

XPS and Electron Microscopy Characterization of The Thermal Decomposition of Ni/K Catalytic Emulsions

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Water/oil emulsions elaboration using soluble metallic salts in the aqueous phase which allows to introduce in a controlled way relatively high quantities of the active element in the load to convert, constitutes a novel catalytic system that at the moment one has come using with success in the development of hydrotreatment technologies of heavy and extra heavy crudes, like it is the case of the commercial processes Aquaconversión[®] and HDH[®] plus[1]. The thermal decomposition of the catalytic emulsion inside the load under operation conditions, allows to generate *in-situ* a ultradispersed phase favoring a bigger catalytic activity [2,3]. However, due to the ultra small size of the generated active particles, it is practically impossible its separation to achieve an appropriate characterization since usually remains blended intimately with the load, reason why it is convenient to opt to model the decomposition process under laboratory conditions. [4]

Thermal decomposition of emulsions and catalytic microemulsiones of Ni and K that have come being used in the process Aquaconversión[®], was carried out under a detailed systematic study with the purpose of knowing the possible active phase that could be formed under the real conditions of process. The experimental methodology began with a study by MET of the internal structure of the emulsion Ni/K, using freeze fracture method. The X-Ray Photoelectron Spectroscopy technique (XPS) to study the derivative solid products of the thermal treatments applied to the different emulsions, between 25 and 450°C in N₂, vacuum and N₂/H₂O atmospheres, additionally these solids were characterized by TEM and EPMA [4].

TEM results allowed to differentiate the dispersed aqueous phase in the GOV (organic phase), as well as to determine that the distribution of the drops size of the aqueous phase is in a range between 1 and 3 μm, figure 1. Chemical analysis by EPMA indicate the formation of a solid phase of Ni, O, K, S, and a minimum quantity of carbon when decomposing of the Ni-K emulsion occurs, figure 2. This could be attributed that in the thermal decomposition, sulfur organic present in the GOV suffers a reaction with the potassium salt added in emulsified form, as it was found by XPS analyses. On the other hand, the presence of Ni and K favors the disappearance of great part of the present carbon in the medium, figure 3.

Additionally, TEM observations on the residuals of the thermal treatment of the emulsion Ni-K in N₂, showed the presence of particles whose crystallinity was evidenced by electron diffraction. Size of the same ones is among 2 and 8 nm.

The results of this work suggest that the combined application of TEM, XPS and EPMA techniques to study the decomposition products of catalytic emulsions, it can extend in the future to analyze systems where other metals are used and even different reactive atmospheres, in order to rehearse other combinations with possible catalytic activity.

References

- [1] P. Pereira et al, *Visión Tecnológica*, 6 (1998).
- [2] N. Panariti et al, *Applied Catálisis A: General*, 204 (2000) 203.
- [3] J. Córdova et al, *US Patent* No.6.043.182. (2000).
- [4] I. González, Undergraduate Thesis, Universidad Central de Venezuela. Caracas. 2002.



FIG. 1.

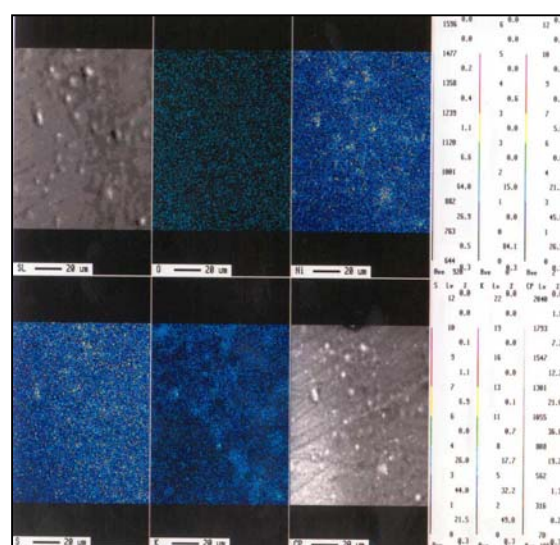


FIG. 2.

FIG.1. Ni-K Emulsion freeze fracture.

FIG. 2. Derivative solid products EDS analysis of Ni-K emulsions thermal decomposition.

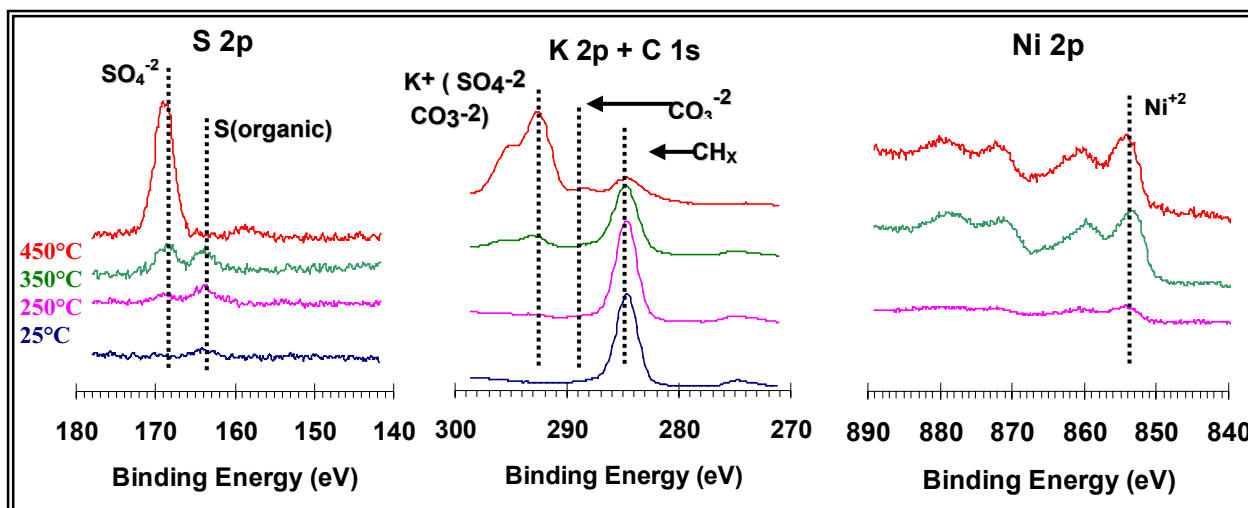


FIG. 3. XPS spectrum series of Ni-K Emulsion thermal decomposition.