms as $Mo_7O_{24}^{6-}$ or $Mo_8O_{24}^{6-}$. During catalyst preparation phosphorus is impregnated as a phosphoric acid. Therefore, during impregnation of molybdenum in presence of phosphoric acid, Mo anions adsorb as polymeric molybdenum anions. There are two ways to deposit Mo on the support surface. One is adsorption and another is precipitation. With addition of phosphorus into support, surface area of the support gradually decreases. Phosphate plugs the pore mouth and hence decreased the surface area. Therefore, phosphate modified surface has fewer pores for adsorption of molybdenum anion and hence molybdenum deposition occurs by precipitation. At very high loading of P, these precipitates of Mo agglomerate and form a bulk MoO_3 [1]. The decreasing trend in surface area on addition of phosphorus is observed in our study. At 3 wt% P loading, surface area of the catalyst reduces sufficiently so that polymeric molybdenum species are agglomerated into the bulk MoO_3 during calcinations of catalyst. It may be the same in the case of the catalyst prepared by first impregnation of P. When P impregnated first and then CoMo, there is less interaction of metals with support. During calcinations active metals may form bulk MoO_3 which is observed in XRD diffractogram. However, the presence of this bulk MoO_3 in the catalyst CoMo-1P is not clear. A plausible explanation for this is the presence of octahedral coordinated polymolybdates. Some of these multilayer molybdates may react with P and form species like $(P_2Mo_5O_{23})^{6-}$ which are converted to crystalline MoO_3.

3.3. Temperature programmed reduction (TPR)

In Fig. 5, the reduction profiles of catalyst prepared by co-impregnation methods are compared with CoMo catalyst whereas in Fig. 6, the reduction profiles of the catalyst prepared by different methods are presented. The catalyst CoMo reduces at temperature maxima 762 K. A shoulder peak also appears at 821 K. With the addition of P the reduction pattern changed. The reduction peak becomes broad in nature of the catalyst 0.3PCoMo. Two comparatively sharp peaks appear at temperature maxima 743 K and 819 K. A small hump also appears at lower temperature, 623 K. The reduction profile of the catalyst 1PCoMo is also broad in nature. The lower reduction peak becomes sharp compared with the reduction peck of 0.3PCoMo. Another peak appears at 742 K. The catalyst 3PCoMo reduces at 744 K and its reduction peak becomes sharp. The temperature maxima and total hydrogen consumed during reduction are calculated and given in Table 3. This table shows that total consumed hydrogen jumps from 585

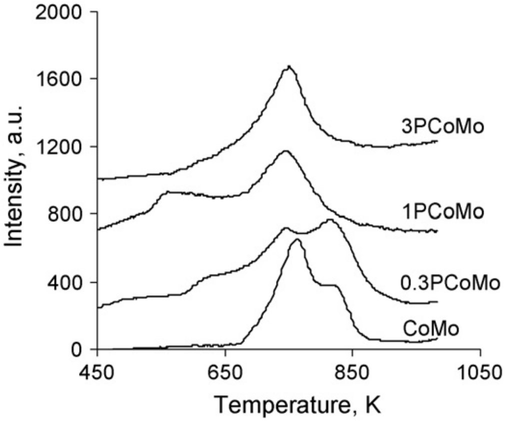

Fig. 5. TPR of CoMo and XPCoMo catalysts.

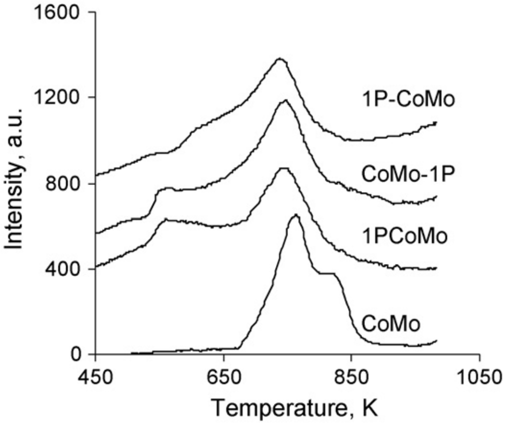

Fig. 6. TPR of CoMo and catalysts prepared by different methods.

