

# COMPARATIVE STUDY OF THE EFFECT OF METAL-BASED DISPERSED CATALYSTS ON THE DEEP HYDROCONVERSION OF A HEAVY OIL RESIDUE.

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## INTRODUCTION

The thermocatalytic hydroconversion process in the presence of dispersed catalysts yields deep conversion ( $\geq 85$  wt. %) of heavy oils into light distillates of good quality with a minimum of toluene insoluble (TI) residues (less than 3%) [1,2].

Experiments were performed on a Safanya vacuum residue with various catalytic precursors having variable amounts of metal and various severity of treatment.

The aim of this study is a better understanding of the role of the dispersed catalysts and of the reactions occurring during the heavy oil transformation by the characterization of the cokefied converted liquid fractions and of the TI residues by various analytical techniques [3].

## EXPERIMENTAL

The conversion experiments were carried out in a batch reactor pressurized with  $H_2$  (7.5 MPa at 20°C) under thermal treatment ranging from 420°C to 460°C and with a reaction time of 2 hours [2]. The catalyst precursors used were phosphomolybdic acid (PMA) and various metal-based naphthenate precursors (Mo, Co, Ni, Fe, Co-Mo, Ni-Mo), and more particularly among them molybdenum naphthenate (MoNaph). After treatment, the converted liquid effluents and the TI residues were separated by centrifugation in toluene. The liquid effluents were observed by optical microscopy after cokefaction at 800°C. The study of the optical textures of the cokefied samples allows an indirect characterization of the structural organisation existing in the converted liquid fractions. The TI residues, as obtained, were characterized by X-Ray diffraction (XRD), optical microscopy (OM), transmission electron microscopy (TEM, STEM), ESR, FTIR and  $^{13}C$  NMR [3].

## RESULTS AND DISCUSSION

*Comparison of PMA and MoNaph catalytic precursors*  
We previously showed [3,4] that the difference of efficiency of the two catalytic precursors in obtaining deep conversion is related to their mode of sulfurization, which is partial with PMA, leading to the formation of

$MoO_2$  and  $MoS_2$  particles, and is complete with MoNaph, leading solely to the formation of the active catalytic entity  $MoS_2$ . This induces strong differences in the physico-chemical and morphological characteristics of the liquid effluents and TI residues.

The TEM data showed that the small stacks of  $MoS_2$  layers (4 to 5 nm in length), and also the  $MoO_2$  particles - which were only observed in the case of PMA- are always associated with an entirely isotropic carbon phase. However, in the case of PMA, and even for high amounts of catalyst, the OM and TEM data showed that the TI residues consist also of anisotropic carbon phases (coalesced mesophase spheres and small anisotropic domains), while in the case of MoNaph, for a Mo content larger than 1400 ppm, the sample is entirely homogeneous and isotropic by OM. Quinoline fractionation of the isotropic carbon phase gives a quinoline insoluble (QI) fraction increasing with the final temperature. The characterization by X-ray diffraction of this QI fraction shows a 002 carbon peak characteristic of a material close to a solid with a misorientation of the basic structural units (BSU). A thermal treatment at 800°C of the TI isotropic carbon phase yields a coke composed of small domains of local molecular orientation of BSU [5], whose size varies from 50 to 150nm. These data indicate, in the case of MoNaph, that the TI isotropic carbon phase corresponds to a material evolving to a strongly cross-linked solid. This was confirmed by the other analytical techniques used.

The ESR results [6], obtained on the TI residues of the experiments performed with decreasing amounts of catalysts, showed that the evolution of the concentration of the stable aromatic radicals is much higher with PMA than with MoNaph, confirming the fact that, with MoNaph, the BSU in the TI residues tend to be cross-linked.

The IRFT and  $^{13}C$  NMR data evidenced with MoNaph that the increase of Mo content and the increase of the final treatment temperature lead to a decrease of the CH aliphatic content, proving that the dehydrogenation is a dealkylation. In the case of PMA, it is more complex since an aromatization and a relative enrichment in aliphatic CH are simultaneously observed. Hence, the hydrogenated molecules are still present in the TI

residues instead of contributing to the converted liquid fractions.

