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Chemical Engineering Journal 132 (2007) 17–26

Chemical Engineering Journal

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Effect of HZSM-5 catalyst addition on the cracking of polyolefin pyrolysis waxes under FCC conditions

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Received 10 November 2006; received in revised form 10 January 2007; accepted 11 January 2007

Abstract

A study has been carried out on the effect of catalyst acidity and composition (mixtures of base catalyst and catalysts provided with HZSM-5 zeolite of different acidity) on the catalytic cracking of polyolefin pyrolysis waxes carried out under standard conditions in a refinery FCC. The experiments have been carried out in a riser simulator, in the 500–550 °C range. The results show that the yields and composition of product stream are acceptable and controlable by refineries without any special adaptation of process conditions. The acidity of the catalysts has a relevant effect on hydrogen transfer capacity, which contributes to decreasing the concentration of olefins in the gases and in the gasoline. The incorporation of HZSM-5 zeolite is very efficient for increasing the yield of gasoline. This gasoline and LPG are more olefinic than those obtained with the base catalyst, given that hydrogen transfer capacity of the catalyst is inhibited.

Keywords: HZSM-5 zeolite; Catalytic cracking; FCC; Waxes; Waste plastics

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1. Introduction

In spite of the increasing interest for upgrading waste plastics, the industrial implementation involves great difficulties that advise a solution that is applicable at large-scale. A feed of polyolefin pyrolysis waxes to FCC units is one of the alternatives for waste plastic with best perspectives from the economic point of view, given that it is based on the use of already existing units for both cracking and subsequent operations of separation and adequation of the product stream [1]. The products will be marketed as fuel or petrochemical raw materials. Another advantage of this strategy is that valorization of waste polyolefins (which account for more than 2/3 of the waste plastics) will be carried out in two steps: (1) polyolefin pyrolysis in small moving units at the waste collection and classification point; (2) transport of waxes to refinery vessels and from here they will be fed to the FCC unit. Furthermore, polyolefin pyrolysis waxes have a composition similar to other residual raw materials, such as Fischer–Tropsch waxes, whose catalytic cracking has good perspectives regarding the yield and composition of the fuels obtained [2,3].

This strategy is an alternative to the dissolution of waste polyolefins directly in the FCC feed (at the point where wastes are collected, in order to make transportation easier) and the subsequent cracking of that dissolution in the FCC unit. The use of light cycle oil (LCO) as solvent has the additional advantage that the solvent, which in this case is a stream of secondary interest in the refinery, is also valorized [4–6]. Furthermore, the synergetic effect of polyolefins in the feed has been proven, given that they improve the composition of LCO cracking products.

The valorization of polyolefins by pyrolysis has mainly been developed in the literature in fluidized bed [7–12], which is a technology that performs well and allows for using a catalyst *in situ* in order to improve product distribution and decrease temperature [13–18]. The main problem of the fluidized reactor is bed defluidization, which is caused by agglomeration of sand particles (inert material) coated with melted polymer [19,20]. To solve this problem, innovative reactors aimed at avoiding particle fusion have been proposed [21–23]. Amongst these reactors, the conical spouted bed reactor (CSBR), of simple design, avoids defluidization provoked by particle agglomeration [24]. This reactor joins the advantages of the spouted bed regime

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doi:10.1016/j.cej.2007.01.012

with those of the conical geometry. The advantages of the conventional spouted bed (cylindrical with conical base) are mainly due to the cyclic movement of the particles, which allows for treating large particles with a wide particle size distributions and providing high heat and mass transfer coefficients between gas and particles. The conical geometry increases versatility in the gas flow and vigorous particle contact [25]. Aguado et al. [26,27] have proven an excellent performance of the CSBR for flash pyrolysis of polyolefins with reduced residence times of primary products (waxes), which allows for obtaining yields of waxes in the 92–97 wt% range with an isothermal bed and at low temperature (400–500 °C). Due to these properties, the conical spouted bed reactor has also been used successfully in the pyrolysis of vegetable biomass, for both thermal [28,29] and catalytic [30,31], and in the pyrolysis of waste tyres [32].

The results of cracking of waxes obtained by polypropylene pyrolysis and the comparison with the results corresponding to the cracking of the typical feed in FCC units, which is VGO (Vacuum Gas Oil), show that the cracking of waxes has a higher yield of gasoline and that this is more olefinic (with a high proportion in the C_5–C_6 range) and less aromatic than the gasoline obtained by cracking of VGO [33]. Nevertheless, the results of previous papers obtained by using a commercial equilibrium catalyst (e-cat) show a significant sensitivity of the results depending on operating conditions (catalyst/feed ratio, temperature and contact time) [34]. In this paper, a study has been carried out on the effect of catalyst properties (physical and chemical) by using a commercial catalyst to which HZSM-5 zeolites of different acidity have been incorporated as additives.

2. Experimental

2.1. Waxes

The waxes have been obtained by flash pyrolysis of polypropylene (PP) at 500 °C. The reaction equipment has been described elsewhere [26,27]. The simulated distillation of the waxes (Table 1) has been carried out in a GC Perkin-Elmer 8500, provided with a semicapillary column, WCOT Unimetal of 5 m × 0.53 mm × 0.17 μm and FID detector. A number average molecular weight of 363 and a weight average molecular weight of 2405 have been determined by gel permeability chromatography. The density is 0.89 g cm^{-3}. A clearly olefinic nature has been determined by FTIR spectrophotometry.

Table 1
Simulated distillation of waxes

(wt%)	T (°C)
I.P.	182
5	241
10	275
30	362
50	440
70	512
90	591
95	618
E.P.	–

Table 2
Catalysts properties

	CAT-1	CAT-Z1	CAT-Z2
Zeolite percentage (wt%)	14	25	25
Particle size (μm)			
0–20 (wt%)	0	37	52
0–40 (wt%)	7	57	74
0–80 (wt%)	58	92	98
Acidity (mmol NH_3 $g^{-1}_{catalyst}$	0.018	0.053	0.024
Acid strength (kJ (mol NH_3)$^{-1}$)	125–140	120	<120
Bronsted/Lewis ratio	6.3	1.6	1.9
BET surface area (m^2 g^{-1})	123	165	182
Zeolite area (m^2 g^{-1})	89	53	63
Average micropore diameter (Å)	7.8	5.5	5.5
average mesopore diameter (matrix) (Å)	146	106	103

