

# Identifying the active sites in catalytic hydrodesulfuration

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## RESUMEN

Este artículo analiza las evidencias de estudios experimentales para deducir un nuevo mecanismo de reacción de hidrodesulfuración (HDS), donde el sitio activo es similar a un carbono sulfurado ("CS") unido a un metal. Además, en base a la ecuación de Chianelli ( $\text{MoS}_{2-x}\text{C}_x$ ), se comprobó que la estructura con composición MoCS es el sitio activo. Esta investigación identifica el mecanismo de reacción (después de la activación inicial) y modifica la ecuación química que tradicionalmente se ha utilizado en la hidrodesulfuración. El artículo ayuda a entender que la presencia de compuestos carbonosos en los catalizadores de HDS desarrolla nuevos sitios catalíticos mejorados. Este trabajo, también ayuda a poner fin a la controversia sobre la naturaleza de la fase activa en HDS, al proponer un nuevo mecanismo nunca antes propuesto.

## ABSTRACT

This article analyzes the evidences of experimental studies to deduce a new reaction mechanism of Hydrodesulfurization (HDS), where the active site is similar to a sulphided carbon ("CS") bonded to a metal. In addition, based on the Chianelli equation ( $\text{MoS}_{2-x}\text{C}_x$ ), the structure with MoCS composition was found to be the active site. This research identifies the reaction mechanism (after the initial activation) and modifies the chemical equation that traditionally has been used in Hydrodesulfurization. The article helps to understand that the presence of carbonaceous compounds in the HDS catalysts develops new improved catalytic sites. This work also helps to end the controversy on the nature of the active phase in HDS, by proposing a new mechanism never before proposed.

## Introduction

The process used in catalysis to remove impurities with hydrogen is called hydrotreatment and this process is widely used in refineries. The hydrotreating process allows the removal of sulfur, nitrogen and oxygen, when sulfur is removed it is called hydrodesulfurization (HDS). The hydrotreating reaction of the gas oil takes place under hydrogen pressure and at high temperature. During the process hydrogen is consumed and the reactions are exothermic. On the other hand, the reactions are carried out in a range of 320-400 °C and at a hydrogen pressure of 10 to 100 bar (Raybaud y Tolhouat, 2013). The catalysts used contain alumina as support in conjunction with molybdenum (Mo) promoted with cobalt (Co) or nickel (Ni) (CoMo/Al<sub>2</sub>O<sub>3</sub> or NiMo/Al<sub>2</sub>O<sub>3</sub>). As discussed above, the catalysts used in hydrotreatment allow the removal of sulfur, nitrogen and other contaminants from the oil in the refinery, so the nature of the active sites and their structure are important in the process (Stanislaus et al., 2010).

Industrially, the HDS catalysts are activated (by pretreatment), usually by "in situ" methods. The HDS conversion is directly related to the temperature and type of activation procedure (Trimm et al., 1989). The activation step is carried out under hydrogen pressure or alternately with a light petroleum gas containing dimethyldisulfide (Dufresne et al., 1996). The most commonly used sulphurizing agents are: H<sub>2</sub>S, dimethyl dimethylsulphide (DMDS), carbon disulphide (CS<sub>2</sub>) or even with the substance to be hydrotreated.

Historically in the catalytic processes the presence of the carbon in catalysts has been related to the deactivation. However, recent studies have shown that the coke (carbon) presence is important in the reactions of the hydrodesulfurization (HDS) (Chianelli and Berhault, 1999; Berhault et al., 2001). Many models have been proposed to explain the activity and the selectivity of the HDS catalysts. Nevertheless, the majority of the researches and the models studied have been made with fresh catalysts.

The characterization in situ of HDS catalysts is difficult and limited due to the conditions of reaction (elevated temperature and high pressure) (Chianelli and Berhault, 1999).

The research of reaction mechanism for hydrodesulphurization on supported Co-Mo or Ni-W stabilized catalyst is complicated experimentally due to the characterization in situ of HDS catalysts (Chianelli and Berhault, 1999). Today, the limited capacity of spectroscopy equipments and the conditions of

reaction (elevated temperature and high pressure) can not oversimplify the identifying experimentally the active phase in these catalysts. Although, Chianelli et al. suggested that active surface of transition metal sulphides is "carbided" (stabilized catalyst composition, MoS<sub>2-x</sub>C<sub>x</sub>), but they did not propose a mechanism of reaction (Chianelli y Berhault, 1999., Chianelli and Pecoraro, 1981., Seiver and Chianelli, 1984). Nevertheless, they demonstrated that the carbon atoms in MoS<sub>2</sub> replace the atoms of sulfur. They also analyzed the catalysts in the transmission electron microscope, proving clearly the presence of carbon in superficial "carbide form" on the stabilized catalyst (after pretreatment).

