SUPPORTED AND SULFIDED Pb-Mo OXIDES: ACTIVE AND STABLE HYDROTREATMENT CATALYSTS

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A newly developed $PbMo/Al_2O_3$ HDS catalyst shows activity and stability that are comparable to or better than the traditional $CoMo/Al_2O_3$. Activity is optimum when the atomic ratio Pb : Mo is 1 : 6. At that ratio, the generated surface phase(s) display maximum degree of Mo coordinative unsaturation, as measured by low temperature oxygen chemisorption.

The industrial success of $CoMo/Al_2O_3$ catalysts for fuel hydrotreatment has impulsed numerous studies on various aspects of their chemistry and catalysis. One aspect, the promotion of Mo by Co or Ni, has been scrutinized from electronic and structural standpoints and its understanding has reached some degree of sophistication [1,2], although still several questions remain [3].

Promotion of the Mo sulfides by elements other than Co or Ni is a fairly virgin domain, as is the stabilization of Mo sulfide phases other than the very stable MoS_2 phase. To fill some of this void, in this article a report is made on the HDS activity of Pb-promoted Mo catalysts and on the correlation between solid state and surface properties, and catalytic activity.

The supported PbMo catalysts were prepared by a two-step impregnation of gamma-alumina (United Catalysts Inc., 215 m^2/g) with aqueous solutions of ammonium heptamolybdate and lead nitrate, to yield typical loadings of about 20 wt% MoO_3 and 5 wt% PbO. Each impregnation step was followed by drying at 120 ° C and calcination at 500 ° C, and the second calcination was followed by in situ reduction at 400 ° C with H_2 for 4 hours, and sulfidation at 400 ° C with 1 vol% thiophene/H_2 for up to 12 hours. Alternative sulfidation with 15 vol% H_2S/H_2 yielded results comparable to those presented here, and are analyzed elsewhere [4]. Reaction with thiophene was carried out in an all-glass and quartz apparatus, using 0.3 g of catalyst, at atmospheric pressure and with a flow of 30 ml/min of 1 vol% thiophene/H_2.

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Table 1
Catalyst composition and surface area

Composition[1] As synthesized	Pb : Mo ratio 1:12	1:9	1:6	2:9	1:3
Surface area[2]					
As synthesized	153	150	147	126	147
After reaction[3]	176	160	132	149	165

[1] Atomic absorption and X-ray fluorescence analysis.
[2] N_2 BET surface area, m^2/g.
[3] 24-h, 1 vol% thiophene/H_2, 400 ° C.

Catalysts were synthesized with the atomic ratios Pb : Mo shown in table 1. The resulting catalysts were amorphous according to powder XRD, indicating fine dispersion of the polycrystalline phases. Nitrogen BET surface areas were determined before and after sulfidation with thiophene (table 1). All the catalysts except the 1 : 6 Pb : Mo sulfided oxide underwent increase in surface area. The surface area of the 1 : 6 Pb : Mo catalyst decreased after sulfidation, possibly because of restructuring of surface phases, the nature of which are currently under investigation. Analysis of the actual surface composition of this 1 : 6 Pb : Mo catalyst, and some evidence of restructuring upon sulfidation, is the object of another publication [4].

The 1 : 6 Pb : Mo catalyst was compared to a commercial CoMo HDS catalyst (United Catalysts Inc. C20-6, 14 wt% MoO_3, 3.5 wt% CoO, 200 m^2/g, pretreated and evaluated as the other samples) over a 24-h period of thiophene HDS, with the results shown in fig. 1. The PbMo catalyst was 80% more active per m^2 than the commercial CoMo catalyst throughout the test period, demonstrating good activity and stability.

The other catalysts shown in table 1 had maximum activities (over a 24-h period) equal to or slightly less than the CoMo catalyst, as depicted in fig. 2. The "volcano" dependence between rate and composition evidences a promotion of Mo by Pb, optimized at a ratio Pb : Mo = 1 : 6. Whether such promotion is textural or structural can not be absolutely ascertained from the data presented.

Nevertheless, an interpretation of the volcano dependence will be offered, although it is being subjected to scrutiny. The 1 : 6 Pb : Mo ratio seems to optimize the amount of the active phases produced upon sulfidation of the supported and reduced mixed oxides. For synthesis ratios other than 1 : 6, smaller amounts of the active phases segregate from relatively inactive phases (such as MoS_2 or PbS). Hence the activity maximum is produced. The active phases are likely to contain coordinatively unsaturated sites of Mo (cus), as in many other Mo-based hydrotreatment catalysts. Some evidence for this argument can be provided by titrating the cus and showing its correlation with activity.