2.2. Catalysts

The behaviour of three catalysts has been studied. CAT-1 is an e-cat supplied by Repsol S.A. (Spain), which has been used in FCC units. CAT-H11 and CAT-H12 are hybrid catalysts prepared by physically mixing CAT-1 (at a rate of 75 wt%) with CAT-Z1 and CAT-Z2, which are catalysts prepared at the laboratory, based on HZSM-5 zeolites supplied by Zeolyst International, with different SiO_2/Al_2O_3 ratio (SiO_2/Al_2O_3 = 30, CAT-Z1, and 50, CAT-Z2). These zeolites have been supplied in ammonium form and have been subjected to calcination at 550 °C in N_2 stream for 4 h for their activation. The calcination temperature has been reached by following a rate of 4 °C min^{-1}. In the preparation of CAT-Z1 and CAT-Z2 catalysts, the corresponding HZSM-5 zeolite (25 wt%) is agglomerated by wet extrusion with bentonite as binder (45 wt%) and with inert alumina (30 wt%) as charge. Prior to use and characterization, these catalysts are subjected to a steaming treatment in a fluidized bed for 5 h, at 760 °C, under atmospheric pressure and 100% steam [35].

The properties of the catalysts are set out in Table 2. The physical properties have been determined by means of N_2 adsorption isotherms in a Micromeritics ASAP 2010. Total acidity and acid strength distribution (Fig. 1) have been measured by combining calorimetry and thermogravimetry (SDT 2960

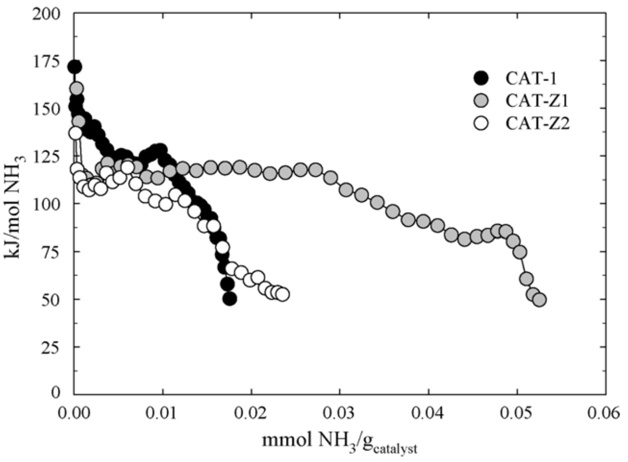

Fig. 1. Acid strength distribution of the catalysts.

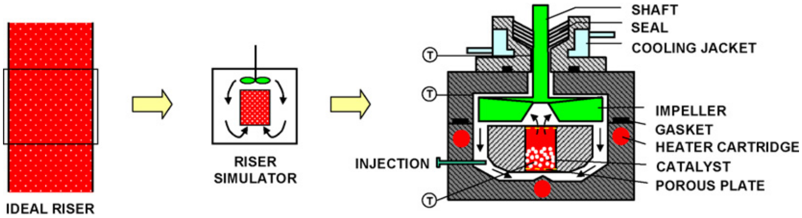

Fig. 2. Diagram of the riser simulator reactor.

Simultaneous DTA-TGA, TA Instruments) in the differential adsorption of NH_3 at 150 °C. The Bronsted/Lewis site ratio has been determined from the intensity ratio of the bands at 1545 and 1455 cm^{-1} monitored by pyridine adsorption and FTIR spectrophotometry (Nicolet 740 SX).

The results in Fig. 1 shows a significant difference in the total acidity and acid strength distribution of the catalysts. CAT-1 is the one that has less sites (total acidity = 0.018 mmol NH_3 $g_{catalyst}^{-1}$), but it has a fraction of very strong sites (in the 125–140 kJ (mol NH_3)$^{-1}$ range). The results show that the treatment of steaming has reduced considerably the total acidity of the HZSM-5 zeolite catalysts when they are compared to the usual values for the same SiO_2/Al_2O_3 ratio [36–38]. This decrease is especially significant for CAT-Z2 catalyst. Furthermore, the acid strength of CAT-Z1 is uniform around 120 kJ (mol NH_3)$^{-1}$, but CAT-Z2 has few sites of this strength and most of the sites are weak.

2.3. Reaction equipment

The equipment used in this work is a riser simulator reactor (Fig. 2). It is an internal recycle reactor specially designed for catalytic cracking and has been previously described [39]. The equipment is easy to operate and its main characteristics are: (1) capability for operating with low and precise values of contact time in the range 1–10 s; (2) a suitable feed–catalyst contact, as the reaction occurs in a dilute fluidized bed regime with perfect mix for the catalyst and for the reaction mixture. The catalyst is in a basket and the gases circulate through the basket, impelled by a turbine located in the upper part. At zero time the established amount of feed is injected and a timer is activated. Once the programmed time has elapsed, a four-port valve is opened and the reaction products pass to a vacuum chamber, maintained at 300 °C. These products are sent through a thermostated line to a gas chromatograph by means of a six-port-valve.

The runs have been carried out at 1 atm, in the 500–550 °C range, with a catalyst/feed ratio C/O = 5.5 by weight and with a value of contact time of 3–12 s. These conditions correspond to those of industrial FCC units. The low value of residence time minimizes the contribution of thermal cracking.

2.4. Product analysis

Product analysis has been carried out by means of a device for reaction product sampling connected to a Hewlett Packard 6890 chromatograph. The sampling is activated by a timer that controls the desired value of contact time. Product identification was carried out on-line by GC–FTIR using a Nicolet/Aldrich library, by means of a FTIR Nicolet 740 SX spectrophotometer connected to a Hewlett Packard 5890 II chromatograph. The results were verified by GC–MS (HP 6890-MS Engine with electronic ionization).

In order to check and assign the retention times in the chromatographic analysis of compounds in the C_5–C_{12} range, pure compounds and mixtures were used as standards. The assignment of the retention times of the components of the gasoline lump has been carried out by using Alphagaz PIANO (Air Liquide) calibration standards, which consist of 8 *n*-paraffins, 39 aromatic components, 35 isoparaffinic, 30 naphthenic and 25 olefinic. The amount of the C_5–C_{12} lump has been determined as that corresponding to the components with boiling point between *n*-C_5 paraffins (*n*-pentane) and *n*-C_{12} (*n*-dodecane).