## Methodology

The literature generally reports an increase in hydrodesulfurization (HDS) activity when using the liquid process. This has been debated and this phenomenon has been attributed to the presence of carbonaceous species. Some studies explain this with the following proposals (Glasson et al., 2002): a) carbonaceous species improve dispersion and inhibit MoS<sub>2</sub> sintering, b) a more efficient heat transfer provided by the liquid phase during the transformation, c) a decrease in the metal/carrier interactions in the presence of carbon, d) an improved catalyst sulfidation due to a better balance between the sulphurization and reduction processes or e) the formation of a new highly active site: Experimental studies have shown that carbon atoms can be introduced into the sulfide phase leading to species similar to carbides such as MoS<sub>x</sub>C<sub>y</sub> (Chianelli y Berhault, 1999). Therefore, the role of carbon as a component of the active phase is controversial and has not been clearly explained. (Tuxen et al., 2001; Berhault et al., 2001).

Improvement of HDS activity by the presence of carbonaceous compounds (on the surface of the catalyst) leads to the conclusion that new improved sites are forming.

## Identification of new catalytic sites

Based on the review of recent studies and publications on hydrodesulfuration, a new reaction has been proposed to explain the active sites that are responsible for the catalytic activity. Here, this work explains that through a reaction mechanism in a stabilized catalyst, the better activity of HDS depends of the ability of the transition metal components of formation of the new active site on the surface of metal (sulphided carbon species, "CS"). The effect of geometric structures is important in the catalysts, which means an efficient accessibility of the MoS groups on the surface to form specific reaction

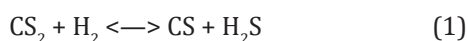
sites. This work is not against the studies of catalytic activity that have shown the importance of the transition metal components or the mixed phases of transition metal sulphides in HDS or the geometric effects of the structures (Berhault et al., 2001; Rueda et al., 1997).

A quantitative study was carried out to verify the accuracy of the proposed catalytic site. Therefore, the equation obtained experimentally by Chianelli ( $\text{MoS}_{2-x}\text{C}_x$ ) was used to verify that the active site (in the HDS reaction) presents the MoCS composition.

## Results and Discussion

### Identification of the nature of the active phase in HDS

Here is proposed the next and new reaction (1) (reaction mechanism) that explains the real reaction in HDS (after pretreatment), considering: 1) the recent studies on the effect of carbon in the reactions of HDS (Chianelli y Berhault, 1999; Berhault et al., 2001), and 2) the reversibility of the reaction when is increased the pressure of hydrogen.



The previous reaction (reaction 1) can explain the true nature of the active phase (responsible reaction in a stabilized catalyst) in the Hydrodesulfurization. In this reaction a new catalytic site (CS) is formed in the presence of carbonaceous compounds.

It is showed in the next part, first the simplified reaction (found in books of refinement of petroleum) of HDS and second the HDS reaction in the base of analyzed evidences:

1) The simplified representation of the reaction of Hydrodesulfurization, as normally is represented in the books (Meyers, 1986):

Desulfurization



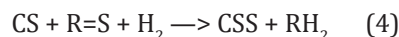
Reactivation



Where R=S = hydrocarbon containing sulfur, MS = active catalytic-metal site and  $\text{H}_2$  = hydrogen.

2) The new proposal that allows to understand the true reaction in the stabilized catalyst (after pretreatment) in HDS reaction:

Desulfurization



Reactivation



Where the CS = new active catalytic site and CSS ( $\text{CS}_2$ ) = deactivated site.

The sites CS (active catalytic site) and CSS ( $\text{S=C=S}$ , deactivated site) are formed in the stabilized catalyst, where the CS site reacts with the organic containing sulfur and with hydrogen (reaction 4) and it becomes in a CSS site. The presence of  $\text{H}_2$  allows forming the catalytic site active in HDS (reaction 5). The previous reaction can help to understand why the sulfating agents are used (the agents contain organic sulfur and alkyl groups) during the pretreatment of the industrial catalysts (Berhault et al., 2001). The pretreatments with sulfating agents lead directly to the formation of CS sites in the HDS reaction. The existence of double bonds between carbon and sulfur lead to have a better reactivity. The  $\text{MoS}_2$  structure reacts forming the MoSC (the real active site) and the presence of R=S and  $\text{H}_2$  forms MoSCS (deactivated site). In Figures 1 and 2, the new mechanism is clarified (reactions 4 and 5). In the figures, the mechanism in detailed steps of the hydrodesulfurization of dibenziothiophene in molybdenum is illustrated.