Low temperature oxygen chemisorption was utilized to determine a quantity

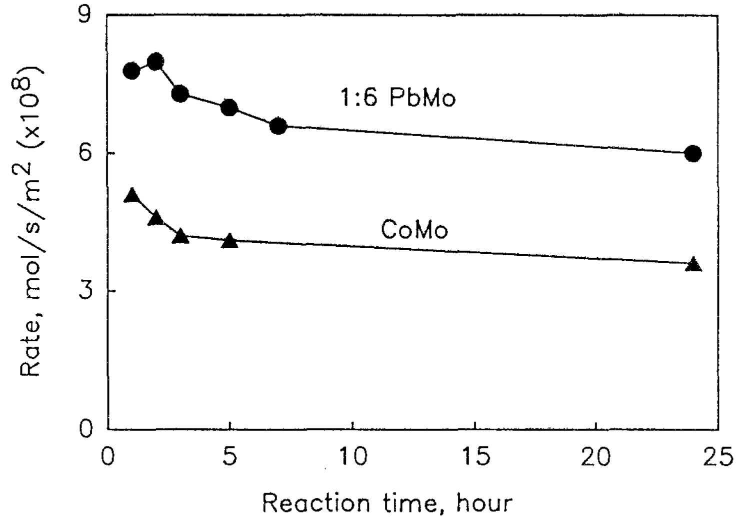

Fig. 1. Activity for thiophene HDS at 400 °C of supported 1:6 Pb:Mo catalyst and commercial CoMo catalyst.

proportional to cus density on the PbMo and CoMo catalysts. The method of Reddy et al. [5] was followed, chemisorbing oxygen at −78 °C on reduced sulfided catalysts. Figure 2 shows the amounts corresponding to 20 Torr without correction for minor physisorption. Except for an abnormally low chemisorption for the 1 : 9 sample, the cus density followed the activity trend.

The argument presented can be reinforced by fig. 3, which depicts an overall

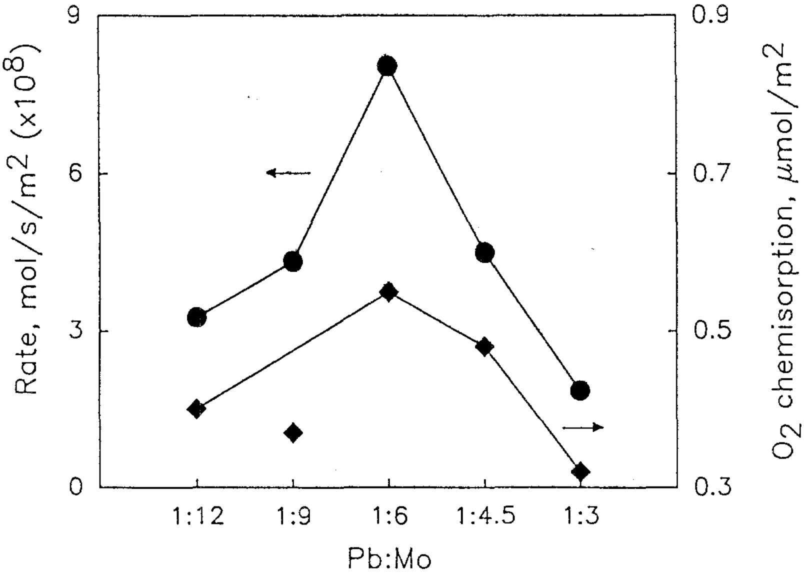

Fig. 2. Activity for thiophene HDS at 400 °C and low temperature oxygen chemisorption of supported PbMo catalysts.

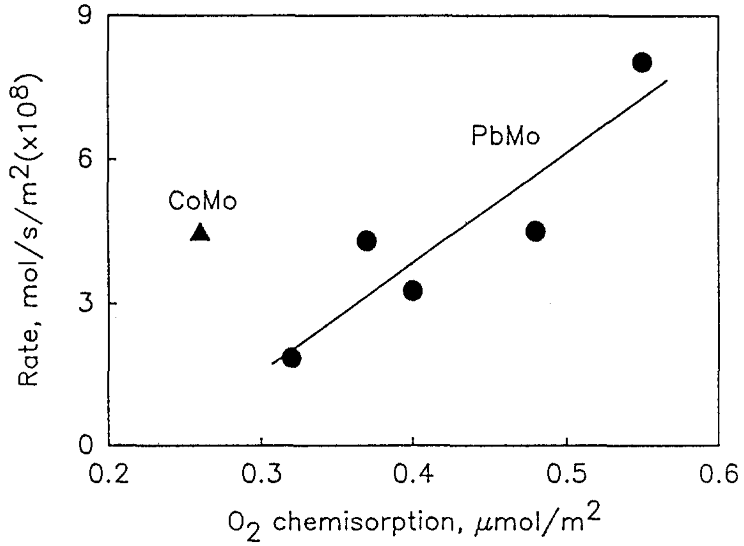

Fig. 3. Correlation between thiophene HDS activity and oxygen chemisorption of supported PbMo and CoMo catalysts.

linear relationship between activity and cus density for the PbMo catalysts. The intercept at null activity does not occur at null oxygen chemisorption, a result that suggests the presence of inactive unsaturated sites able to chemisorb oxygen, as discussed elsewhere [4]. For reference, the activity and oxygen chemisorption measured for the commercial CoMo have also been indicated in fig. 3. The single point for CoMo lies away from the PbMo correlation, a result compatible with different extents of promotion of Mo by Co and Pb. This inference is under deeper investigation.

In conclusion, it has been demonstrated that supported and sulfided PbMo oxides are very active catalysts for thiophene HDS, a result consistent with promotion of Mo by Pb. The active phases formed upon sulfidation attain the largest coordinative unsaturation of Mo when the Pb : Mo ratio is 1 : 6. At this composition, the activity is maximum.

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