The coke deposited on the catalyst was measured by thermogravimetric analysis in a Setaram TG-DSC 111 calorimeter-thermobalance. The deactivated catalyst from the reactor is dried at 110 °C in a nitrogen stream and is subsequently subjected to combustion with air at a programmed temperature ramp (5 °C min^{-1}) up to 700 °C.

3. Results

3.1.1. Conversion and yields

The main quality of the HZSM-5 zeolite is shape selectivity, which limits the access of multisubstituted aromatics.

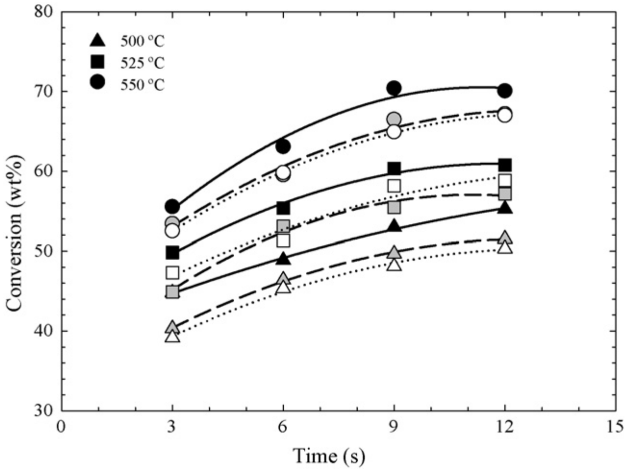

Fig. 3. Comparison of conversions obtained with a HY zeolite catalyst (base catalyst) and with hybrid catalysts (with HZSM-5 zeolite), for different temperatures and contact times. Black points–solid lines, CAT-1. Grey points–dashed lines, CAT-H11. White points–dotted lines, CAT-H12.

Nevertheless, the tridimensional nature of the pores allows, according to several authors [40–42], circulation within the porous structure of linear compounds of higher molecular weight than those in the gasoline range. This accessibility explains the high conversion in the cracking of polyolefins dissolved in LCO [5]. Under FCC conditions, the polyolefins undergo thermal cracking within matrix mesopores and macropores and on the external surface of catalyst particles. If the concentration of polyolefins in the feed is not excessive, this thermal cracking is enough for the resulting chains to be accessible to the porous structure of the HZSM-5 zeolite, where catalytic cracking takes place.

Fig. 3 compares the conversions for catalyst CAT-1 (containing HY as active phase), CAT-H11 and CAT-H12, being the two latter hybrid catalysts (made up by 25 wt% of a catalyst based on HZSM-5 zeolite and the remaining 75 wt% of CAT-1), for different temperatures and contact times. Conversion has been determined as the sum of yields to dry gases (C_1–C_2), LPG (C_3–C_4), gasoline (C_5–C_{12}) and coke. Each yield is calculated as:

$$\text{yield of lump}\, i = \frac{\text{mass of lump}\, i}{\text{total mass in the feed}} \times 100 \qquad (1)$$

It is observed in Fig. 3 that under all conditions the conversion order is: CAT-1 > CAT-H11 ≈ CAT-H12. A comparison of both hybrid catalysts shows that their behaviour is similar at 525 and 550 °C, and that CAT-H11 is slightly more active at 500 °C.

The explanation of these results of conversion lies in the factors that condition catalyst activity in the cracking: (1) accessibility to the zeolite structure; (2) acid strength of the sites; (3) total acidity or number of potentially active sites. The higher activity of CAT-1 is explained by factors 1 and 2. The greater accessibility of CAT-1 is due to the microporous structure of the HY zeolite (Table 2) with pores of 7.8 Å diameter, to which reactants access by diffusion into the mesoporous structure of the matrix. CAT 1 is the one with less acid sites (Table 2 and Fig. 1), but of higher strength, in the 125–140 kJ (mol NH_3)$^{-1}$ range.

Although the hybrid catalysts are of higher total acidity (Table 2), their lower activity must be attributed, firstly, to the lower accessibility to the micropores of the HZSM-5 zeolite [43], whose size is between 5.4 and 5.7 Å. Secondly, only a fraction of HZSM-5 zeolite sites have a high acid strength, to same order as that of CAT-1. The stronger acid sites of CAT-Z1 (constituent of CAT-H11 hybrid catalyst) have a homogeneous

