Effect of acidity, hydrogenating phases of catalysts in the molecular structure evolution of asphaltenes during hydroconversion

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Introduction

The aim of this work is to investigate the influence of the catalyst acidity in vacuum residues hydroconversion processes and particularly in the refractory asphaltenes compounds. A grafting procedure was applied to incorporate silicon at the surface of alumina carriers which is suspected to enhance acidity [1,2]. Comparatively to Ancheyta *et al.* [3] this original method is expected to keep unchanged the textural properties and sulphided metal active phase due to the low amount required [4]. The corresponding NiMo catalysts with different silicon amounts are evaluated using a multi-techniques set of analyses in order to assess the conversion rate and mechanism. Then it is attempted to describe the molecular structure and to establish a link with catalysts properties.

Materials and Methods

Aluminosilicate carriers were obtained by grafting silica on the trilobic alumina surface [4]. The grafted alumina was consecutively hydrolyzed overnight, dried at 120 °C (24 hours) and calcined at 550 °C (4 hours). In order to increase the silica amount grafted over the support, the complete grafting process was repeated two or three times. It allows us to obtain carriers up to 2.3 wt.% of silicon (Table 1). The catalysts prepared for this study were obtained from the incipient wetness impregnation with a NiMo solution followed by a drying and calcination under air for 2 hours at 450 °C. XRF analysis are in agreement with the target values (Table 1).

Table 1. textural and XRF	properties of catalysts
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carriers				catalysts			
	Si (wt.%)	APD [*] (nm)	Pore Volume	Sbet	MoO ₃	NiO	P ₂ O ₅
			(normalized)	(normalized)	(wt.%)	(wt.%)	(wt.%)
NiMoP 0%	-	$14,5 \pm 0.1$	100 ± 3	100 ± 3	$\textbf{14.1} \pm 0.4$	3.0 ± 0.1	$\textbf{3.6}{\pm}~0.2$
NiMoP 2.3%	$\textbf{2.3} \pm 0.3$	$\textbf{14.5}\pm0.1$	91 ± 3	95 ± 3	$\textbf{14.4} \pm 0.4$	3.1 ± 0.1	3.3 ± 0.2

The catalytic test was carried out in an isothermal batch reactor filled with 90 mL of Safaniya Vacuum Residue (VR) and 15 mL catalyst (sulphided ex-situ) introduced inside a stationary perforated basket. The test is performed at 370 °C and 9.5 MPa for 3 to 7 hours. At the end of the test, the final product is recovered and asphaltenes are recovered by a derived method of the NF T60-115. NMR ¹³C is performed using a 600 MHz Bruker Avance spectrometer to determine the proportion of the different types of aromatics and aliphatic carbons. Asphaltenes molecular weight distribution was performed using Size Exclusion Chromatography (SEC) on a Waters Alliance 2695 system by using a refractive index detector and THF as eluent.

Results and Discussion

First, it appears (NMR ¹³C) that increasing acidity induces some cracking/isomerizing transformations as for thermal reaction but without any change in aromaticity (figure 1). In a

molecular point of view, after 3 hours under reaction, the NiMo catalyst modified with silica exhibit more condensed aromatic rings and shorter aliphatic chains (figure 2). This difference is even magnified after 7 hours of reaction.



Figure 1. Evolution of polarity (Cali/Caro) of asphaltenes with the cracking of aliphatic chains (diminution of CH₂/CH_x _{Aliphatic}) with acidity vs. thermal conversion (NMR data).



Figure 2. Evolution of asphaltenes molecular structure with time and acidity

Significance

The aim of this work was to investigate the influence of the catalyst acidity in a vacuum residues hydroconversion process. Grafting procedure allows us to both control textures but also the rate of hydrogenating active phase. Our results reveal that acidity can enhance cracking of aliphatic chains of asphaltenes and, some cracking reactions are enhanced, but are not linked to significant changes in the asphaltenes aromaticity. These catalysts give hope to a new catalyst type for hydroconversion of heavy petroleum fractions and to maximize their conversion yield.

References

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