**ENHANCEMENT OF HYDROCRACKING ACTIVIY OF DISCARDED FCC CATALYST BY MEANS OF ACIDITY MODIFICATION**

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**Highlights**

* Noble metal‑based catalysts with different acidities are employed
* Acidity plays a key role in the second stage of the LCO upgrading
* Lifespan of equilibrated FCC catalysts is extended

**1. Introduction**

Nowadays the oil market is especially volatile, thus the refining industry is working hard to find the most optimum way to process the heavier and sourer crude while maintaining its economics and profitability together with meeting the growing demand of high‑quality fuels [1]. With the aim of intensifying the oil valorization, high efforts are being done to adapt the already installed and amortized units for the processing of non-conventional feedstocks, such as LCO. Considering the units available in the refineries, the best perspectives are focused on the usage of hydroprocessing units due to their multiple advantages [2]. Moreover, hydroprocessing in two stages, a first stage of hydrotreating (HT) with transition metal‑based catalysts and a second stage of hydrocracking (HC) with noble metal‑based catalysts, has proved to be a very suitable way of upgrading these streams [3]. In this work, the possibilities of using equilibrated FCC catalysts as support for catalysts used in the second hydrocracking stage of LCO valorization has been studied, extending, in this way, the life cycle of one of the highly produced residua of the refineries.

**2. Methods**

The feedstock consists of a previously hydrotreated light cycle oil (LCOHT). Two in-house prepared catalyst have been used: (i) Pt‑Pd/HY and (ii) Pt‑Pd/HY‑Al2O3, with the same Pt‑Pd metal loading (0.5-0.5 wt%) and using as supports a HY ultra-stable zeolite (SiO2/Al2O3 = 12) and an equilibrated commercial FCC catalyst (HY- Al2O3), respectively. In this work, apart from these two catalysts a physical mixture of them (50 wt%) has been employed, also. A deep characterization of the catalysts have been done [3]. Hydrocracking runs have been carried out in a down-flow fixed bed reactor in the following conditions: 400 °C; 65 bar; H2/LCOHT ratio, 1000 NmLH2 mLLCO-1; space velocity (WHSV), 0.21 h-1; time on stream (TOS), 8 h. Products have been analyzed by chromatographic means.

**3. Results and discussion**

In the studied process, all the catalysts, before reaching a pseudo‑equilibrium state, show an initial fast deactivation period as a consequence of both coke deposition and the stabilization of the metallic phases [4]. The length of this initial period has varied depending on the catalyst employed: the Pt-Pd/HY catalyst reached it after 2 h, whereas both Pt‑Pd/HY‑Al2O3 catalyst and the physical mixture of catalysts needed c.a. 4 h. Since the metallic phase is the same for the three catalysts, the coke formation rate seems to be related to the properties of the support, i.e., acidity and porous structure. Besides, as it has been widely demonstrated, the acidity of the catalyst is a key factor controlling the hydrocracking activity and selectivity of noble metal‑based catalysts in the hydrocracking of secondary streams [5]. Figure 1 depicts the dependence between the hydrocracking (HC) and hydrodearomatization (HDA) conversions and the acidity of the catalyst employed. This way, the HC activity of the catalysts is linearly dependent of their acidity in the pseudo‑stationary state, reaching for acidities higher than 0.16 mmolNH3 g-1 total conversions at zero time of reaction. On the other hand, the HDA activity has not clear acidity dependence, so, for this route, porous structure appears to be a key factor. One more time, at zero time of reaction values of 100 % of HDA conversion are achieved. Comparing the performance of the different catalysts, the intermediate behavior of the physical mixture offers promising results, as the products stream is composed of c.a. 50 wt% of naphtha and diesel fractions with high HDA and HC activities. This fact reveals that adding a high acidity catalyst to the spent FCC catalyst is a good way of improving the behavior of the discarded FCC support and extending its lifespan.

XHDA

Acidity (mmolNH3g-1)

**Figure 1.** Dependence between the hydrodearomatization (HDA) and the hydrocracking (HC) conversions with the acidity of the catalysts.

XHC

XHC, zero time

XHDA, zero time

**4. Conclusions**

Using the spent FCC catalyst mixed with a high acidic fresh catalyst in the second stage of hydrotreatment of LCO is a good way of extending the life cycle of highly produced residua of the refineries. The addition of this highly acidic catalyst leads to an enhancement of the acidity, which is the key factor controlling the hydrocracking activity and selectivity, producing a stream with a good quantity of naphtha and diesel. Besides, the hydrodearomatization activity, controlled also by other physical properties of the catalyst like pore volume, is improved.

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