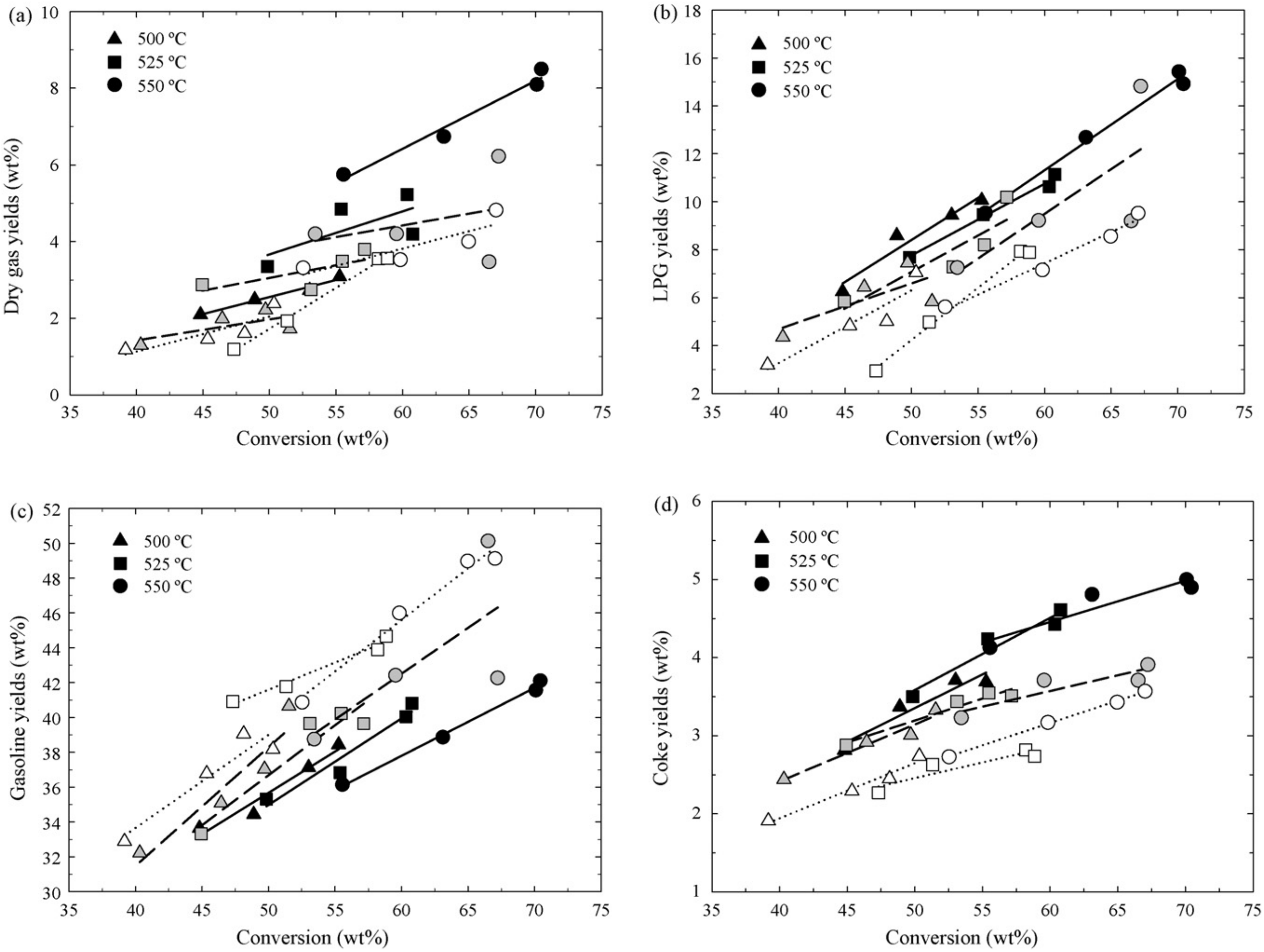

Fig. 4. Comparison of the yields of different product fractions obtained using a HY zeolite catalyst (base catalyst) and hybrid catalysts. Black points–solid lines, CAT-1. Grey points–dashed lines, CAT-H11. White points–dotted lines, CAT-H12.

acid strength around 120 kJ (mol NH_3)$^{-1}$, whereas the sites of CAT-Z2 (constituent of CAT-H12 hybrid catalyst) are weaker acid sites (Fig. 1). When the conversions of CAT-H11 and of CAT-H12 are compared, it is clear that the total acidity of the HZSM-5 zeolite does not have significant incidence on the activity of hybrid catalysts. Catalyst CAT-Z2, which makes up CAT-H12 (with $SiO_2/Al_2O_3 = 50$), has a total acidity that is half of that corresponding to CAT-H11 ($SiO_2/Al_2O_3 = 30$) (Table 2) but, nevertheless, this effect is only significant in Fig. 3 for the conversion at the lower temperature studied, 500 °C.

In Fig. 4, the yields of gases, LPG, gasoline and coke obtained with the three catalysts are compared. The results are evidence of the importance of the acid strength of the catalyst. Thus, CAT-1, having sites of higher acid strength, gives higher yields of LPG and lower of gasoline, as a consequence of its greater capacity for gasoline overcracking. This increase in the yield of gasoline is relevant for a positive valuation of HZSM-5 zeolite incorporation in the catalysts for wax cracking. The lower yield of dry gases and of coke when HZSM-5 zeolite is incorporated in the catalyst is also very positive, which is due to the moderate acid strength of the sites. Shape selectivity of the microporous structure of the HZSM-5 zeolite also contributes to the low coke generation, which at the same time hinders polyaromatic generation.

It is noteworthy that this behaviour of HZSM-5 zeolite of increasing the yield of gasoline is different to the effect of this additive in the cracking of gas–oil, in which the capacity of HZSM-5 zeolite for gasoline overcracking is well-documented. The consequence is a decrease in the yield of gasoline and an increase in the yield of LPG compared to the base catalyst [40–42,44]. This apparently different role of the zeolite is explained by the difference in the feeds. In the case of waxes all the feed may be cracked to gasoline, whereas for the gas–oil, the catalyst is in excess over that required for cracking the non-refractory fraction of the feed to gasoline and the active sites in excess activate the overcracking of gasoline [1].

Regarding the fraction of dry gases, hybrid catalysts give way to lower concentrations of all the components of this fraction, especially at high temperature. This result is consistent with that of Buchanan and Adewuyi [45] and is contrary to that obtained by Aitani et al. [46] by cracking VGO with hybrid catalysts. The difference in the results is attributable, firstly, to the difference in the severity of the equilibration treatment of the hybrid catalysts, which in this paper is very pronounced and, to a lesser degree, the different composition of the feed (as was previously commented for the yields of LPG and gasoline) and the different reaction conditions.

The higher yield of gasoline with the hybrid catalysts is evidence that in the cracking of waxes the yield of gasoline is not affected by diffusion of polyolefinic chains produced in the primary cracking of waxes. This previous cracking, which will take place in the matrix of the bentonite and on the external surface of HZSM-5 zeolite crystals, will be mainly thermal and only partially catalytic and the products formed, although voluminous (in the range of gasoline and LCO), are linear and accessible to the internal channels of the HZSM-5 zeolite. This scenario, in which the steps of thermal and catalytic cracking of waxes are considered to take place partially in series, is coherent with the results of thermal cracking on silica [47] and of catalytic cracking of polyolefins dissolved in LCO [4–6,48].