Table 3
Reduction temperature and reduction peak area of catalysts

Catalysts	Peak maxima (K)			Total peak area (μmol H_2/g cat)
	T1	T2	T3	
CoMo		762	821	585
0.3PCoMo	623	743	819	984
1PCoMo	572	742		618
1P-CoMo	653	738		350
CoMo-1P	563	743		362
3CoMo		744		388

unit to 984 unit with the addition of only 0.3 wt% P. Hydrogen consumption is also higher in 1PCoMo catalyst compared with phosphorus free catalyst. However, with the addition of higher amount of P (3PCoMo) the total hydrogen consumption reduces.

The TPR profiles of phosphorus containing catalysts prepared by different methods are compared with phosphorus free catalyst in Fig. 6. The reduction patterns for catalyst 1P-CoMo and CoMo-1P are almost similar. However, peak area of catalyst CoMo-1P at lower temperature is higher than that for catalyst 1P-CoMo. Total hydrogen consumption of these two catalysts is almost the same; however, it is less than that of the catalyst 1PCoMo and CoMo. The temperature maxima and total hydrogen consumption are also given in Table 3. The reduction of the P containing catalysts has started at lower temperature than that started for CoMo catalyst. So it can be said that with the addition of P, reducibility may increases; however, it is different for the different methods used for the preparation and it also depends on the amount of P added.

In general, the reduction profiles of P containing catalysts are broad in nature. It indicates that several reducible species are formed in the presence of P. The higher reduction peak (at 821 K) may be reduction of strongly bonded tetrahedral molybdenum species. Whereas the lower reduction peak (at 762 K) is reduction of octahedral molybdates. With the addition of 0.3 wt% P the amount of octahedral with tetrahedral species increases. Moreover, a hump appears at lower temperature (623 K). This lower temperature shoulder peak may be due to the reduction of very loosely bonded multilayer polymobdates species. These species increase with increasing concentration of P at the expense of tetrahedral. Reduction profile of these species is shifted towards lower temperature (1PCoMo). The shifting of reduction maxima at lower temperature was also observed by Maity et al. [10] in the presence of P. However, in their case, total reduction area is less compared with phosphorus free catalyst. Authors conclude that polymobdate phases are formed at the expense of tetrahedral molybdate phases. These polymolydates are converted to crystalline molybdenum when the interaction of these phases with support reduces to a certain level. It was also reported that at higher P loading these multilayer polymobdates may convert to crystalline MoO_3 or form $(P_2Mo_5O_{23})^{6-}$ complex which is very difficult to reduce [12]. We have observed that total reduction area is less in catalyst 3PCoMo. Our XRD results also reveal the presence of bulk MoO_3 species.

When we compared the reduction behavior of the catalysts prepared by three different methods, it is found that more reducible species are available in the catalyst prepared by co-impregnation method. Moreover, the presence of polymeric species is abundant in this catalyst compared with that in catalysts 1P-CoMo and CoMo-1P. The results indicate that with the addition of P, more reducible polymolybdate-like species are formed. But at higher loading these polymeric species may be converted to crystalline MoO_3-like species or it may form a complex molybdate species with phosphorus which is very difficult to reduce. The formation of bulky molybdate depends on the preparation method. When phosphorus is impregnated separately, i.e. in case of 1P-CoMo and in case of CoMo-1P, these bulky species may easily form. Even from our XRD results we have observed the presence of these species.

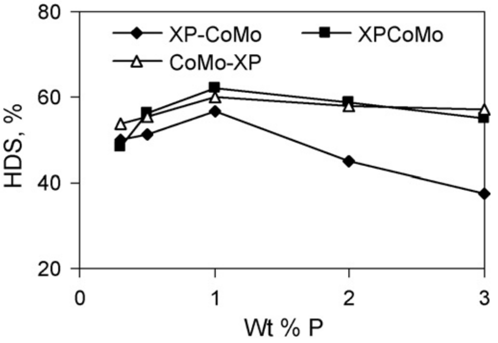

Fig. 7. Effect of phosphorus loading on thiophene HDS.

