

## Synthesis of alkaline (K, Li) modified CoMo/Al<sub>2</sub>O<sub>3</sub>-MgO-(X) catalysts, potentially useful for selective HDS of gasoline

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### Introduction

In order to fulfill the restrictions on sulfur content for transport fuels, it is necessary to adequate the hydrotreatment (HDT) catalysts and processes. Although, sulfur compounds present in the gasoline are not difficult to eliminate, in some industrial installations it has been reported that after hydrotreatment of the FCC naphtha, there is some hydrogenation (HYD) and loss of octane number<sup>1</sup>. To diminish the HYD activity the use of CoMo phases and a less acidic support is proposed. Klimova et al.<sup>2</sup> reported that the use of less acidic support, obtained by the addition of a small quantity of MgO to the alumina, causes a decrease on the HYD activity, while the HDS activity is preserved. However, in another work has been reported<sup>3</sup> that those mixed oxides had a low specific area and the inconvenience of the low textural stability in the water presence and also at exposition at room conditions, showing that Mg(OH)<sub>2</sub> and also Mg(CO<sub>3</sub>)<sub>2</sub> are obtained on the support surface; however, the catalytic performance did not change a lot. Taking this into account, it is advisable that the hydrotreatment catalysts supported on magnesia and also on hybrid supports containing MgO should be prepared by non-aqueous impregnations. Besides, on pure magnesia it has been supposed the existence of undesirable interactions between MgO and the promoter metal (Co or Ni) when aqueous solutions are used, obtaining a solid solution which has been reported before<sup>2</sup>. In this work CoMo catalysts for selective HDS of gasoline were prepared over hybrid supports of MgO-Al<sub>2</sub>O<sub>3</sub> doped with alkaline (K or Li) oxides, which were added in small quantities up to 5 wt %, to get a more stable magnesia structure and to maintain the low HYD activity. The main objective of this work is to study the effect of the alkaline addition to the structure formulation and to the acidic sites on one hand, and to the other, the study of the changes on the catalytic performance in selective HDS.

### Materials and Methods

The Al<sub>2</sub>O<sub>3</sub>-MgO support was prepared by the impregnation of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> from the pseudo-boehmite Catapal B<sup>TM</sup> with an aqueous solution of Mg(NO<sub>3</sub>)<sub>2</sub>·6 H<sub>2</sub>O (Aldrich) in the required amount to reach the 5 % wt as MgO. The alkaline-modified supports were prepared by two single ways: a) Simultaneous mixture of Mg(OH)<sub>2</sub> plus the corresponding salt of Li or K to alumina by using a binder of Catapal B according to the method described elsewhere<sup>4</sup>. Hereafter, these support were called Al<sub>2</sub>O<sub>3</sub>-MgO-Li<sub>2</sub>O or Al<sub>2</sub>O<sub>3</sub>-MgO-K<sub>2</sub>O, b) once the support Al<sub>2</sub>O<sub>3</sub>-MgO was thermally treated by a drying (12 h, 100 °C) and calcination (4 h, 550 °C) steps the addition of Li or K was made by impregnation of an aqueous solution containing the alkaline salt, henceforth, this supports will be identified as Li<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub>-MgO or K<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub>-MgO. Over these two series of supports, the impregnation of the precursors of the active

phases CoO and MoO<sub>3</sub> was done simultaneously using the pore volume impregnation technique by using an amoniacal solution obtained, according to the method described before<sup>5</sup>. Catalysts performance was evaluated in HDS, HYD and HCY simultaneous reactions with a model mixture and its structural, textural and acid-base properties were characterized for several techniques, such as powder X-ray diffraction, surface area (BET), Infrared and Raman spectroscopies, an by Py thermodesorption.

### Results and Discussion

The addition of an alkaline (K or Li) oxide to the hybrid Al<sub>2</sub>O<sub>3</sub>-MgO support causes a slight decrease in the TNAS (No se ha definido) for the support and the corresponding CoMo catalysts determined by the Py thermodesorption. Also the alkaline addition promotes the textural and structural stability of the MgO, that possibly could be attributed to the solid solution formation (Li o K)<sub>x</sub>Mg<sub>1-x</sub>O. The decrease in the TNAS is related to activity reduction for HCY and also to the decrease in HYD activity.

**Table 1. Catalytic performance and overall conversions for benzothiophene and n-decane, and conversion and yield for 1-octene.**

Catalysts	Conversion (%)			Yield to octane
	octene	benzothiophene	decane	
CoMo/Al <sub>2</sub> O <sub>3</sub>	100	96.9	3.9	97.0
CoMo/Al <sub>2</sub> O <sub>3</sub> -MgO	98.6	98.2	0.6	90.7
CoMo/Al <sub>2</sub> O <sub>3</sub> -MgO-K <sub>2</sub> O	98.7	97.3	0.7	85.7
CoMo/K <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub> -MgO	93.0	95.1	1.8	83.7
CoMo/Al <sub>2</sub> O <sub>3</sub> -MgO-Li <sub>2</sub> O	99.3	98.5	0.7	92.0
CoMo/Li <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub> -MgO	97.1	96.7	0.9	83.7

From table 1, We observe that the better performance for the selective HDS was obtained for the catalyst CoMo/Li<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub>-MgO, where is obtained the lower yield to octane and the benzothiophene conversion is maintained.

### Significance

The objective of this work is to contribute of the understanding of the effect of alkaline addition to the structure formulation and to the acidic sites by one hand, and to the other to contribute in the performance of a better catalyst for selective HDS.

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