

# Spectroscopic study of the electronic interactions in titania supported ruthenium sulfide HDS catalysts.

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## Introduction

Comparative studies on the activity of transition metal sulfides (TMS) in the thiophene, dibenzothiophene and 4,6-DMDBT hydrosulfurization (HDS) reactions revealed that the HDS activity of the sulfides of the second and third rows is higher than that of the sulfides of the first row. A maximum is found in Ru and Os [1,2]. One of the proposals to explain this trend correlates the number of *d* electrons in the highest occupied molecular orbital (HOMO) of the TMS with the HDS activity. The proposal is based in theoretical calculations that indicate that in the best catalysts the TMS should have a HOMO filled with as many electrons as possible and have  $t_{2g}$  character instead of  $e_g$  [3]. From this point of view, it is not surprising that  $RuS_2$  is the most active HDS catalyst since ruthenium has an HOMO of  $t_{2g}$  nature filled with 6 electrons. The importance of the *d* population in TMS is corroborated by the fact that electronic transfer towards the TMS enhances the HDS activity. An example is the increase in activity experienced by Mo in CoMoS or NiMoS catalytic systems. The promotion effect has been defined as the capacity to inject electronic density into the *d* levels of the TMS [4]. The electronic density may also arrive to the TMS coming from supports like titania, and in that sense titania can be defined as a promoter [5]. The possible electronic interactions between titania, able to donate electronic density, and  $RuS_2$ , that already has the optimum configuration with 6 electrons at the  $t_{2g}$  HOMO, is clearly of great interest since it may help to better understand the role of *d* electrons in the HDS activity of TMS.

The object of the present work is to study the characteristics and behavior of  $Ru/TiO_2$  HDS catalysts when the sulfidation temperature is varied between 573 and 873 K.

## Materials and Methods

A series of  $Ru/TiO_2$  sulfided at different temperatures were characterized with X-Ray Diffraction (XRD), Temperature Programmed Reduction (TPR-S), UV-Visible-NIR spectroscopy and EPR spectroscopy. The characterization was made with freshly sulfided samples and with catalysts after reaction. The results were related to the activity in the thiophene, DBT and 4,6-DMDBT HDS reactions.

## Results and Discussion

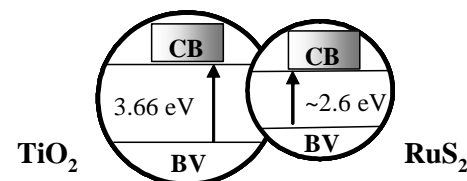
The thiophene HDS results evidenced that titania acts as a promoter or ruthenium sulfide only when the catalyst is sulfided at low temperature (573 K). Surprisingly, titania acts in detriment of the thiophene HDS activity when ruthenium is sulfided at high temperature (873 K). To explain this trend we analyzed the role and behavior in reaction of each species present in the sulfided catalysts, that is,  $TiO_2$ ,  $RuS_2$ -amorphous and  $RuS_2$ -pyrite [6].

In the case of sulfidation at high temperature, the species present in the catalyst after reaction are  $TiO_2$  and  $RuS_2$ -pyrite. The electronic spectroscopy evidenced partial

reduction of titania with the appearance of  $Ti^{3+}$ . It also showed that in the sulfided catalyst the conduction bands of titania and ruthenium sulfide are connected (Scheme 1). It is then most likely that the electron density that arrives to the titania conduction band via reduction is delocalized both in titania and in pyrite ruthenium sulfide. The net effect is the appearance of electron density in the  $E_g$  conduction band of pyrite ruthenium sulfide, which may have negative effects on the activity since it alters the already optimum configuration of 6 electrons at the full  $T_{2g}$  valence band. Besides, the electronic density is received in  $d_{x^2-y^2}$  and  $d_z^2$  orbitals of ruthenium, which are oriented towards the sulfur vacancies at the surface of the cubic particle. This negative charge in the  $e_g$  orbitals may play an inhibiting role in the adsorption of the sulfur containing molecule on the sulfur vacancies. The results from theoretical calculations showed that the interaction between the sulfur 3p lone pair of the thiophene molecule with the metal *d* orbitals greatly influences the activity of the catalysts [7].

In the case of sulfidation at 573 K, the catalytic system is different to that of  $Ru/TiO_2$  sulfided at 873 because after reaction the species present at the surface are  $TiO_{2-x}$  ( $Ti^{3+}$ ), small domains of metallic ruthenium (product of  $RuS_2$ -amorphous reduction during reaction) and  $RuS_2$ -pyrite with sulfur depleted surface [6]. The activity enhance can be explained by metallic ruthenium-support interactions. The electronic spectroscopy suggested the transfer of electron density from titania to metallic ruthenium, that causes weakening of the Ru-H bond, augmenting the capacity of the Ru-H groups to supply hydrogen to the HDS reaction. This effect may substantially increase the HDS activity of  $Ru/TiO_2$  sulfided at 573 K.

**Scheme 1.** Band gap transitions in titania and ruthenium sulfide.  
CB – Conduction Band  
VB – Valence Band



## Significance

The findings of this work provide experimental evidence to the theoretical correlations found between electronic structure and HDS activity since they show that the electronic transitions towards a TMS that already has full HOMO of nature  $t_{2g}$  populates  $e_g$  orbitals and diminishes its catalytic activity. They also contribute to better understand that the role of the promoter is to provide electronic density in *d* orbitals of metals with electron deficiencies in the  $t_{2g}$  orbitals.

## References

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