The reduction behavior of P containing NiW catalysts was also studied by Cruz et al. [5]. It was said that more reducible octahedral coordinated tungsten species such as polytungstates were formed in presence of P in the catalyst. Hellgardt et al. [13] also reported that the more reducible species were present in P containing catalysts.

3.4. Thiophene HDS Activity

The thiophene hydrodesulfurization activity of P containing catalysts is studied and the results are presented in Fig. 7. This figure shows that with increasing P loading the HDS activity increases and it reaches maximum at 1 wt% P loading. The HDS activity decreases with further increase in P loading. This trend is observed for all the catalysts irrespective of the catalyst preparation method. A comparison is also made between P free and P containing catalysts in Fig. 8. It shows that the HDS activity increases with the addition of phosphorus into the catalyst. Increment is higher in the catalyst prepared by co-impregnation method. However, differences of HDS activity of 1PCoMo and CoMo-1P are minimal. It is worth to mention that HDS activity of pure alumina and P/alumina is also performed and it is found that there is no activity of these two samples. Therefore, the possibility of thermal cracking of the catalysts can be eliminated.

3.5. Cumene HC activity

The hydrocracking activity of cumene is studied and the results are presented in Fig. 9. The hydrocracking activity

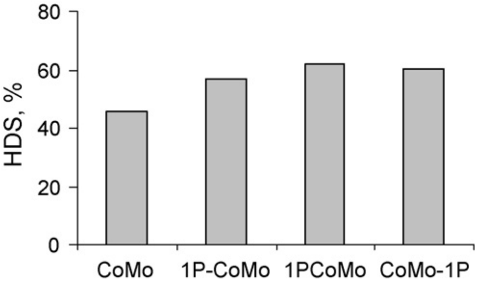

Fig. 8. Effect of catalysts preparation methods on thiophene HDS.

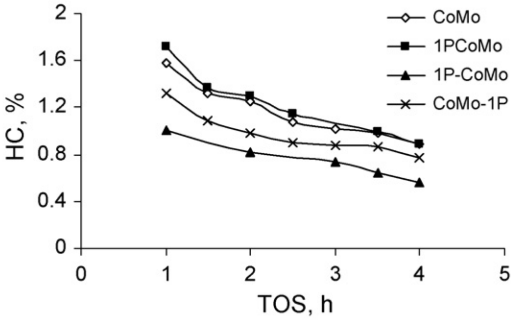

Fig. 9. Cumene hydrocracking activity of CoMo and P containing catalysts.

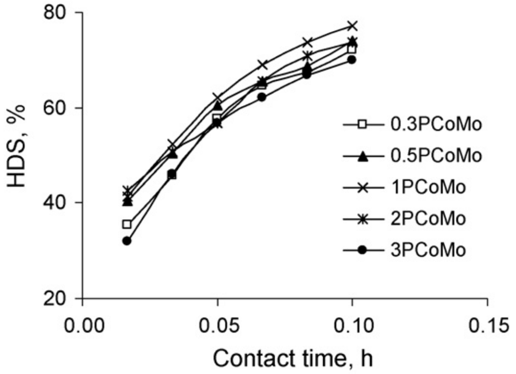

Fig. 10. Gas oil HDS of *X*PCoMo catalysts with contact time.

decreases with time-on-stream (TOS). Moreover, the HC activity is very low compared with the HDS activity of thiophene. Two blank tests are also performed on pure alumina and P/alumina samples. These two catalysts do not have any HC activity. The results show that only 1PCoMo catalyst has slightly higher HC activity compared with CoMo catalyst. Other two catalysts 1P-CoMo and CoMo-1P have lower HC activity than P free catalyst.

3.6. Gas Oil HDS activity

In Fig. 10, gas oil HDS activity of the catalyst having different P content is presented. It is observed that with contact time, the HDS activity increases for all the catalysts in the series *X*PCoMo. The effect of P loading on the HDS activity can be seen from Fig. 11. In this figure activity results at 6 h are compared. It is observed that with increasing concentration of P into the catalyst the diesel activity also increases and reaches maximum at 1 wt% P loading. The HDS activity decreases with further increase in loading.

