ESRF	**Experiment title:** Structural characterization of dispersed catalysts for heavy crudes conversion.	**Experiment number**: 30.02.991
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Contexte de l'étude

An alternative to the use of supported catalysts for the processing of highly contaminated feeds is the addition of **dispersed** catalysts which may be discarded along with the ultimate residue where nonreactive metallic and coke-like species concentrate. Highly dispersed solids are generally unstable and tend to sinter under the normal conditions of hydrotreatment reactions. As a consequence, efforts have been dedicated to the preservation of the state of dispersion of finely divided catalysts particles. Such a process, studied at IRCELYON in the late 80's [1], concentrates know the interest of refining community [2]. We are currently performing the conversion of heavy crudes containing precursors such as Mo octoate or Mo napthenate at 19 MPa of H_2 and T close to 400°C and analyzing the resulting gas, liquid and solid products. Depending on the concentration of the metal and the reaction parameters, we can control the quality and stability of the hydrogenated products. The quantity of Mo added in the residue is in the range of 100-600 ppm. Due to the nature of the sample (black solid or liquid matrix) and the small concentrations of metal involved, only XAS can provide characterization of this active element. Therefore, XAS experiments were performed on BM30B in fluorescence mode on the sample in the liquid hydrocarbons or solid form obtained after some experiments. The purpose of the study was also to get information on the activation of the catalysts upon heating treatment.

Expériences au seuil K du molybdène

At first, organic precursors (Mo naphtenate, Mo octoate were analyzed) and compared to the starting hy characterization of this active element. Therefore, XAs experiments were performed on BM30B in fluorescence mode on the sample in the liquid hydrocarbons/dispersed catalysts mixture or solids obtained after some experiments. Fig 1. evidences that the dissolution procedure (at 150°C) does not affect the local environment of Mo and that the precursor state (at 600ppm) is kept since the FT of the reference is similar.

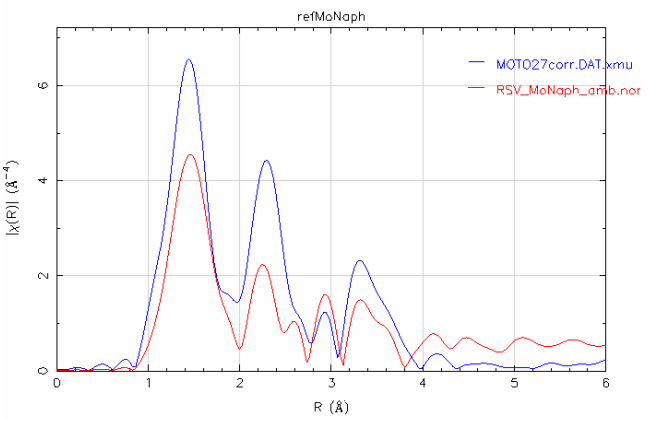


Fig 1 :Precusor (bleue and diluted salt in RSV)

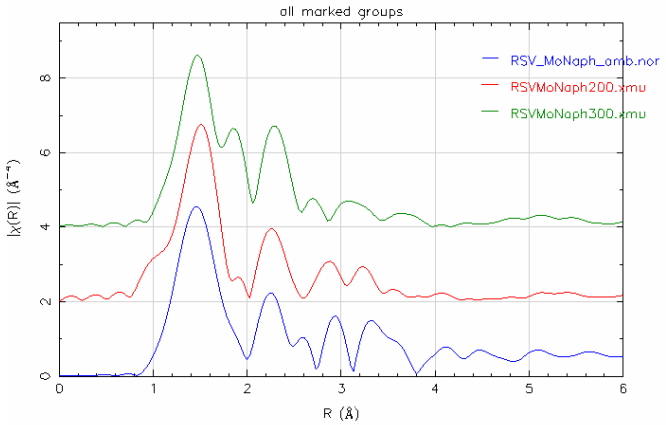


Fig 2 : Evolution of the precursor with temperature

At higher tempratures MoS_2 is formed and evolution of the nanoparticles is given by the number of Mo atoms (second sphere of coordination) N(Mo) obtained from the simulation of the XAS.

Expériences au seuil K du nickel

Attempts to characterize Ni were also performed. Ni can also be used as a cocatalyst. Similar experiments with Ni content of 80 ppm allowed to get XAS spectra which can be analized in term of XANES or EXAFS as illustrated by Fig 2.

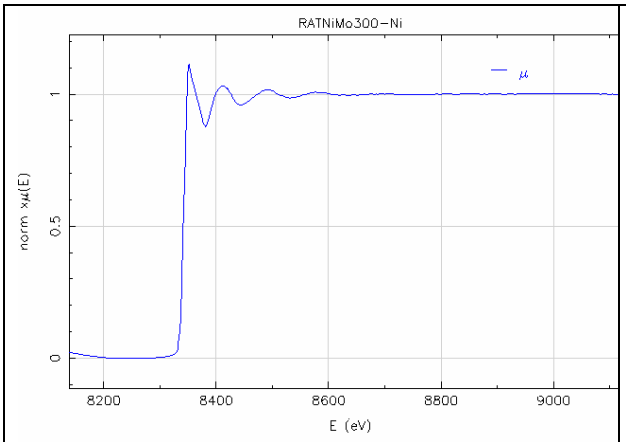
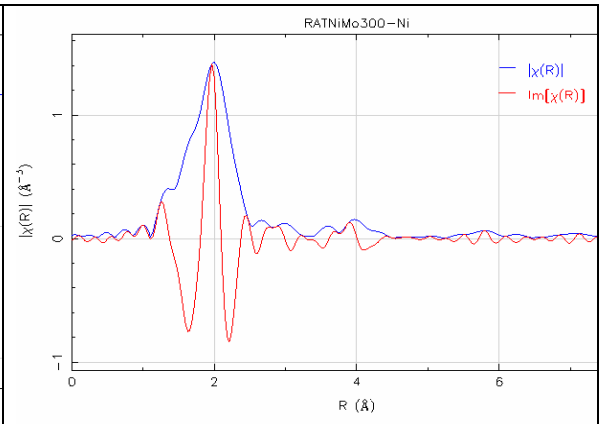


Fig 2. a) XAS spectra of 80 ppm of Ni catalysts in an atmospheric residue



a) FT at Ni K edge of left side spectra

Conclusions

For the first time structural information were obtained from catalysts diluted (below 500ppm) in an hydrocarbon matrix. Unique data on the activation and reacting state of the catalysts are obtained.

References

1- *New Developments in Deep Hydroconversion of Heavy Oil Residues with Dispersed Catalysts. 1. Effect of Metals and Experimental Conditions* Bernard Fixari, Sylvie Peureux, Jeanne Elmouchnino, Pierre Le Perchec, Michel Vrinat, Frederic Morel *Energy Fuels*, **1994**, *8* (3), pp 588–592

2-*A review of recent advances on process technologies for upgrading of heavy oils and residua* Mohan S. Rana , Vicente Sa´mano , Jorge Ancheyta , J.A.I. Diaz *Fuel* 86 (2007) 1216–1231