Moreover, the  $^{13}\text{C}$  NMR results show a good fit of the aromatic lines distribution with a simulation of chemical shift anisotropy. In the experiments performed without catalyst or with low catalyst content, the best fit corresponds only to symmetrical lines.

The results with PMA differ from those with MoNaph in that the asymmetrical line has its center of mass near the benzene reference, indicating hole doping due to  $e^-$  acceptor defects and/or to a moderate time averaging. With MoNaph, the center of mass is going nearer to 55 ppm/ $\text{C}_6\text{H}_6$ ; this corresponds to a specific decrease of the orbital contribution parallel to the external magnetic field, perhaps related to some bad aromatic organization. In this case, the wider aromatic distribution means less mobility of aromatic BSU.

The OM data obtained on the cokefied liquid fractions and expressed as frequency histograms of optical textures are a criterium of quality of the liquid effluents: the larger the size of the domains seen by OM, the more hydrogenated the liquid fractions.

#### *Comparison of various metal-based naphthenate precursors [3]*

Two series of experiments with low metal content were performed. The first one compares the catalytic activity of MoNaph, CoNaph, NiMoph and FeNaph, at a metal content of 1400 ppm. Deep conversion ( $\geq 85\%$ ) is only obtained with MoNaph, CoNaph and NiNaph.

The characterization by OM of the cokefied liquid fractions and the comparison of the frequency histograms of the optical textures showed more hydrogenated liquid fractions in the presence of MoNaph and CoNaph (this latter being slightly less efficient) than in the presence of NiNaph. The characterization of the TI residues showed that all the catalysts exist as sulfides. The crystals are 7-8 nm in size, in the case of CoNaph and 10 to 60 nm with NiNaph. In both cases, the sulfides are always associated with an isotropic carbon phase, as previously observed with  $\text{MoS}_2$ , but large crystals (0.2  $\mu\text{m}$  in size) were observed with FeNaph, never associated with an isotropic carbon phase. In the latter case, the microtexture of the TI residue is very similar to the one obtained without catalyst.

The second series of experiments compares the catalytic activity of MoNaph to that of bimetallic (Co-Mo, Ni-Mo) naphthenates at very low metal content (230 ppm). The conversion yields are still high and are similar (85-86%); however, the characterization of the cokefied liquid fractions shows differences. The metal association Co-Mo yields more hydrogenated liquid fraction than

Ni-Mo, both being more efficient than MoNaph alone. The characterization of the TI residues by TEM shows a close association of the  $\text{MoS}_2$  layers and of the crystals of Co or Ni sulfides. In the case of the Co-Mo catalyst, the smaller size of the Co sulfide crystals seems to lead to a better dispersion of the  $\text{MoS}_2$  layers: the  $\text{MoS}_2$  stacks are loose and form distorted columns. The size of the Co and Ni sulfide crystals seems to affect the dispersion of the  $\text{MoS}_2$  layers, which could explain the difference of efficiency of these bimetallic catalysts.

### CONCLUSION

The various analytical techniques used showed that the efficiency of MoNaph, as compared to PMA, is the result of its complete sulphidation, leading to deep conversion ( $\geq 85\%$ ) and the occurrence of a smaller proportion of cross-linked dehydrogenated TI residues, to the benefit of a larger proportion of hydrogenated liquid fractions.

The comparison of various metal-based (Mo, Co, Ni, Fe) naphthenate catalysts brings out strong differences in the quality of the liquid fractions. The more hydrogenated are obtained with MoNaph, followed by CoNaph, these catalysts being slightly more efficient than NiNaph and much more efficient than FeNaph.

The efficiency of the bimetallic (Co-Mo, Ni-Mo) as compared to the monometallic catalysts, is due to the close association of their metal sulfides on the scale of the aggregates, leading to deep conversion even with low metal contents (230ppm), retaining well hydrogenated liquid fractions and low content of TI residues (2 - 3%).

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