Molybdenum Phosphide as Catalyst for the Thiophene Hydrodesulfurization

R. M. Leite[1], J. L. Zotin[2], V. Teixeira da Silva[1]
[1]Instituto Militar de Engenharia, Praça General Tibúrcio, 80, Rio de Janeiro, 22290 – 270, Brazil; [2]CENPES/PETROBRAS, Q7, Ilha do Fundão, Rio de Janeiro, 21949 – 270, Brazil

Introduction

The need for more active hydrotreating catalysts due to the tightening in the allowed sulfur content in fuels has led to the search of catalysts more active than the traditional ones. Basically, the studies have focused new active phases (carbides, nitrides, sulfides promoted by noble metals), new supports (TiO_2-Al_2O_3, ZrO_2-Al_2O_3, molecular sieves) or combination of new active phases on new supports. In a series of recent papers, Oyama's group has shown that a new active phase, transition metal phosphides, present an excellent potential for use in hydrotreating reactions[1-4].
In face of these recent results, the main aim of this work was to synthesize, characterize and evaluate the performance of bulk molybdenum phosphide (MoP) in the thiophene hydrodesulfurization reaction.

Experimental

Unsupported MoP was prepared in two steps has previously described elsewhere[1]. In the first, a homogeneous solution with a Mo/P atomic ratio equal to one was made by mixing previously prepared solutions of ammonium heptamolibdate (Alfa–Aesar) and diammonium hydrogen phosphate (Alfa–Aesar). After evaporation, a white solid was obtained and a subsequent calcination at 773 K for 5 h lead to the formation of a dark blue solid herein referred as molybdenum phosphate, $Mo_2P_2O_{11}$. In the second step, 0.5g of $Mo_2P_2O_{11}$ were reduced by heating from room temperature up to 923 K at a rate of 1 K min^{-1} in flowing H_2 (150 mL min^{-1}–AGA, 99,999%). The temperature was dropped to room temperature under flow of pure He (100 mL min^{-1}) and the sample present in the reactor (MoP) was either used directly in thiophene HDS reaction or passivated for five hours in flow of 0.5% O_2/He mixture (50 mL min^{-1}) to further characterization.
Thiophene HDS activity measurements at 533, 553 and 573 K were carried out using an atmospheric pressure flow reactor with an on-line FID gas chromatograph (Shimadzu GC-17A) equipped with an automatic injection valve. The feed current consisted of a 10 mol% thiophene/H_2 mixture.

Results and Discussion

The XRD diffraction pattern of the synthesized $Mo_2P_2O_{11}$ shows that the synthesized material is essentially amorphous with the presence of small quantities of MoO_3. In fact, XPS results show that the molybdenum photopeak is constituted by two dublets with maxima at 232.4 – 235,5 eV and 233,6 – 236,7 eV which can be assigned to Mo^{+6} as in MoO_3 and in $Mo_2P_2O_{11}$, respectively. Additional evidence that the $Mo_2P_2O_{11}$ is not constituted by a pure phase is obtained by UV-vis DRS which shows

the presence of several absorption bands indicating that molybdenum has different coordination and several degrees of condensation. The reason for this heterogeneity is probably associated with the synthesis method which does not allow a good control of phosphate formation during the evaporation step.

After reduction at 923 K under flow of pure H_2, the XRD diffraction pattern of the passivated sample presents only the characteristic diffractions of MoP[5]. Variation of the heating rate (1, 5, 7.5 and 10 K min^{-1}) during the reduction permitted to conclude that the $Mo_2P_2O_{11} \rightarrow$ MoP solid-state transformation occurs according to the nucleation model with activation energy of 100 kJ mol^{-1}.

Surface characterization by XPS of the passivated MoP reveals that the molybdenum photopeak can be deconvoluted into three dublets with maxima at 228.0 – 231.1, 232.3 – 235.3 and 229.3 – 232.4 eV which can be associated to Mo^{+6}, Mo^{+4} and Mo^{o}, respectively. While the presence of molybdenum in +6 and +4 oxidation steps can be explained by the passivation step which conducts to a surface oxidation, the zero state can only be explained by the presence of a covalent Mo – P bond. In fact, when the P2p photopeak is analyzed there is the presence of two maxima at 133.8 and 129.4 eV, the first associated to phosphorous bonded to oxygen such as in phosphates and the second related to phosphorous directly bonded to the metal as in the MoP.

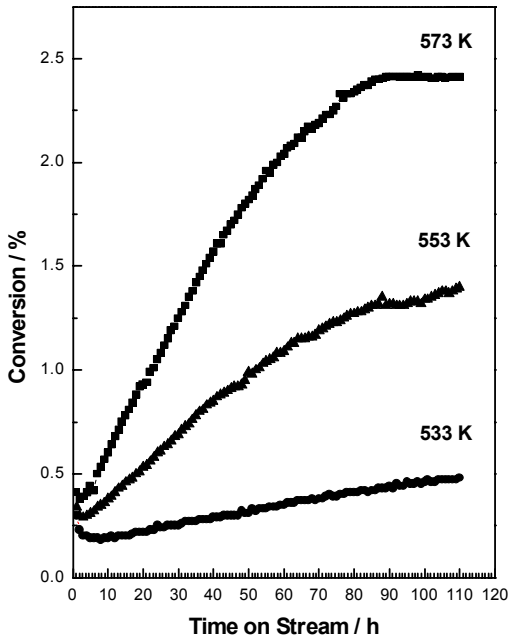

Figure 1 – Thiophene HDS activity of MoP at different reaction temperatures.

When used in the thiophene HDS reaction, the MoP presents the trend shown in Figure 1 with activity increasing substantially over time on stream, the rate of augment being higher for superior temperatures. In particular, for reaction temperature of 573 K there is a 5.8 times increase in conversion.

This trend in HDS activity clearly indicates that the surface of the MoP evolves into a more active structure during the course of the reaction. XPS and TEM results of the sample submitted to catalytic testing permit to conclude that during the reaction there is a surface sulfiding which conducts to the formation of a more active phase.

References

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