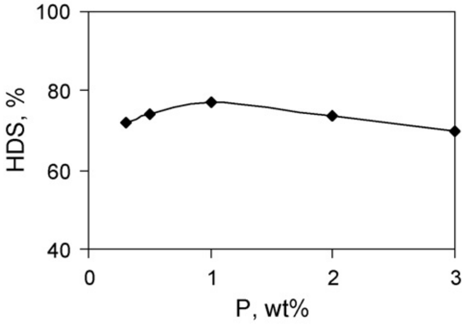

Fig. 11. Effect of phosphorus loading on gas oil HDS.

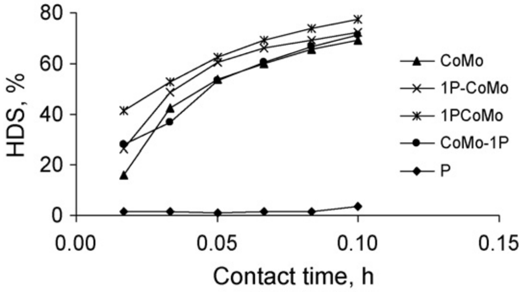

Fig. 12. Gas oil HDS of different catalysts with contact time.

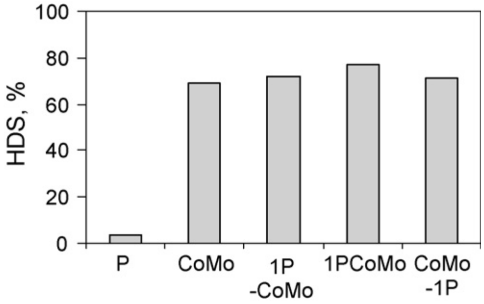

Fig. 13. Effect of catalyst preparation methods on gas oil HDS.

Gas oil HDS activity of the catalysts prepared by different methods was studied and activity is plotted against contact time in Fig. 12. In every hour product is collected from the batch reactor and its sulfur content is analyzed. The activity increases with contact time. A comparison of activity of the different catalysts is shown in Fig. 13 by taking result at 6 h. It shows that P/alumina has almost negligible HDS activity. The P containing catalysts have slightly higher gas oil HDS activity compared with P free catalyst. In this case also, the catalyst prepared by co-impregnation method shows the highest HDS activity.

3.7. Maya crude HDS and HDM activities

The effect of P on hydrodemetallization and hydrodesulfurization activities of Maya heavy crude is also studied and the results are given in Fig. 14. This figure shows that 1PCoMo

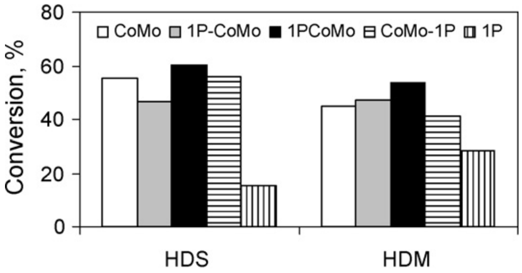

Fig. 14. Effect of catalyst preparation methods on Maya HDS and HDM activities.

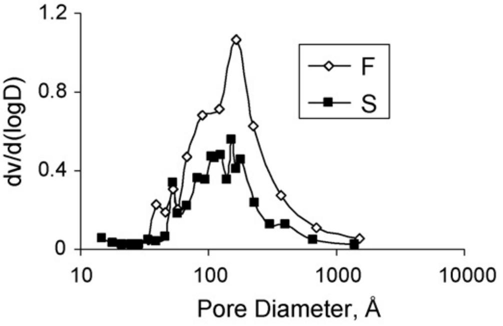

Fig. 15. Pore size distribution of fresh (F) and spent (S) CoMo catalyst.

