EFFECT OF CATALYST ACIDITY ON RESIDUES HYDROTREATMENT

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Introduction

Worldwide trends indicate a decline in the availability of conventional crude oil which is balanced by the increasing exploitation of heavy crude. This trend makes it crucial to have modern refineries adapted to the upgrading of distillation petroleum residues. Petroleum residues contain high quantities of sulfur that can be eliminated by hydrotreatement (HDT) using fixed-bed units. From this process an ultra-low sulfur fuel can be obtained, as well as a product that can be further upgraded in a Residue Catalytic Cracker (RCC).

The presence of high molecular weight asphaltenic molecules, resins and organometallic compounds in residues makes the hydrotreatment of these feedstocks markedly different from that of light feeds. By definition, asphaltene is the most polar fraction of crude oil and it precipitates in the presence of an high excess of normal alkanes (nC5, nC6 or nC7), although it is soluble in toluene [1]. The remaining fraction called maltenes contains saturates, aromatics and resins. The heavier fractions of resins and asphaltenes concentrate most metals and impurities such as sulfur and nitrogen. Asphaltenes and metals like Ni and V are poisons for the hydrodesulphurization (HDS) catalysts used in hydrotreatment processes.

The presence of such complex compounds makes the designing of residue hydrotreatment catalysts a hard task and a challenge to define optimum parameters (carriers porosity, acidity and active phase properties).

This study is focused on the impact of hydrotreatment catalysts acid properties in residues hydrotreatment activities (HDV, HDNi, HDS, HDAsC7, HDN, HDCCR).

It was shown that only fluorine introduced after the active metals impregnation, allowed to develop the most enhanced Brønsted acidity without a major impact in the active phase.

A catalytic test was performed in a lab scale batch reactor at hydrotreatment conditions and using a Safaniya vacuum residue feedstock. Hydrotreatment functions were followed to show the effect of catalysts acidity on hydrotreatment performances.

Experimental

NiMoP catalysts carried on multimodal alumina porous distribution were used. The acid properties of alumina carriers were modified (in terms of nature, number and strength of acid sites) in a wide range of acidity. This was achieved by doping the carriers using different additives (F, SiO2) at different contents. The active phase is introduced by incipient wetness impregnation of carrier grains with a solution containing simultaneously Ni, Mo and P (solution prepared under reflux at 90°C from MoO_3, H_3PO_4 and $Ni(OH)_2$ as precursors). Impregnation is followed by a maturation step during 12h in a water saturated atmosphere at room temperature. After impregnation it follows a drying step for 12h at 120°C and calcination at 500°C in a 1.5 $nL_{dry\ air}/h/g_{catalyst}$ flow with a 5°C/min heating ramp. The active phase target content in oxidic form for all catalysts is 1.9 wt% NiO, 9 wt.% MoO_3 and 2.2 wt.% P_2O_5 (Ni/Mo~0.39 at/at and P/Mo~0.46 at/at). In this system, surface acidity is modified by incipient wetness impregnation of F or SiO_2 precursors. Fluorine was added after the active phase impregnation using NH_4F as a precursor. SiO_2 is inserted before the active phase impregnation using *Rhodorsil* E1P (emulsion containing 35 wt.% of polydimethylsiloxane oil) as a precursor. After impregnation, follows a maturation step for 12 h in a water saturated atmosphere at room temperature, a drying step for 12 h at 120°C and a calcination at 500°C in a 1.5 $nL_{dry\ air}/h/g_{catalyst}$ flow with a 5°C/min heating ramp.

The distribution of Brønsted and Lewis acid sites were distinguished by infrared spectroscopy (IR) using respectively lutidine and pyridine as probe molecules. The sulfided samples were also analysed by Transmission Electron Microscopy (TEM) in order to evaluate MoS_2 nanoculsters dispersion.

A catalytic test was performed in a lab scale batch reactor at hydrotreatment conditions and using a Safaniya vacuum residue feedstock. The test was performed at 370°C, total pressure of 95 bar, for 2 hours length. The hydrotreatment functions: HDV, HDNi, HDS, HDAsC7, HDN and HDCCR were followed, as well as hydrogen consumption. Carbon and hydrogen content in spent catalysts were analyzed.

