

## Effect of sulfur compounds on the HDS/HYDO selectivity in the transformation of a model FCC gasoline over Mo based catalysts

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### Introduction

Reduction of the sulfur level in gasoline (10 ppm S in 2009) requires the elaboration of new catalysts or the optimization of conventional ones. Consequently, hydrotreating catalysts must meet the selective criteria (hydrodesulfurization/hydrogenation) HDS/HYDO, i.e. achieve a deep HDS with a minimum of olefin saturation.

This work reports the effect of H<sub>2</sub>S and 2-methylthiophene over unsupported molybdenum based sulfide catalysts, promoted or not by nickel or cobalt in the transformation of a FCC model feed: hydrodesulfurization of 2-methylthiophene (2MT) and hydrogenation of 2,3-dimethylbut-2-ene (23DMB2N). A comparison between each reactant studied separately and the full model mixture has been done. Microkinetic modelling has also been used to correlate the HDS and HYDO activities as well as HDS/HYDO selectivity vs the metal-sulfur bonding energy of the catalyst and to include the effect of H<sub>2</sub>S and 2MT.

### Materials and Methods

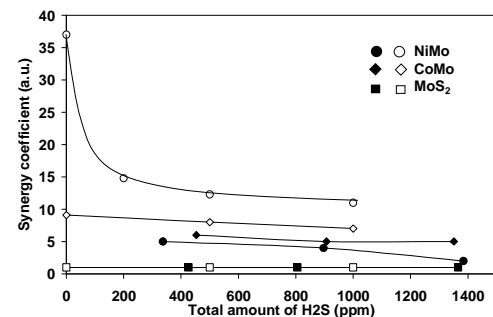
The three unsupported molybdenum based catalysts (MoS<sub>2</sub>, NiMo and CoMo) were synthesized and characterized as already described in previous papers<sup>1,2</sup>. Catalytic activity measurements were carried out in a fixed-bed reactor at 250°C under a total pressure of 20 bar. The feed was composed of 20 wt% of 23DMB2N or 0.3 wt% of 2MT in n-heptane for the study of each model molecule alone. The full model mixture was composed of 20 wt% of 23DMB2N, 0.3 wt% of 2MT and 30 wt% of ortho-xylene, representative of an aromatic molecule, in n-heptane. The impact of sulfur was studied by adding different quantities of H<sub>2</sub>S (from 0 to 1000 ppm of sulfur).

### Results and Discussion

Figure 1 represents the evolution of the synergy coefficient in hydrogenation of the olefin alone or when present in the model FCC gasoline feed, as a function of the total amount of H<sub>2</sub>S in the reactor. The total amount of sulfur comes from either the added H<sub>2</sub>S in the feed and/or the H<sub>2</sub>S resulting from the 2MT HDS (between 30 and 40% for each catalyst). The promoting effect of cobalt and nickel is found for the hydrogenation reaction, as reported in the literature by Miller *et al.*<sup>3</sup>, but is more pronounced when nickel is the promoter and mainly for low amount of H<sub>2</sub>S in the feed. However the activity strongly depends on the H<sub>2</sub>S amount, NiMo being more sensitive than CoMo<sup>2</sup>. The comparison of the results between the model feed and the olefinic feed indicates that the presence of both 2MT and H<sub>2</sub>S has a deeper negative impact on hydrogenation reaction than H<sub>2</sub>S alone. Indeed, NiMo and CoMo present the same

promoting effect which is lower than the one calculated for the olefin hydrogenation alone in the presence of the same total amount of H<sub>2</sub>S. These results highlight the competition of adsorption with the olefin depending on the sulfur amount. These results could be explained with a single microkinetic model involving the hydrogenation and hydrodesulfurization activity and also the HDS/HYDO selectivity integrating the metal-sulfur bond energy of bulk transition metal sulfide<sup>1,4</sup>. These two reactions were considered in competition on the same active site. From this model we reproduced the inhibiting effect of 2MT on the transformation of 23DMB2N due to a competitive adsorption between these two compounds, the covering level of 2MT being higher than the olefin on the catalysts surface. On the one hand, the increase of the 2MT partial pressure increased the optimum of the HDS/HYDO selectivity. On the other hand, the increase of the H<sub>2</sub>S partial pressure lead to a decrease of the selectivity and the optimum was moved to lower metal-sulfur bond energies. Depending on the feed composition it would be possible to modify the position and the magnitude of the maximum of the selectivity. This study gives a new insight on the HDS/HYDO selectivity behavior correlating experimental work and the recent DFT study of Krebs *et al.*<sup>5</sup>.

**Figure 1.** Impact of H<sub>2</sub>S on the transformation of 23DMB2N alone or in the model feed over molybdenum based catalysts (T= 250°C, P=20bar, full symbol: model feed, empty symbol: olefinic feed).



### Significance

The combination of experimental results and kinetic modelling helped explaining and determining the effects of various parameters in HDS and HYDO activity and especially on the selectivity HDS/HYDO which is the determining parameter for the treatment of FCC feeds. It is then possible to use this combined approach to evaluate the performance of new catalysts in order to optimize the selectivity.

### References

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