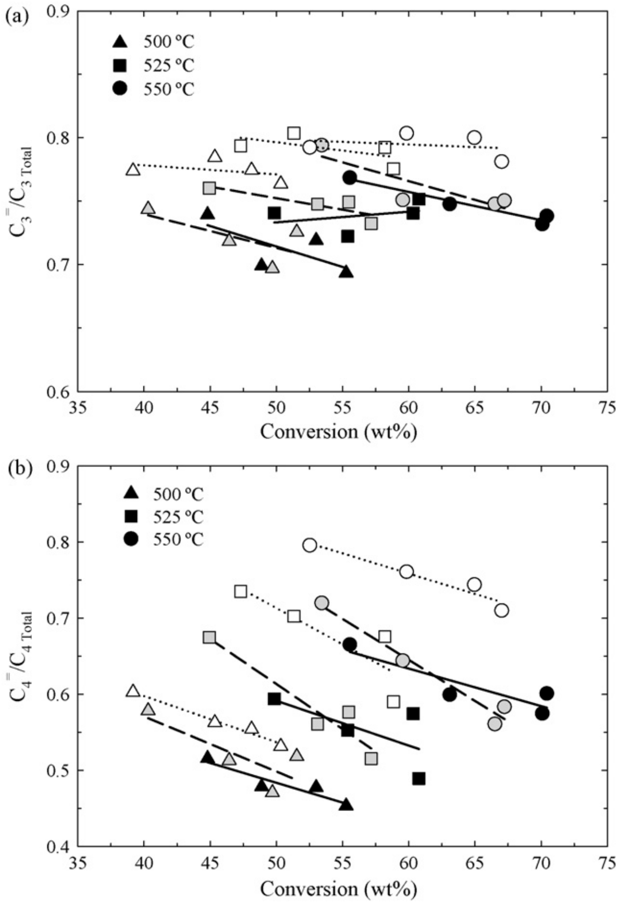

Fig. 5. Olefinicity comparison of C_3 (graph a) and C_4 (graph b) components in the LPG fraction, for HY zeolite catalyst (base catalyst) and hybrid catalysts, for different conversions and temperatures. Black points–solid lines, CAT-1. Grey points–dashed lines, CAT-H11. White points–dotted lines, CAT-H12.

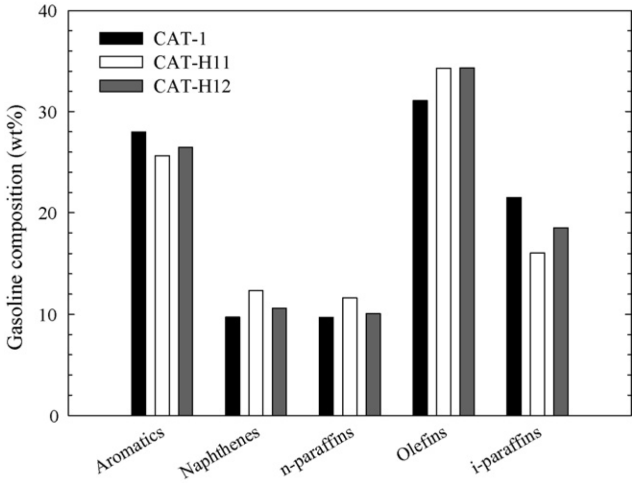

Fig. 6. Comparison of the gasoline composition for a HY zeolite catalyst and hybrid catalysts. 500 °C. $t = 6$ s.

Moreover, when the results for the two hybrid catalysts shown in Fig. 4 are compared, it is evident that the HZSM-5 zeolites of both hybrid catalysts are also active for cracking gasoline to LPG, although less than HY zeolite (due to the severe steaming). Thus, the higher acidity and acid strength of the HZSM-5 zeolite contained in CAT-H11 justifies its lower yield of gasoline and higher of LPG, dry gases and coke compared to CAT-H12.

The hybrid catalysts produce greater quantities of olefins than CAT-1, especially at low temperatures, which is due to the low activity of HZSM-5 zeolites in bimolecular reactions, such as those of hydrogen transfer. Consequently, the concentration of linear and branched paraffins in the LPG decreases when hybrid catalysts are used. Contrarily to what Buchanan and Adewuyi [45] obtained in the cracking of VGO, the hybrid catalysts give a higher concentration of butadiene, which increases with temperature.

It is well-documented that HZSM-5 zeolite is active for the production of olefins in the LPG range by cracking olefins in the gasoline range [46,49] and, furthermore, it has been proven that it has a significant capacity for cracking LCO-HCO range olefins [41–43]. In the cracking of waxes, which are linear and, consequently, accessible to the HZSM-5 zeolite, a high cracking capacity for direct cracking of the feed to olefins in the LPG range is feasible This fact and a reduced capacity for hydrogen transfer of the HZSM-5 zeolite explains the low yields of paraffins and the high olefinicity of C_3 and C_4 fractions in the LPG when the hybrid catalysts are used (Fig. 5).

Fig. 6 shows that the gasolines obtained with the hybrid catalysts have a higher concentration of naphthenes, *n*-paraffins and olefins and a lower concentration of aromatics and isoparaffins than those corresponding to the base catalyst. The behaviour of CAT-H12 is intermediate to other ones, as corresponds to the lower activity of its HZSM-5 zeolite constituent and, consequently, to its lower incidence on product distribution. Nevertheless, the activity of the HZSM-5 zeolite contained in CAT-H12 is sufficient to give the same concentration of olefins than CAT-H11, given that the production of olefins by cracking olefins of heavier fraction requires lower acidity than that for other reactions involved in the cracking.

Concerning component distribution in the gasoline, essential role is played by the reduce capacity for hydrogen transfer of the HZSM-5 zeolite (due to the limitations of shape selectivity to form the intermediates required in bimolecular reactions). Consequently, the olefins and naphthenes directly obtained by cracking of heavier fractions (LCO-HCO) are not transformed into isoparaffins and aromatics.

