

## Trimetallic NiMoW, CoMoW unsupported catalysts for HDS

Amelia Olivas<sup>1\*</sup>, Gabriel Alonso<sup>2</sup>, Donald H. Galvan<sup>1</sup> and Sergio Fuentes<sup>1</sup>

<sup>1</sup>Departamento de Catálisis, Centro de Ciencias de la Materia Condensada, Universidad Nacional Autónoma de México, Apdo. Postal 2681, Ensenada, Baja California, México.

<sup>2</sup>Centro de Investigación en Materiales Avanzados, Miguel de Cervantes No 120, Chihuahua, Chih. C.P. 31109, México.

\*aolivas@ccmc.unam.mx

### Introduction

New unsupported catalyst called Nebula[1], presented in 2001 are reported to be four times more active for HDS than typical supported CoMo catalysts and two times more than advanced formulations. These catalysts are multimetallic based on transition metals as Ni, Co, Mo and W in a sulfided form. According with existing models for HDS the improved catalytic properties of multimetallic catalysts should be related with the appropriate combination of transition metals during preparation and the final arrangement of atoms at the border of crystallites. Trimetallic precursors (Ni-Mo-W) have been synthesized using several methods including direct precipitation and pH controlled precipitation [2], among others. It was reported that when Mo is substituted at least partially for W, an amorphous phase is produced, whose decomposition and sulfidation produces catalytically active materials. The method of thiosalt decomposition is an interesting alternative preparation since it provides a simple and reproducible method to obtain MoS<sub>2</sub> catalysts with controlled stoichiometry, wide range of surface areas and improved catalytic activity [3, 4, 5]. Some patents have reported the use of tetralkylammonium thiometalates to generate carbon-containing MoS<sub>2</sub> y WS<sub>2</sub> catalysts with high surface area and improved activity [6, 7]. In the field of nanomaterials Mo<sub>1-x</sub>W<sub>x</sub>S<sub>2</sub> nanotubes have been prepared by the decomposition of thiometalates solid solutions [8]. In this work, we report the preparation of trimetallic NiMoW and CoMoW sulfides derived from the impregnation of bimetallic ammonium thio-molybdate-tungstate (ATMW) salts, which are further decomposed both *ex situ* and *in situ*. The catalytic activity in the HDS of DBT and computational calculations using Extended Huckel methods, were also carried out.

### Materials and Methods

The NiMoW trimetallic sulfide catalysts were obtained by impregnation of (NH<sub>4</sub>)<sub>2</sub> (Mo<sub>x</sub>-W<sub>1-x</sub>)S<sub>4</sub> bimetallic thiosalts (ATMW) with Ni and Co nitrate solutions, according with reference [9]. The bimetallic ATMW complexes were obtained from ammonium heptamolybdate and ammonium metatungstate in ammonia solutions in contact with flowing H<sub>2</sub>S gas during 4 h. Bimetallic thiosalts with Mo/W atomic ratios (R1) = 0.5 (experimental values) were prepared. These thiosalts were impregnated with nickel and cobalt nitrates to form trimetallic Ni (Co) catalysts with atomic ratio [R2 = Ni (Co)/(Mo+W) = 0.5]. The *ex situ* activation of catalysts was made by treating the NiMoW (CoMoW) trimetallic precursor in 15% H<sub>2</sub>S/H<sub>2</sub> gas mixtures at 400 C during four hours. The *in situ* activation was done in the reaction media previous to the catalytic activity test. The catalytic activity in the HDS of DBT was evaluated in a batch reactor according to the experimental procedure reported in reference [2].

### Results and Discussion

Catalytic activity results for Ni-catalysts activated *in situ* and *ex situ* showed that the highest synergistic effect of Ni was observed for *ex situ* sample, also this catalyst had high selectivity to hydrogenation. The activity of this catalyst was two times higher than a NiMo/alumina industrial catalyst under the same conditions. The activation treatment has a great effect in selectivity. The HYD/HDS ratio is higher for *ex situ* than for *in situ* samples. It is suggested that the best distribution of Ni and W in the MoS<sub>2</sub> poorly crystalline structure of the Ni(Mo-W)S<sub>2</sub> *ex situ* catalyst was obtained under such conditions. The results for Co-catalysts showed that the sample has a higher catalytic activity than the Ni-catalyst but the HYD/HDS ratio was almost a half. The Extended-Huckel calculations showed the formation of metallic states in the N-Mo-W-S system due to the electronic interaction of Mo with W and Ni or Co that could explain the catalytic behavior of Ni and Co trimetallic catalysts.

### Significance

The trimetallic Ni(Co)MoW sulfide catalysts prepared by the impregnation of bimetallic ATMW thiosalts yield very promising unsupported catalysts with good Ni distribution, adequate mesoporosity, significant synergistic effect and two times more activity (in a weight basis) than an industrial NiMo/alumina catalysts. The optimal composition and distribution of atoms in the precursor obtained by controlling the reactions occurring during the preparation steps led to a very active catalyst.

### References

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