Influence of the Support on the Deactivation of Bifunctional Catalysts (Pt-Pd/support) in the Hydrocracking of LCO

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The deactivation of bifunctional catalysts (Pt-Pd/support) has been studied on the hydrocracking of LCO (light cycle oil, which is a highly aromatic byproduct in the FCC unit). The reactions were performed in a fixed bed reactor using a Pt-Pd catalyst prepared with supports of different acidity and pore structure: B (H-beta zeolite), Y_5, Y_{12} (H-USY zeolites with SiO_2/Al_2O_3=5 and 12), F (commercial FCC catalyst) and A (γ-Al_2O_3). The operating conditions were: 350 ºC, 50 bar, WHSV= 4 h^{-1}, H_2/LCO ratio (n_{H2}) =8.9 and time on stream (TOS) = 300 min. The results show that, once the initial deactivation has been elapsed, the catalyst reach a pseudo-stable state subsequent to TOS = 250 min, with a considerable residual activity that is maintained constant. This residual activity increases as catalyst acidity is increased.

1. Introduction

A critical goal of the refineries is satisfying the growing demand for high-quality middle distillates, while lowering the contents of sulphur and aromatics (Babich and Moulijn, 2003). The reserves of crude are declining so heavy and secondary streams have to be converted into lighter products. As a result, the importance of hydrocracking (HDC) in refineries is rising (Lee et al., 2010), as it can intensify the valorization of secondary streams, lowering the boiling point and sulphur and aromatic content of the mixture.

Light cycle oil (LCO) is a secondary stream from the fluid catalytic cracking (FCC) unit, which is suitable for the production of higher quality fuels and light olefins whose demand is increasing. The boiling point range of LCO is similar to diesel, but its high content of poly-aromatic hydrocarbons (PAH) and sulphur make it inappropriate as diesel-blending (Corma et al., 2001). Considering the fact that most of the refractory-aromatic and sulphur molecules in the LCO have the highest boiling point in the mixture, the heavier fraction of the LCO can be hydrotreated separately. However, the hydrocracking of a LCO complex stream over bifunctional catalysts (noble metal-acid support) is more interesting (but more expensive) (Calemma et al., 2010).

The hydroprocessing of LCO has been studied in the literature using Ni-Mo or Ni-W catalysts under mild conditions (Ding el al., 2009). These catalysts are able to upgrade sulphur and aromatics, but more active catalysts can enhance the conversion at the expenses of more significant deactivation. In previous papers we studied the influence of the support type and acidity on the hydrocracking of toluene (Castaño et al., 2008) and pyrolysis gasoline (Castaño et al., 2006, 2007, 2009), with 70 wt% of aromatics,

concluding that a correct selection of these properties can optimize the conversion, selectivity and stability of the process. The deactivation of the catalyst is a key aspect controlling the viability of the hydroprocessing of LCO with noble metal supported catalysts. Thus, the aim of this paper is to study this deactivation and explore the influence of the support (of different porous structure and acidity).

2. Experimental

2.1 Catalyst preparation and characterization
Catalysts have been prepared using five supports called: B (based on Hβ zeolite, Zeolyst International, CP814E, $SiO_2/Al_2O_3=25$), Y_{12} (with HUSY zeolite, CBV712, Zeolyst International, $SiO_2/Al_2O_3=12$), Y_5, (with HUSY zeolite, CBV500, Zeolyst International, $SiO_2/Al_2O_3=5$), F (with FCC commercial catalyst, Albemarle) and A (with amorphous alumina, Stem Chemicals). The catalysts have been prepared by ionic exchange at 80 ºC of the supports (previously calcined at 550 ºC for 2 h) with an aqueous solution of $Pt(NH_3)_4(NO_3)_2$ (Alfa Aesar) and $Pd(NH_3)_4(NO_3)_2$ (Stem Chemicals). The interest of the bimetallic function of Pt-Pd lies in its higher tolerance to S than the monometallic functions (Yoshimura et al., 2007). The catalysts have been dried for 24 h at 120 ºC and finally calcined at 450 ºC with air for 2 h (5 ºC/min). The metal content of the catalysts (digested at 90 ºC with HF) has been measured by ICP-AES (Inductively Coupled Plasma - Atomic Emission Spectroscopy) in a Horiba Yobin Yvon Activa.

The textural and superficial properties of the catalysts have been determined by adsorption-desorption isotherms of N_2 at -196 ºC in a Micromeritics ASAP 2010. The samples have been previously degassed at 150 ºC for 8 h. The surface area has been estimated by means of BET equation and the pore volume and pore distribution according to BJH method. The properties of the metallic phase have been determined by means of H_2 adsorption in a Micromeritics ASAP 2010 according to the method of the double isotherm. The analysis has been carried out at 100 ºC.