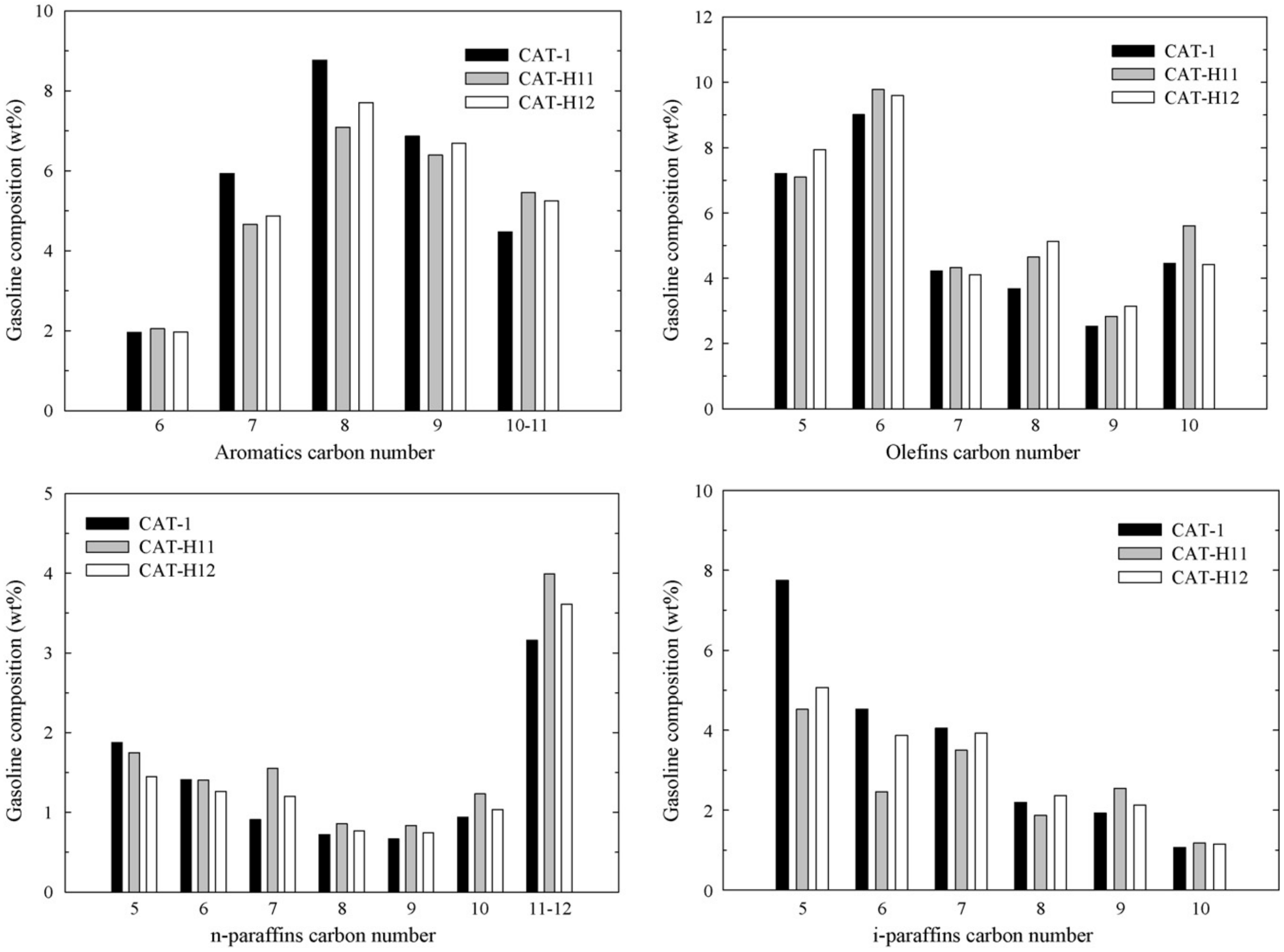

Fig. 7. Comparison of gasoline lump compositions obtained using the HY zeolite and hybrid catalyts, according to their components with different number of carbon atoms. 500 °C. $t = 6$ s.

In the hybrid catalysts studied in this paper, the base catalyst CAT-1 has a very low value of TCU, 24.27 Å Consequently, it is less active for hydrogen transfer reactions and so for the generation of aromatics than a standard FCC catalyst. Under these circumstances, a high capacity for cracking olefins in the gasoline range to LPG by the HZSM-5 zeolite is expected [50]. Nevertheless, the nature of the waxes should be taken into account, which are made up of linear paraffins and olefins in the LCO-HCO ranges, whose selective cracking occupies active sites and, consequently, inhibits the subsequent cracking of olefins in the gasoline fraction to LPG. This priority in the cracking of heavy olefins [40], together with the limitation for hydrogen transfer explains the high concentration of olefins in the gasoline for hybrid catalysts. These results of the effect of HZSM-5 zeolite as additive agree with those of Nalbandian et al. [51] for the cracking of VGO.

Furthermore, when the composition of the gasoline obtained with both hybrid catalysts is compared, the results agree with those of Liu et al. [50] for the cracking of VGO, who also confirmed that the HZSM-5 zeolite with higher SiO_2/Al_2O_3 ratio (and consequently with lower acidity) is less active under cracking and so it yields more aromatics and isoparaffins.

Concerning the distribution of components of different carbon atom number in each gasoline lump, Fig. 7 shows that CAT-1 produces a higher concentration of aromatics in the whole range of carbon atom number, but especially in the C_7–C_9 fraction. CAT-1 also produces higher concentrations of C_5 *n*-paraffins but smaller of C_{7+} *n*-paraffins. The explanation of this latter effect (contrary to that expected by the higher hydrogen transfer capacity of CAT-1 than the hybrid catalyst) must be attributed to the low reactivity for cracking heavy paraffins, which together with the difficulty for diffusion in the HZSM-5 zeolite limits the cracking of these paraffins over the hybrid catalysts.

Due to this lower capacity for hydrogen transfer, higher concentrations of olefins are obtained with the hybrid catalyst in the whole range of carbon atom numbers. The formation of isoparaffins takes place by means of hydrogen transfer reactions, which are unfavoured for C_5–C_8 light olefins on the hybrid catalysts. The reverse happens with C_9 isoparaffins and the results are similar for C_{10}.

The results in Fig. 7 are partially different to those by den Hollander et al. [41,42], which obtained lower yields of C_{7+} olefins and higher yields of C_5–C_6 isoparaffins by using hybrid catalysts than by using a HY zeolite catalyst. Nevertheless, these authors compared yields and not concentrations and the feed was different (VGO). Furthermore, the equilibration of catalysts was less severe than in this paper. As was aforementioned, the effect of adding HZSM-5 zeolite on the gasoline yield and composition is closely related to the composition of the feed. Thus, for a feed made up of only gasoline, the HZSM-5 zeolite cracks almost all the olefins of high molecular weight [41,42].

A higher SiO_2/Al_2O_3 ratio in the HZSM-5 zeolite contained in the hybrid catalyst, and the resulting lower total acidity and acid strength (Table 2 and Fig. 1) as corresponds to CAT-H12, produces higher concentrations of aromatics and isoparaffins in the whole range of gasoline. This is due the fact that CAT-H12 is less active in the cracking reactions [40], which increases its capacity for the reactions of isomerization and hydrogen transfer. Consequently, CAT-H12 produces higher proportion of aromatics and isoparaffins than CAT-H11. These results agree with those obtained by Buchanan [40] by comparing the behaviour of hybrid catalysts with different acidity in the cracking VGO.

