



Avoiding over-cracking reactions in hydrocracking processes by means of desilication treatment of zeolites

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1. Introduction

The utilization of zeolites as support for noble metals-based catalysts in hydrocracking is well known. However, these catalysts can lead to an overcracking of the feed [1], which results in a decrease of the yields of the lumps of interest, i.e., naphtha and diesel.

A decrease on temperature or pressure can affect not only the cracking capacity of the system, but also the yields of naphtha and diesel, thus being a need of finding out an alternative way to reduce the over-cracking without reducing those yields. In this context, a modification of the catalysts employed appears as a feasible option. As the metal function of the catalyst promotes the hydrogenation function, modifying the support is a better path, which has been already tested by desilication in a process different to hydrocracking [2], observing a decrease on total acidity and a modification of the mesoporous structure. This procedure consists on immersing the zeolite in a NaOH aqueous solution 0.1 M, stirring at 25 °C during 15 min. Then the suspensions are neutralized with HCl, exchanged with NH₄Cl solutions and finally washed with deionized water, dried at 110 °C during 16 h and calcined at 550 °C for 4 h.

The selection of n-hexadecane (n-C₁₆) as a model compound of hydrocracking processes has some specific reasons: on one side, the products of its conversion are quite relatable to those obtained in the hydrocracking of vacuum gasoil; and on the other side, the application of a primary and secondary cracking analysis (PASCA) to n-C₁₆ hydrocracking has been previously assessed [3]. This analysis is based on the idea that primary cracking leads to equal amounts of the products, while secondary cracking (that of primary cracking products) would result in larger amounts of compounds with less carbon atoms due to the cracking of the compounds with more carbon atoms. The ratio between the extension of primary and secondary cracking (mol of product molecules cracked with respect to the reactive molecules cracked, A_{SC}/A_{PC}) can be applied to measure the overcracking of the model compound. This parameter is an effective index to quantify the over-cracking, as values over 0 indicate that the average number of carbon atoms is lower than 8, and values below zero are related to a higher number of carbon atoms in the products. Therefore, a decrease on this index is expected in the search of a minimization of the n-C₁₆ over-cracking.

2. Methods

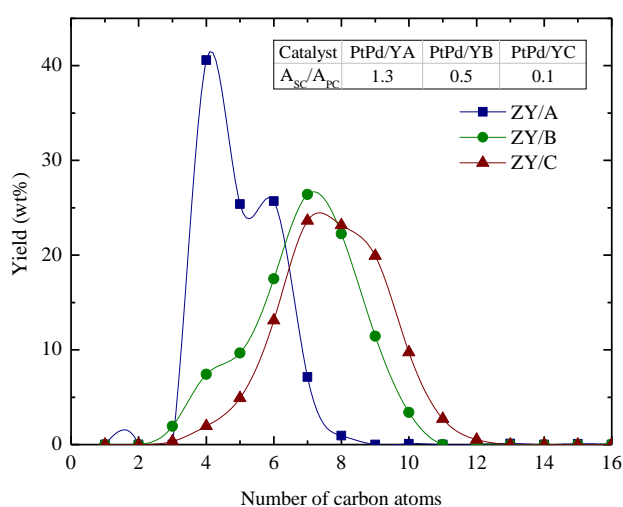
A zeolite Y was used as parent support and then the same zeolite was once and twice-treated for its use as support. After the metal deposition these catalysts have been named PtPd/YA, PtPd/YB and PtPd/YC, respectively. Textural and acidic properties of the catalysts have been measured by means of N₂ adsorption-

desorption isotherms and NH_3 -TPD, respectively. This treatment affect in a different way the first and second time in terms of acidity and surface properties, which are collected in Table 1.

Table 1. Properties of the catalysts employed.

	PtPd/YA	PtPd/YB	PtPd/YC
$S_{\text{BET}}, \text{m}^2 \text{g}^{-1}$	613	590	518
Micropore volume, mL g^{-1}	0.231	0.222	0.184
Total acidity, $\text{mmol}_{\text{NH}_3} \text{g}^{-1}$	0.55	0.49	0.43

Hydrocracking runs have been carried out in a fixed bed reactor under the following conditions: 300 °C; 40 bar; H_2 :n- C_{16} ratio, 1000 $\text{mL}_{\text{N}_2} \text{mL}_{\text{n-C}_{16}}^{-1}$; space time, 0.25 $\text{g}_{\text{cat}} \text{h g}_{\text{n-C}_{16}}^{-1}$; and time on stream (TOS), 8 h. Reaction products have been analysed on-line by means of a GC equipped with an FID detector. The absence of coke in the catalysts has been checked through TPO.



3. Results and discussion

The results of the hexadecane hydrocracking show a complete conversion of this compound for the three studied catalysts, regardless of the time on stream (no deactivation was observed), with different distribution on the number of carbon atoms in the products, as shown in Fig.1. The ratio between primary and secondary cracking, also indicated in Fig. 1, shows a noticeable decrease after the first desilication treatment and also a slight effect on the second one.

Figure 1. Distribution of the number of carbons in the products and ratio of primary and secondary cracking extension.

As shown in Fig. 1, the modification of the catalysts allows to avoid the high production of light compounds (40.6 wt% of C_4 and ca. 25 wt% of C_5 and C_6) that are relatable to an over-cracking situation and concentrate the products on C_5 - C_9 (with concentrations of 17.5, 26.4 and 22.3 wt% for C_6 , C_7 and C_8) and C_6 - C_{10} (23 wt% of C_7 and C_8 and 20 wt% of C_9) ranges by using the PtPd/YB and PtPd/YC catalysts, respectively. The content of coke of the spent catalysts was imperceptible, which is consistent with the literature.

The PASCA index is nearly zero in the last case, which would be a negligible over-cracking without losing the hydrocracking activity of the catalyst. In fact, the first treatment also triggers a great displacement on the curve to higher carbon number products, varying this parameter from 1.3 to 0.5.

4. Conclusions

The modification of the catalysts results in a consistent decrease on their total acidity and an alteration of their internal structures depending on the times that the catalyst has undergone the treatment. The desilication treatment seems to be a right path for avoiding overcracking situation keeping other good properties of PtPd/zeolite catalysts, i.e. the hydrocracking conversion. A two-subsequent treatment achieves the maximum reduction on the over-cracking parameter for this catalyst, with a high production of n- and iso-compounds in C_7 - C_9 range.

References

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