The acid properties have been estimated by coupling isothermal-adsorption analysis with temperature programmed desorption (TPD) of NH_3. The experiments have been carried out in TG-DSG Setaram 111 calorimeter with a Harvard syringe (for NH_3 injection) and a Balzers Quadstar 422 mass spectrometer (for NH_3 detection). The isothermal-adsorption analysis was performed at 150 ºC, after the removal of impurities at 550 °C for 30 min in a flow of He. The NH_3 desorption is monitored under a temperature programmed ramp (150-450 ºC, 10 ºC/min) (Aguayo et al., 2005).

2.2 Feedstock properties
The LCO (provided by Repsol YPF) was analyzed using a GC-MS (Shimazdu-QP2010-S) (Table 1). The LCO has a 67 wt% content of aromatic, with the concentration of components of 1, 2, 3 and 4+ rings being, 16, 28, 16 and 5 wt%, respectively. The concentration of sulphur (determined by X ray fluorescence in a Philips MiniPhal PW-4025) is 0.55 wt%. The elemental analysis (Euro EA Elemental Analyzer from EuroVector) of LCO is as follows: C = 88.68 wt%, H = 10.22 wt%, N = 0.24 wt% and S = 0.55 wt%. The density, determined according to ASTM D4052, is 0.94 kg/L and the cetane indices, according to ASTM D4737 and D976, are 27.64 and 27.61, respectively.

Table 1: Composition of LCO determined by GC-MS.

Lump	Concentration (wt%)	Lump	Concentration (wt%)
i-paraffins	5.18	acenaphthenes	0.19
n-paraffins	5.43	fluorenes	2.08
olefins	1.55	indanes	5.49
cycloalkanes	0.39	indenes	0.04
dicycloalkanes	0.42	biphenyls	5.15
aromatics	66.83	sulphur compounds	2.22
monoaromatics	*16.40*	unknown	5.03
diaromatics	*28.32*		
triaromatics	*16.44*		
polyaromatics	*5.12*		

2.3 Reaction equipment and conditions

The reactions have been carried out in an isothermal fixed bed reactor at 350 ºC, 50 bar, WHSV= 4 h^{-1}, H_2/LCO ratio (n_{H2}) =8.9 and time on stream (TOS) = 300 min. The products were separated in a gas-liquid separator. The analysis of the gas was carried out on-line in a Varian CP-4900 micro-gas-chromatograph. The liquid products were analyzed off-line in a Hewlett Packard 6890 gas chromatograph with a FID detector and a PONA (50 m x 2 mm x 0.5 mm) column.

The conversion has been determined as the disappearance of the fraction of LCO with a boiling point higher than 343 ºC (normally assigned to HCO or heavy cycle oil).

2.4 Coke measurement

Coke has been studied quantitatively and qualitatively using thermogravimetric analysis of its combustion (TG-TPO) (Elordi et al., 2011). The experiments were performed on a TG analyser (TA Instruments, SDT 2960), with an on-line mass spectrometer (Balzers Quadstar 422s). Each sample (30 mg) was heated up to 150 ºC in an inert atmosphere and then calcined up to 650 ºC (3 ºC/min).

3. Results

3.1 Catalyst properties

The properties of the catalysts are shown in Table 2. Y_5 catalyst has the highest values of metallic content, surface area, micropore volume, acidity and acid strength. Y_{12} catalyst has similar support type as Y_5 (HUSY), but given that it has a lower Si:Al ratio, its acid properties are milder. Figure 1 shows the acid strength distribution of the fresh catalyst (integrating the area of the TPD curve in the desorption ranges of 150-280 ºC, 280-420 ºC and 420-550 ºC, for weak, mild and strong acidity, respectively). Using pure-zeolitic supports (Y_5, Y_{12} and B) lead to more acid catalysts with acidities close to 600 µmol NH_3/g_{cat}. Y_{12} and B catalysts have similar acid strength distribution, whereas the proportion of weak acid sites is higher for A and F catalysts.

Table 2: Main properties of the catalysts used.

Catalyst	Pt-Pd content (wt%)	Pore volume (cm^3/g_{cat})	Micropore volume (cm^3/g_{cat})	Surface area (m^2/g_{cat})	Acidity ($\mu mol\ NH_3/g_{cat}$)	Acid strength ($J/mmolNH_3$)
F	0.45-0.42	0.14	0.02	90	65	65
A	0.46-0.37	0.48	0.06	285	347	80
B	0.67-0.57	0.8	0.15	562	598	87
Y_{12}	0.63-0.58	0.34	0.18	511	550	98
Y_5	1.12-0.46	0.40	0.25	668	686	109
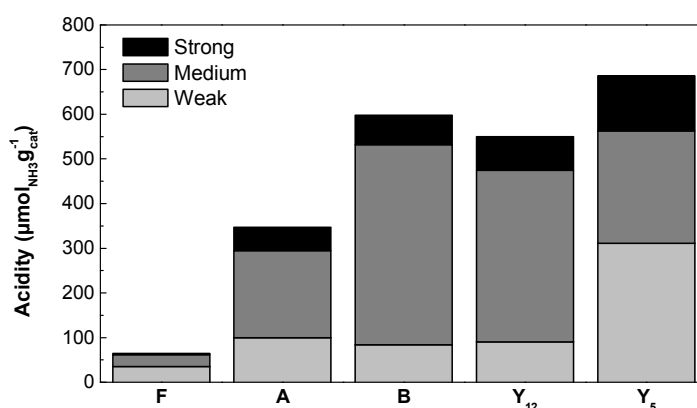
Figure 1: Acid strength distribution of the catalysts.