Results and Discussion

Catalysts characterization results obtained by IR-pyridine and IR-lutidine are presented in Table 1.

Table 1 – Sulfided Catalysts Acid Sites Quantification by IR-pyridine (Lewis Sites) and IR-Lutidine (Bronsted Sites)*

	Lewis		Brøsnted	
	Weak	Strong	Weak	Strong
Ref.	1.3±0.22	0.9±0.22	1.2±0.14	0.2±0.14
3%F	0.6±0.13	0.7±0.13	2.6±0.41	1.5±0.41
10%SiO2	0.3±0.06	0.3±0.06	1.4±0.17	0.3±0.17

*Results in arbitrary units.$cm^{-1}.g^{-1}$

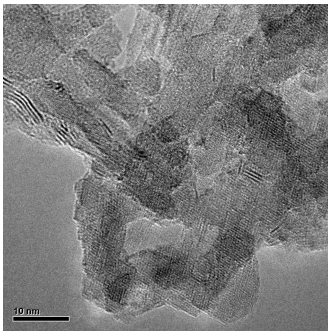
These results show that the reference catalyst (ref.) presents a higher amount of weak Lewis sites (1.3 a.u.$cm^{-1}.g^{-1}$) and identical amount of strong Lewis sites (0.9 a.u.$cm^{-1}.g^{-1}$) in relation to fluorine doped catalysts (0.6 and 0.7 a.u.$cm^{-1}.g^{-1}$ respectively). This is in agreement with other works suggesting that low quantities of fluorine could interact with Lewis acid sites [2]. In order to explain these trends, we propose that either fluorine occupies preferentially the weak sites, or if the strong Lewis sites are taken by fluorine, it enhances adjacent weak Lewis acid sites by its electro-attractor effect converting weak into strong Lewis sites.

Lewis acidity is also lower in SiO_2 catalysts. In this case, SiO_2 is deposed on Al_2O_3 surface and therefore alumina Lewis sites should be inaccessible.

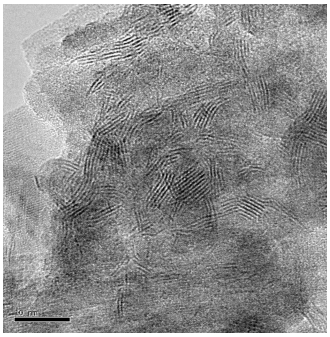
Brønsted acidity is higher in terms of number and force in fluorine doped catalysts (3%F). The increase of Brønsted acidity is interpreted as the result of the electronegativity carried by the fluorine element. Fluorine attracts the electrons towards itself reducing the electronic density of adjacent OH groups existing on alumina support. This is consistent with the proposals from other research works [2,3].

In the case of SiO_2 catalysts, no significant increase of Brønsted sites is observed in relation to reference catalyst.

TEM images presented in Figure 1 reveal that SiO_2 affects molybdenum dispersion resulting in a bulky sulfided active phase.



a. Ref AMM
(dispersed MoS2 nanoclusters)



a_3. AMM-10%SiO_2
(bulky nanoclusters)

Figure 1. TEM images of sulfided reference catalyst $NiMoP/Al_2O_3$ and SiO_2 doped catalyst $NiMoP/Al_2O_3$-10%SiO_2

Figure 2 presents the hydrotreatment performances of the reference alumina supported NiMoP catalyst and acid catalyst obtained through the Safaniya vacuum residue catalytic test.

