

# Synthesis, Characterization and Evaluation of NiMo/ Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> Catalysts prepared by the pH-swing method

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## Introduction

The increasing production of clean middle distillates <sup>[1]</sup> generates a field of important application in the design of new catalysts with balanced hydrodesulfurization (HDS), hydrogenation (HYD), hydrodenitrogenation (HDN) and hydrocracking (HCK) able to fulfill the environmental regulations <sup>[2,3]</sup>.

In this work we propose the use of NiMo/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts with an optimal SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio (SiO<sub>2</sub>) synthesized by the pH-swing method <sup>[4]</sup>, for hydrotreatment of middle distillates, which contain high amounts of aromatics (25~78.6 w,% ), with important amounts of sulfur and nitrogen (1.328~3.171 w,% and 61~2000 ppm respectively) <sup>[5]</sup>.

## Experimental.

NiMo/ SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts with different SiO<sub>2</sub> loading (0, 10, 25 and 50 wt %) were synthesized by the pH swing method. All catalysts were prepared with 13 wt % of MoO<sub>3</sub> and an atomic ratio (Ni+Mo)/Ni = 0.3. The sulfided samples were characterized by CO adsorption and analyzed by FTIR. Before the catalytic activity test, the catalysts were sulfided with a H<sub>2</sub>S/H<sub>2</sub> mixture at 400 °C during 4 hours. The experiments were performed in batch reactor at 325°C and 1200 psia under hydrogen atmosphere during 6 hours. Three catalytic activities were tested separately. For testing HYD activity a solution of 5 wt% Naphthalene in n-decane was employed. In the case of HDS a solution of 4,6- Dimethyldibenzothiophene in n-decane containing 1000 sulfur ppm was used and a solution of 70 ppm of N for HDN activity, that was prepared by adding Carbazole to a mixture of n-decane and m-xylene (70/30).

## Results.

In order to compare kinetic parameters the following simple model for each reaction was established:

$$-r_i = \frac{k_{APi} C_i}{1 + K_{Ai} C_i}$$

where (-r<sub>i</sub>) = ration rate of i component (Carbazole, 4,6-DMDBT and naphthalene, **k<sub>APi</sub>**=apparent reaction constant of i component, **K<sub>Ai</sub>**= equilibrium adsorption constant of i component and **C<sub>i</sub>**= concentration of i component. The results obtained by fitting the data to the proposed model are shown in table1.

**Tabla1.** Apparent reaction constant and Equilibrium adsorption constant.

Catalyst	<b>k<sub>api</sub> [L/gmol h]</b>			<b>K<sub>Ai</sub> [L/gmol]</b>		
	Carbazole	4,6DMDBT	Naphthalene	Carbazole	4,6DMDBT	Naphthalene
Al <sub>2</sub> O <sub>3</sub>	0.774	0.767	2.5	190	102	9.25
NiMo/10SiO <sub>2</sub> -90Al <sub>2</sub> O <sub>3</sub>	1.37	3.2	6.07	577	208	24.7
NiMo/25SiO <sub>2</sub> -75Al <sub>2</sub> O <sub>3</sub>	1.07	3.14	5.64	505	200	11.2

The catalyst NiMo/10SiO<sub>2</sub>-90Al<sub>2</sub>O<sub>3</sub> shows the higher value of apparent reaction constant for the three reactions, which means that it has the highest activity for the three reactions studied. Besides, In this catalyst the reactivity of the different species shows the order; **k<sub>NAF</sub> > k<sub>46DMDBT</sub> > k<sub>CARB</sub>**.

It was also found that the values of equilibrium adsorption constants for the three species also are maxima for the NiMo/10SiO<sub>2</sub>-90Al<sub>2</sub>O<sub>3</sub> catalyst. In this case, the order in the value of equilibrium adsorption constants is  $K_{A\text{carb}} > K_{A46} > K_{A\text{NAFT}}$ .

After three hours of reaction, NiMo/10SiO<sub>2</sub>-90Al<sub>2</sub>O<sub>3</sub> catalyst results to be 13% more active than that supported on Al<sub>2</sub>O<sub>3</sub> for HYD of naphthalene. For HDS of 46-DMDBT and HDN of Carbazole, we observe an increase in activity of 12% and 7% respectively (Table 2).

**Tabla 2.** Conversion at three hours of reaction

Catalyst	Carbazole Conversión %	4,6DMDBT Conversión %	Naphthalene Conversion %
Al <sub>2</sub> O <sub>3</sub>	41	61	81
NiMo/10SiO <sub>2</sub> -90Al <sub>2</sub> O <sub>3</sub>	48	74	94
NiMO/25SiO <sub>2</sub> -75Al <sub>2</sub> O <sub>3</sub>	41	69	88

Table 3 presents the intensity ratios of the IR bands after CO adsorption. For molybdenum promoted sites, CUS-NiMoS, we considered the band at 2080 cm<sup>-1</sup> and for unpromoted CUS-MoS<sub>2</sub> sites that at 2112 cm<sup>-1</sup> [6]. The highest ratio is obtained for the NiMo/10SiO<sub>2</sub>-90Al<sub>2</sub>O<sub>3</sub> catalyst indicating a greater level of molybdenum promotion by nickel. These results are in agreement with those obtained in the catalytic experiments.

**Tabla 3.** CUS-NiMoS/CUS-MoS<sub>2</sub> ratio after CO adsorption.

Catalyst	CUS-NiMoS/CUS-MoS <sub>2</sub> (2080 cm <sup>-1</sup> /2112 cm <sup>-1</sup> )	CUS-NiMoS/ g cat.
Al <sub>2</sub> O <sub>3</sub>	0.5303	226
NiMo/10SiO <sub>2</sub> -90Al <sub>2</sub> O <sub>3</sub>	0.9840	453
NiMO/25SiO <sub>2</sub> -75Al <sub>2</sub> O <sub>3</sub>	0.5242	235

To analyze the effect of silica loading in the support surface, experiments of FTIR in the hydroxyl region were performed. The results show that 10% of SiO<sub>2</sub> loading eliminates OH groups bonded to Al<sup>3+</sup> in tetrahedral coordination (3775 cm<sup>-1</sup> band)<sup>[7]</sup>. 25 % SiO<sub>2</sub> in the support, causes almost the complete disappearance of the alumina OH' s groups giving rise to typical silanol groups.

## Conclusions

The catalyst with 10% of SiO<sub>2</sub>, showed higher activities for naphthalene hydrogenation, 4,6 DMDBT hydrodesulfurization and carbazole hidrogenitrogenation than that supported on alumina. This behavior is explained as follows: 10 wt% of silica modifies alumina surface eliminating the OH' s groups bonded to Al<sup>3+</sup> in tetrahedral coordination. This results in a less interacting surface that could give rise to well dispersed and sulfided molybdenum species which are adequately promoted by Ni as shown by the CO adsorption experiments.

## References

1. Moreira Rodríguez H. Perspectivas del Uso de los hidrocarburos a nivel México. Informe técnico abril 2005, México Secretaria de energía SENER.
2. M Breyse; J.L Portefaix; Catalysis Today 10, (1992), 489-505.
3. R Gray Murray. Upgrading petroleum residues and heavy oil.. Marcer Dekker. New York, 1996.
4. T Ono; Togari O. Preparation of Catalysts III. Elsevier Science Publisher the Netherlands, 1983.
5. Teh C. Ho. Applied Catalysis A: General 244 (2003) 115-128.
6. Digne M., Sautet P. Journal of Catalysis 211 (2002) 1-5.
7. Mauge F; Duchet J.C; Lavalley J.C. Catalysis Today. 10, (1991), 561-577.