3.2 Deactivation of the catalysts

Figure 2 shows the conversion of LCO as a function of time on stream (TOS) for each catalyst studied. F and A catalysts undergo severe deactivation for the initial 2 h on-stream; B, Y_{12} and Y_5 catalysts deactivate less in this period due to the use of catalyst in excess. Nevertheless, after 5 h on-steam all catalysts reach a pseudo-stable regime.

The deactivation is a combination of fouling (coke formation) and poisoning (nitrogen compounds adsorbed on the acid sites and sulphur adsorbed on the metallic sites). There is evidence of this result during the TG-TPO of coke combustion, where we detect the presence of CO_2, NO_x and SO_2 in the exhaust gases. As a result, deactivation is a combination of reversible steps; (i) of poisoning with sulphur and nitrogen, and (ii) coke fouling. When the pseudo-stable regime is reached all these deactivation steps are in equilibrium and so the performance of the catalyst is steady. Hence, the strongest acid and metallic sites are poisoned first, whereas weak sites continue to convert the feed.

3.3. Relationship between remaining activity and catalyst acidity

Figure 3 shows a linear dependency of the conversion in the pseudo-stable regime and amount of coke deposited on the catalyst for 5 h time on stream with the initial acidity of the catalyst. Y_{12} and B catalysts have a different shape selectivity of their support.

However, as they have very similar acid properties (see Figure 1), they perform similarly (in terms of conversion and coke formation). This result illustrates the importance of the number of acid sites of the catalyst for the conversion of LCO when the catalyst reaches a pseudo-stable state with a constant remaining activity.
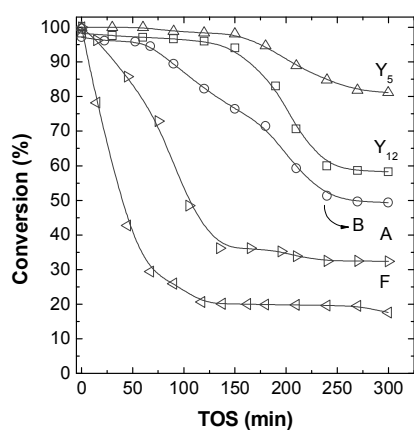

Figure 2. Evolution with time of the conversion of LCO hydrocracking using different catalysts. 350 °C, 4 h^{-1}, 50 bar, n_{H2} =8.9, TOS 300 min
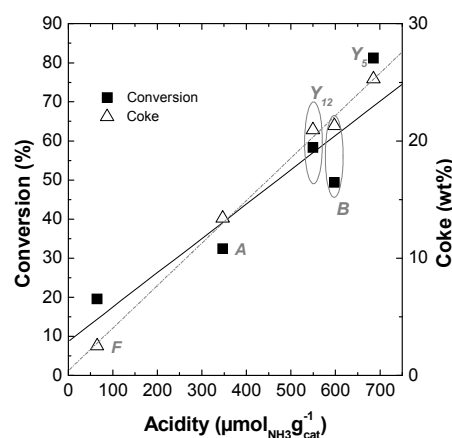
Figure 3. Relationship between conversion (in the pseudo-stable regime) and coke content with the acidity of the fresh catalysts.

The conversion of LCO is higher for catalysts with higher content of coke (Figure 3). This result is evidence that coke formation is related to the conversion in pseudo-stable state but it is also linearly related to catalyst acidity, which is consistent with the reported effect of acidity on the mechanisms of coke growing (Guisnet et al., 2009).

4. Conclusions

Although catalysts of Pt-Pd on acid supports have a rapid initial deactivation in the hydrocracking of LCO, they reach a pseudo-stable state in less than 5 h with a significant remaining activity that is constant throughout time on stream, which is higher as catalyst acidity level is higher. Consequently, a USY zeolite of high acidity level (low Si/Al ratio) is a suitable support.

This result evidences that a pseudo equilibrium state is reached in the deactivation steps by sulphur and coke, which is enhanced by catalyst acidity. Consequently, the acidity level of the support is of high relevance for preparing stable catalysts of noble metals for LCO hydrocracking.

Acknowledgements

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