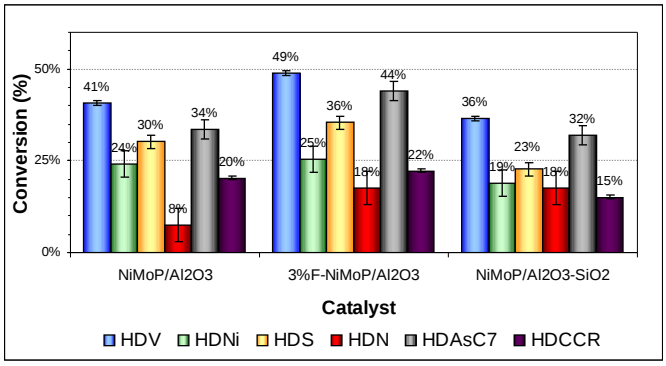


Figure 2. Hydrotreatment performances of reference catalyst NiMoP/Al2O3 and doped catalysts 3%F-NiMoP/Al2O3, NiMoP/Al2O3-10%SiO2

These results show that HDV, HDNi, HDS and also in lower degree HDAsC7 performances are lower with SiO_2 doped catalyst in comparison to the reference catalyst ($NiMoP/Al_2O_3$). This is explained by the loss of active hydrogenating sites probably due to the bulky MoS_2 nanoclusters as observed by MET results. HDCCR follows this trend by decreasing from 20wt% (reference catalyst) to 15wt% (SiO_2 doped catalyst). Moreover, the hydrogen consumption decreased from 3.6NL (ref. catalyst) to 2.7NL (AMM-10%SiO_2), which clearly demonstrate that hydrogenation is limiting the hydrotreatment performances. Surprisingly, the lower HYD activity resulted in no supplemental coke as it is revealed by the elemental characterization results of spent catalysts presented in Table 2.

Table 2 – Spent Catalysts C, H Elemental Analysis

	Ref AMM	3%F-AMM	AMM-10%SiO2
C (wt.%)	9.8±0.5	10.1±0.5	8.4±0.4
H (wt.%)	1.4±0.1	1.3±0.1	1.3±0.1

It can be proposed that HYD is limiting the bifunctional conversion mechanisms but not the hydrogenation of radicals precursors of coke. HDN conversion increases from 8 to 18% this increase is however low in relation to HDN uncertainty. HDN increase could be explained by the adsorption of basic organic nitrogen on SiOH sites.

The results present in Figure 2 show that fluorine increased HDV (from 41 wt.% to 49 wt.%) and HDAsC7 conversions (from 34 wt.% to 44 wt.%) in relation to the reference alumina supported catalyst. HDS also increases from 30 wt.% to 36 wt.% and HDN increases from 8 wt.% to 18 wt.%.

The hydrogen consumption (3.6-3.8 NL) and the HDCCR (20-22 wt%) were conserved. Moreover, the increase of HDAsC7 did not result in higher contents of carbon deposits (C ~ 10 wt.%, Table 2).This results confirm that the active phase was indeed not distressed by fluorine.

Although the performance improvements are moderate, these results demonstrate that HDT catalysts can be upgraded by means of enhancing Brønsted acidity (number and/or force) in order to promote an asphaltene bifunctional type conversion mechanism.

Conclusion

Acid catalysts were prepared with identical pellets shape, porous distribution and identical active phase in relation to a reference alumina supported catalyst. Catalysts differing in the acid nature (Brønsted / Lewis) and strength of acid sites were obtained by means of using different acidifying agents.

Regarding to SiO_2 doped catalysts, TEM characterization results reveal that a bulky sulfided active phase is obtained. As a result, hydrogenation activity is limited and lower hydrotreatment performances are obtained.

Catalysts doped with fluorine revealed no hydrogenation activity limitations. Furthermore, acidity characterization by IR revealed that fluorine reduces Lewis acidity and it increases significantly the number of weak and strong Brønsted acid sites.

Residue hydrotreatment catalytic tests have shown that the acidity enhanced by fluorine (strong Brønsted sites), increased HDAsC7 and overall hydrotreatment activities without resulting on supplemental coke. These results suggest that hydrotreatment catalysts acidity could be adjusted in order to improve hydrotreatment performances.

References

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(3) Fischer, L. Modification de catalyseurs sulfure pour l'hydrotraitement par ajout de fluor. 1999. PhD Thesis, Université Pierre et Marie Curie.