

## Study of the hydrodenitrogenation reaction with PtMo/NaY catalysts

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### Introduction

Catalytic hydrotreating has become an important process for removal of sulfur and nitrogen from petroleum due to increasing environmental constraints. Heterocyclic compounds containing sulfur and nitrogen are relatively stable structures because the S or N atoms are multiply bonded to their neighbors. Even though the hydrotreating process removes sulfur and nitrogen simultaneously, nitrogen compounds are more resistant than sulfur compounds and require more severe reaction conditions.[1,2]

The aim of this work is to investigate the behavior of PtMo catalysts supported on NaY zeolite in the hydrodenitrogenation of quinoline. In order to better understand the structural properties of the catalysts and to verify possible interactions between the metals and their interaction with the support, these catalysts have been characterized by different techniques such as temperature programmed reduction (TPR) and “in situ” X-Ray Diffraction. The behavior of the catalyst was investigated on the hydrodenitrogenation of quinoline, with different sulfur content. The results show the real possibilities of use of this system.

### Materials and Methods

The catalysts have been prepared by using NaY zeolite as support. Molybdenum has been incorporated by wet impregnation using  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  and platinum by dry impregnation with  $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ , with a metal loading of 1 wt%. The bimetallic catalyst was prepared by adding Pt on Mo/NaY catalyst, with the same metal loading. In order to better understand the structural properties of the catalysts and to verify possible interactions between the metals and their interaction with the support, these catalysts have been characterized by different techniques such as  $\text{H}_2$  chemisorption, UV-Vis DRS and “in situ” X-Ray Diffraction. For the catalytic tests, 200 mg of the catalysts were reduced with pure  $\text{H}_2$  at 573 K during 2 hours and then evaluated by using quinoline as reaction model at 673 K. The selectivities were calculated considering the formation of propylbenzene, propilcyclohexene and propilcyclohexane. Additionally, a higher tolerance of the bimetallic catalyst has been ascertained in the reaction using different amounts of sulfur.

### Results and Discussion

The results obtained for the activity of 1Pt/NaY and 1Pt1Mo/NaY catalysts are presented on Figure 1. It has been observed that the activity of bimetallic catalyst is four times higher than that of the monometallic catalyst. It can be explained considering the results of the Temperature Programmed Reduction (TPR) experiments, that indicated that the Pt addition enhance the reduction of molybdenum, as well as it favors possible interactions between the metals species presents on the catalyst, occurring significant formation of  $\text{Mo}^{4+}$  species. This species of molybdenum possibly interact with the sulfur of the feed stream, inhibiting the poisoning of the platinum and therefore enhancing the activity of the catalyst. Moreover, it is

important to report that the results of UV-Vis DRS analyzed in accordance with the procedure disclosed by Weber (3) and “in situ” X-Ray Diffraction, indicated the formation of a new active phase Pt-Mo on the bimetallic catalyst, possibly formed by the reorganization of the superficial molybdenum after the platinum addition.

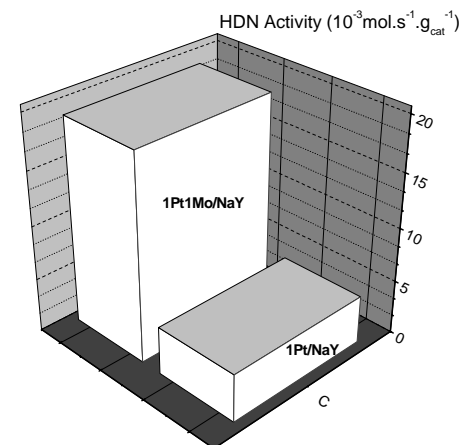


Figure 1. HDN activities for HDN of quinoline

### Significance

Many specialists are of the opinion that, in the near future, the nitrogen content on the middle distillates will be regulated to even below 100 ppm, which would ensure sufficient stability of middle distillate fuels.

### Conclusions

The 1Pt1Mo/NaY catalyst is more active and selective for the hydrodenitrogenation reaction. Moreover, it has been observed that the possible interaction between the Pt and Mo species favors the route of the reaction with less consumption of  $\text{H}_2$ , once it was observed significantly formation of propylbenzene.

These better results of activity and selectivity of bimetallic catalyst as well as its higher tioreistance can be expalined be explained by the interaction between platinum and molybdenum with the formation of a new active phase, which has been identified by DRS and DRX “in situ”.

### References

1. Prins, R., *Adv. Catal.*, 46, 399-405, (2001).
2. Liu, C., Yu, Y., Zhao, H., *Fuel Process. Tech.*, 86, 449-460 (1998).
3. Weber, R.S., *J. of Catalysis*, 151, 470- 474, (1995).