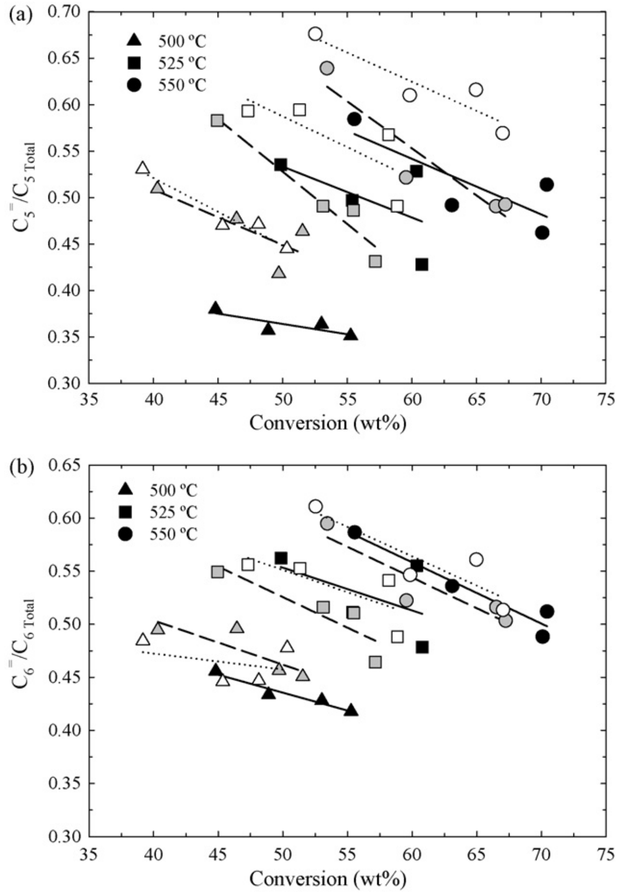

Fig. 8. Comparison of olefinicity of C_5 (graph a) and C_6 (graph b) components in the gasoline obtained using a HY zeolite catalyst and the hybrid catalysts, for different conversions and temperatures. Black points–solid lines, CAT-1. Grey points–dashed lines, CAT-H11. White points–dotted lines, CAT-H12.

Fig. 8 shows the important effect of HZSM-5 zeolite addition on the olefinicity of C_5 (graph a) and C_6 (graph b) gasoline components. It is observed that, as is documented in the literature [52], at 500 °C, the hybrid catalysts produce a higher concentration of C_5 and C_6 olefins, which explains the fact that at low temperature the shape selectivity of HZSM-5 zeolite is a determining factor in the inhibition of hydrogen transfer reactions. Nevertheless, as temperature is increased these exothermal reactions are inhibited in the HY zeolite catalyst (CAT-1) and the cracking reactions are favoured. Consequently, at 550 °C there are no significant differences between the results of olefinicity corresponding to CAT-1 and those corresponding to the hybrid catalysts (CAT-H11 and CAT-H12). Furthermore, when the results for both hybrid catalysts are compared, there is no significant effect of HZSM-5 zeolite acidity on the olefinicity of C_5 and C_6 components in the gasoline.

In the olefinic fraction, the hybrid catalysts give way to higher concentrations of light isoolefins, C_5 and C_6 (Fig. 9) which is

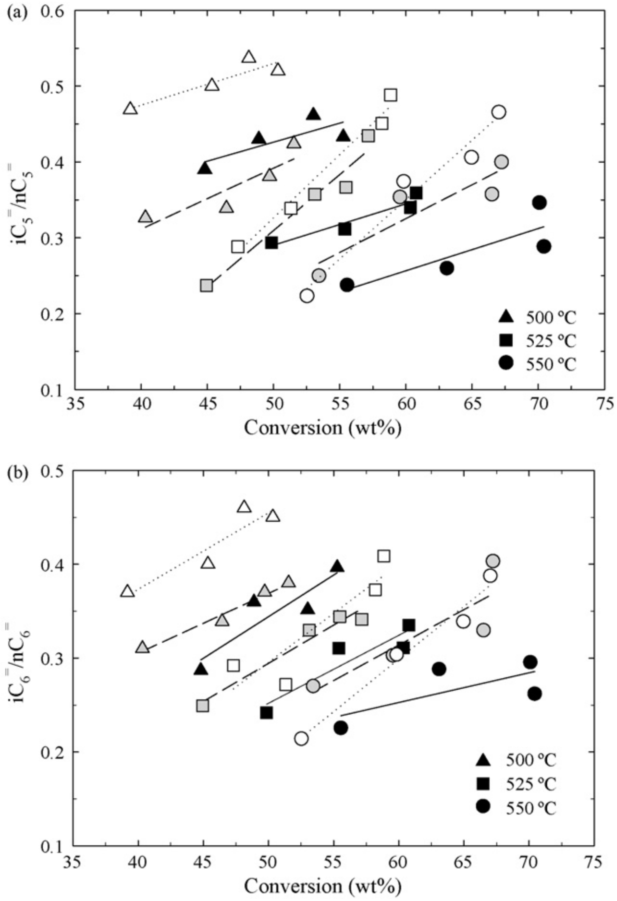

Fig. 9. Comparison of C_5 (graph a) and C_6 (graph b) olefinic component branching in the gasolines obtained using the HY zeolite catalyst and hybrid catalysts, for different conversions and temperatures. Black points–solid lines, CAT-1. Grey points–dashed lines, CAT-H11. White points–dotted lines, CAT-H12.

very interesting from the commercial point of view of these products for the synthesis of oxygenate gasoline additives. This result is consequence, firstly, of the higher capacity of HZSM-5 zeolite than HY zeolite for isomerization of light olefins. Furthermore, the conversion of isoolefins to isoparaffins by hydrogen transfer is severely hindered by shape selectivity and the low acid sites density of the tested samples. The results are consistent with those obtained in the cracking of VGO by several authors [41,42,44,45].

The effect of HZSM-5 zeolite addition to the catalyst on the branching of paraffins has been studied (Fig. 10) because of its interest in the quality of the gasoline. It is observed that this effect is different for C_5 and C_6 components in the gasoline. Thus, the hybrid catalysts produce a lower concentration of C_5 branched paraffins (graph a) than CAT-1, whereas there are no significant differences between the results of C_6 branched paraffins obtained with the HY zeolite catalyst and hybrid catalysts (graph b). These results are coherent with that expected for HZSM-5 zeolite in the sense that it limits hydrogen transfer and the subsequent isoparaffin production. The results show that in the case of C_5 the first effect is more important, whereas in the case of C_6 the second is determining. When the results in Fig. 10 are compared with those in the literature, a noteworthy fact is that the effect of HZSM-5 zeolite on the isoparaffinicity of C_5 and C_6 components in the gasoline depends on the feed. Thus, the results obtained in the cracking of VGO are different to those obtained in the cracking of gasoline [41,42]. The results of this paper are consistent with those of VGO cracking [41,42,44]. The values of isoparaffinicity obtained by Buchanan and Adewuyi [45] using hybrid catalysts are very similar to those of the base catalyst. In fact, they are slightly higher for C_5 and slightly lower for C_6 than those obtained here.