catalyst has higher HDS and HDM activities than that of CoMo catalyst. Though HDM activity of 1P-CoMo catalyst is higher than that of CoMo, but it shows lower HDS activity. It indicates that both functionalities of HDS and HDM do not follow the same mechanism. It is also found that P/Al_2O_3 catalyst has HDS and HDM activities. Its HDM activity is higher than HDS activity, indicating that hydrotreating of heavy crude oil not only depends on active sites but also on the pore structure, particularly for removal of metals. Support material provides pore structure of the catalyst and hence P/Al_2O_3 has HDS and HDM. It also proves that removal of sulfur from heavy crude depends on active sites more preferably whereas for removal of metals, pore structure is an important factor to be considered. Maity el al. [9,10] observed synergic effect of P on HDM activity of Maya crude; however, the beneficial effect of it on HDS was not consistent. The HDS and HDM activities of Kuwait atmospheric residue increased with P loading and it reached maximum at 0.5–1 wt% P [8]. It was also observed that these activities are high on the catalyst prepared by co-impregnation method than that of catalyst P-CoMo.

3.8. Deactivation

The pore size distributions of fresh and spent CoMo and 1PCoMo catalysts are presented in Figs. 15 and 16, respectively. The pore size distributions of the spent catalysts are changed with respective to their fresh one. This change in pore size distribution is mainly due to the coke formation during the heavy oil hydrotreating. The changes are more prominent in the P free catalyst. It suggests that the P inhibits coke formation. Maity et al. [10] and Kushiyama [8] also reported the inhibition effect of P on deactivation of the catalyst. However, Kang et al. [6] did not find any suppression of coke formation with P addition.

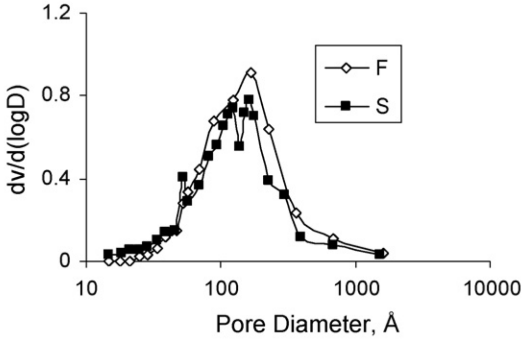

Fig. 16. Pore size distribution of fresh (F) and spent (S) 1PCoMo catalyst.

The formation of octahedral coordinated polymolybdates is favorable in P loaded catalysts. It has logic that the formation of these molybdates is more if P is impregnated first and then CoMo; so that there is no direct strong interaction between active metal and support. However, if the interaction is too weak, these polymolybdates can be agglomerated into the bulk MoO_3 phases. Therefore, the presence of more or less polymolybdate depends on support–metal interactions. In literature, several researchers found that the presence of these polymeric molybdates is more in the catalyst when P impregnated first compared with the catalyst prepared by co-impregnation method. In this study, we have observed from TPR experiment that more polymolybdates are present in the catalyst 1PCoMo. It suggests that these species, which are formed easily in catalyst 1P-CoMo, may be agglomerated into the crystalline MoO_3, assuming that metal–support interaction is not sufficiently strong. We have found from XRD that there is a small peak due to the presence of bulk MoO_3 in the catalyst 1P-CoMo and CoMo-1P.

From TPR result, it is also noticed that the total peak area increases drastically by impregnation of 0.3 wt% P. However, it reduces when 1 wt% P is loaded into the catalyst. It also observed that the amount of polymolybdates increases at the expense of strongly tetrahedral coordinated molybdates (shifting of peak maxima at lower temperature). It is possible that when P loading increases from 0.3 to 1 wt%, some of the loosely bonded multilayer molybdates may react with phosphate and form $(P_2Mo_5O_{23})^{6-}$ complex which is very difficult to reduce [12]. The concentration of these bulky molybdates increases with increasing concentration of P loading at the expense of polymolybdates and upon calcination it agglomerated into the crystalline MoO_3 which is detected by XRD.