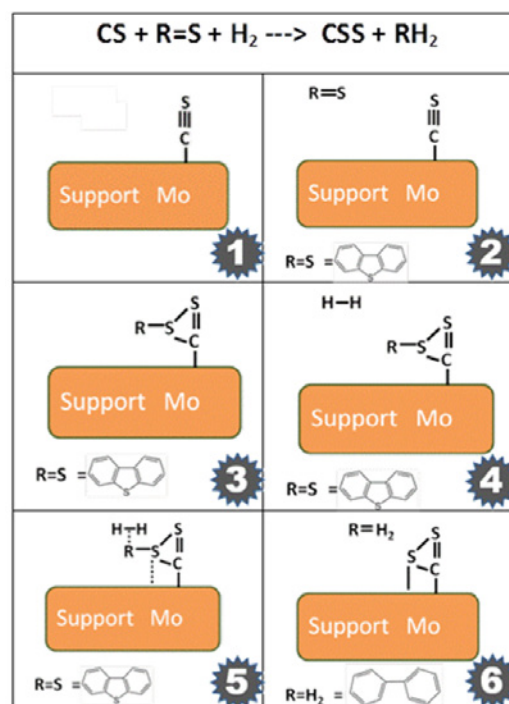
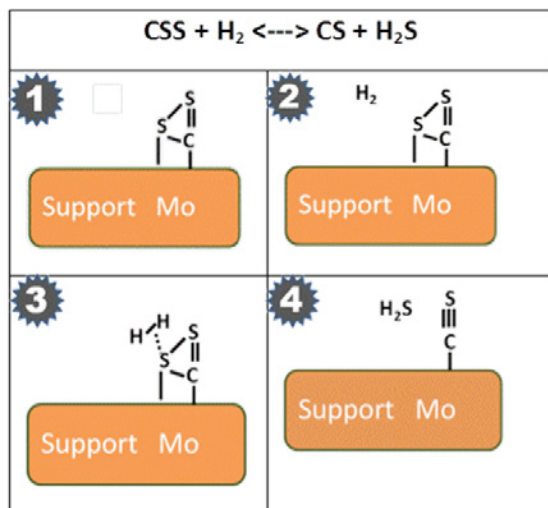


Figure 1. Reaction mechanics of  $\text{CS} + \text{R=S} + \text{H}_2 \longrightarrow \text{CSS} + \text{RH}_2$ .



**Figure 2.** Reaction mechanics of  $\text{CSS} + \text{H}_2 \rightleftharpoons \text{CS} + \text{H}_2\text{S}$ .

This means that SCS atoms in  $\text{MoS}_2$  replace the atoms of sulfur. These conclusions are in complete agreement with the recent studies of HDS (Chianelli y Berhault, 1999). In the catalyst composition suggested by Chianelli et al.  $\text{MoS}_{2-x}\text{C}_x$  (Chianelli y Berhault, 1999), for compounds formed of carbon with sulfur,  $x$  does not allow values of 0 or 2, only the option of  $x = 1$  is possible, which leads to the  $\text{MoSC}$  composition. Exactly, as the site proposed in this work. When  $x = 0$ , the result is  $\text{MoS}$  and when  $x = 2$ , the result is  $\text{MoC}$  (sulfur and carbon are separated).

## Conclusions

The presence of carbon and sulfur on the surface of the HDS catalysts allows the formation of a new species with better catalytic properties. The new catalytic site is responsible of HDS, it is the CS obtained after the pretreatment and after exposure of the catalyst to the hydrogen. Therefore, it is confirmed that the activation methods (pretreatment) have a great importance in the activity of the catalysts. This signifies that is necessary to improve the techniques of the synthesis or change the pretreatment agents, because the excess or deficiency of carbon or sulfur during pretreatment can diminish the amount of active sites (catalytic activity).

Then, the function of the promoters used in HDS (Ni, Co, etc.) is the formation of CS active sites in the stabilized catalyst in efficient form and with a better accessibility. In addition, based on the analysis of the Chianelli equation ( $\text{MoS}_{2-x}\text{C}_x$ ), the possible resulting molecules were calculated and it was found that structure with  $\text{MoCS}$  composition is the active site in hydrodesulfurization.

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