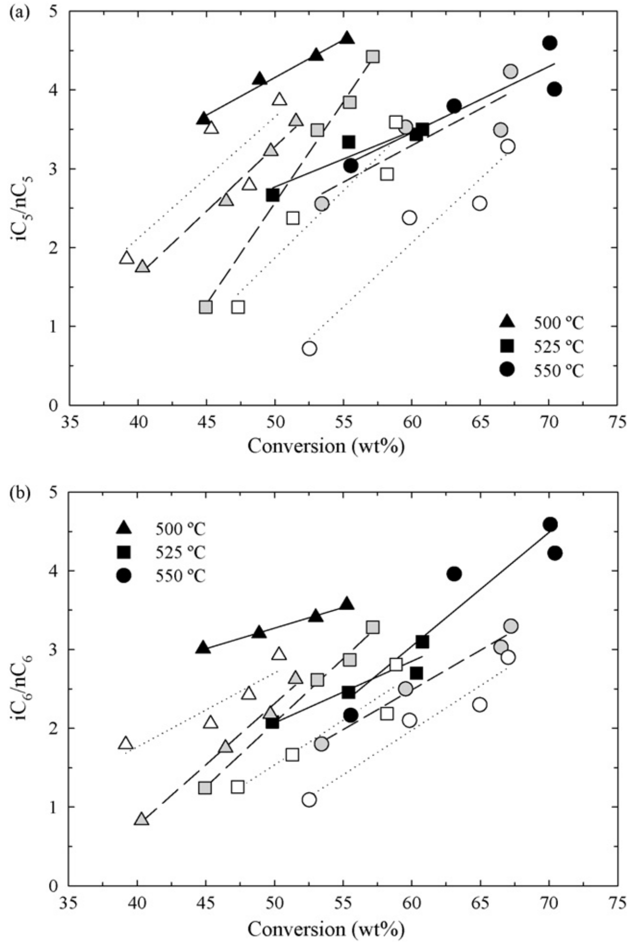

Fig. 10. Comparison of C_5 (graph a) and C_6 (graph b) paraffinic component branching in the gasolines obtained using the HY zeolite catalyst and hybrid catalysts, for different conversions and temperatures. Black points–solid lines, CAT-1. Grey points–dashed lines, CAT-H11. White points–dotted lines, CAT-H12.

Table 3 shows the values of RON for the gasoline obtained with base and hybrid catalysts. It is observed that the hybrid catalysts provide slightly higher RON values and this difference increases with temperature. In other words, the higher concentration of olefins in the gasoline obtained with the hybrid catalysts favourable compensates the lower concentration of aromatics and isoparaffins.

A significant fact is the importance of rapid deactivation of the catalyst and the different deactivation of HZSM-5 and HY zeolites in this paper's results. The lower deactivation of HZSM-5 zeolite [53] and the attenuation of coke deposition by moderating the acid strength by treating with phosphorous [54,55] are

Table 3
Octane index (RON) of the gasoline obtained using the base and hybrid catalysts, for different temperatures and contact times

	t (s)	500 °C	525 °C	550 °C
CAT-1	3	95.1	96.8	97.9
	6	95.5	96.4	97.9
	9	95.4	97.8	98.5
	12	95.2	95.6	98.5
CAT-H11	3	95.0	96.1	98.0
	6	96.7	97.0	98.5
	9	95.1	97.4	98.9
	12	95.5	97.0	98.1
CAT-H12	3	94.8	95.7	98.0
	6	95.2	96.4	98.5
	9	95.2	97.6	98.9
	12	95.7	96.6	98.7

well-known. These improvements in the behaviour of HZSM-5 zeolites open future pathways for the improvement of the process studied here.

4. Conclusions

Polyolefin pyrolysis waxes provide acceptable results for refineries when used as a FCC feed, given that the effect of operating conditions is similar to that corresponding to standard feeds (such as VGO). The properties of the catalyst have great influence on product yield and composition. The magnitude of this influence is similar to that of the standard feed, although there are certain aspects attributable to the composition of the waxes.

The incorporation of a catalyst based on HZSM-5 zeolite (by partially substituting the catalyst based on HY zeolite) decreases the conversion to waxes, due to the shape selectivity of the HZSM-5 zeolite (more severe than that of HY zeolite) and to the lower acid strength of the hybrid catalyst. The total acidity of the HZSM-5 zeolite used has no significant incidence on the activity of the hybrid catalyst.

The lower conversion provided by the hybrid catalyst is the result of lower yields of LPG, dry gases and coke, although the yield of gasoline is higher than that with the base catalyst, which is a consequence of its lower capacity for overcracking gasoline. This result of increase in the yield of gasoline is a relevant fact to take into account for a positive evaluation of HZSM-5 zeolite incorporation in the wax cracking catalyst. It is noteworthy that, for this purpose, the catalyst based on HZSM-5 zeolite must have a moderate acid strength.

On the whole, hybrid catalysts produce higher olefins concentrations in the LPG than the base catalyst, especially at low temperatures, due to their capacity for cracking higher olefins and to the low activity of HZSM-5 zeolites in bimolecular reactions, such as those of hydrogen transfer.

The gasoline obtained in the cracking of waxes with hybrid catalysts has a higher concentration of naphthenes, *n*-paraffins and olefins and a lower concentration of aromatics (especially in the C_7–C_9 range) and of isoparaffins than the gasoline corresponding to the base catalyst. The difference between the results for the different catalysts is higher as the acidity of the HZSM-5 zeolite is higher. From the point of view of minimizing the concentration of aromatics in the gasoline, a HZSM-5 zeolite with a minimum level of acidity is required in order for hydrogen transfer reaction not to be relevant.

Acknowledgements

This work was carried out with the financial support of the University of the Basque Country (Project 9/UPV 00069.310-13607/2001) and of the Ministry of Science and Technology of the Spanish Government (Project PPQ2003-07822). We are indebted to Repsol-YPF S.A. (Petronor refinery) and Dow Chemical S.A. for their generous provision of materials.

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