Gisti et al. [14] observed the increases in Lewis acidity of support whereas Lewis et al. [2] reported the increment in Brønsted acidity with the addition of P into the catalyst. Cumene hydrocracking activity was studied in this work to see if there is any change in the catalyst acidity. We have observed that 1PCoMo catalyst shows slightly higher HC activity than that of P free catalyst CoMo. It suggests that P increases catalyst acidity either Lewis or Brønsted. Cumene cracking activity is also studied in pure alumina and P/Al_2O_3. These catalysts do not have activity, indicating that P does not modify any support acidity. It was reported by Topsøe [15] that at reaction conditions, Brønsted acidity was generated at sulfided catalyst by dissociation of H_2S on anion vacancies of MoS_2. Rana et al. [16] also observed the cumene cracking activity of Mo/Al_2O_3 sulfided catalysts and they concluded that it was due to Brønsted acidity generated at reaction conditions. From our TPR experiment, it is observed that 1PCoMo catalyst has more reducible species compared with that in CoMo catalyst. Moreover, P containing catalyst reduces at lower temperature. It suggests that 1PCoMo catalyst may have higher quantity of anion vacancies which leads to produce more Brønsted acidity by dissociation of H_2S. It is in agreement with that found by Lewis et al. [2]. However, the catalyst 1P-CoMo and CoMo-1P show lower HC activity. It is observed that these catalysts have fewer amounts of reducible molybdenum species compared with that of CoMo catalyst and this is the reason these catalysts show lower HC activity.

The catalysts having low concentration of P show higher HDS activity. From our earlier discussion it is noticed that P does not modify support acidity. So increment in HDS activity is related with molybdenum active sites. It is noted from TPR that addition of P indeed increases total amount of polymolybdate species and reducibility of these species. However, catalysts prepared by two-step impregnation method, either P impregnated first or latter, have less polymolybdate species, but these molybdate species reduce at lower temperature. Therefore, it can be said that P increases number of sites as well as sites strength and it is the reason for showing higher activity of 1PCoMo catalyst. Although 1P-CoMo and CoMo-1P catalysts have fewer sites, but the strength of these sites are modified by P, so that these catalysts show slightly higher HDS activity.

Catalyst 1P-CoMo shows higher HDM activity, but shows lower HDS activity compared with CoMo catalyst. Sulfur and metal content in heavy crude oils are different in nature. Generally heavy crude oil contains bigger as well as smaller sulfur compounds. But metal compounds are bigger in size. Therefore, removal of metal and sulfur compounds does not follow similar mechanism. Removal of these heteroatoms not only depends on active sites but also on the pore structure. For that we have observed hydrotreating activities of P/Al_2O_3 catalyst. Therefore, effect of P on hydrotreating of heavy crude oils is not so far well defined. More studies are necessary in this area. But there are good numbers of evidences that phosphorus suppresses coke formation during hydrotreating of heavy crude oils.

4. Conclusions

The presence of phosphorus in hydrotreating catalyst facilitates the formation of multilayer polymeric molybdates which are active sites for hydrodesulfurization. A promotional effect of phosphorus is observed on HDS of thiophene and gas oil. However, the effect of it on Maya crude is mixed. The promotional effect on HDS is observed for all the catalysts irrespective of the preparation method. However, the catalysts prepared by co-impregnation method show higher hydrotreating activity compared with the catalysts prepared by two-step impregnation methods. The activity increases with increasing concentration of phosphorus into the catalysts and it reaches maximum at 1 wt% P loading. At higher loading polymolybdates are agglomerated into the crystalline MoO_3 which are not the active sites and hence the activity decreases. Phosphorus can also modify the Brønsted acidity of the catalyst and hence cumene hydrocracking activity slightly increases in 1PCoMo catalyst. Although 1PCoMo catalyst shows higher HDS and HDM activities of Maya crude, other two catalysts 1P-CoMo and CoMo-1P show mixed behavior compared with phosphorus free catalyst. The HDS of heavy crude preferably depends on the active sites whereas for the HDM reaction, the pore structure of the catalyst is an important factor to be considered. Therefore, the effect of phosphorus on hydrotreating of heavy crude is not solely related to active sites. However, it is confirmed that P inhibits coke formation on the catalyst during hydrotreating of heavy crude oil. As a result, P containing catalyst shows higher hydrotreating activities in long run since the deactivation by coke is less in this catalyst compared with that in P free catalyst.

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