

# Performance of ZSM-5 as a Fluid Catalytic Cracking Catalyst Additive: Effect of the Total Number of Acid Sites and Particle Size

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The performance of ZSM-5 as a fluid catalytic cracking (FCC) catalyst additive has been tested in a microactivity test unit for the cracking of gas oil. Laboratory-synthesized ZSM-5 samples, with various Si/Al ratios, fresh or hydrothermally dealuminated were tested. A 2 wt % ZSM-5, on total catalyst weight, found by previous investigators to be the optimum additive concentration, was used for all of the experiments. It has been found that a direct and smooth correlation exists between the product yields and the total number of ZSM-5 acid sites measured by ammonia temperature-programmed desorption tests. This is a unique function of the aluminum content of fresh samples as well as the temperature of the hydrothermal deactivation of steamed ZSM-5 zeolite samples. Previous works have been qualitatively compared to the results of this work and have been classified on the basis of different total acidity regions of the ZSM-5 used in each case. Higher total acidity results in gasoline loss, liquified petroleum gases (LPG) and ethylene increases, and research octane number gain. The  $C_5$  aliphatics are increased in the low acidity region because of cracking and isomerization of larger alkenes, while an increase of the total ZSM-5 acidity resulted in a monotonic decrease of all of the gasoline range hydrocarbons, except of  $n$ - $C_5$  alkane,  $C_6$ – $C_7$  aromatics, and  $C_5$  naphthenes. The branched/linear (B/L) ratios for  $C_5$ – $C_6$  alkenes were found to increase with acidity, while the B/L ratios for  $C_5$ – $C_9$  alkanes decrease. The number and strength of the additive's acid sites control the contribution of the different reaction paths, through which cracking, isomerization, and aromatization occur, to the final product distribution. The sizes of the ZSM-5 particles have a strong effect on the changes in product yields and gas and gasoline compositions. Smaller particles favor a decrease in gasoline and an increase in LPG yield more than larger particles. The effect is more pronounced in the high acidity region where the decrease in the yields of  $C_7+$  isoalkanes, naphthenes, and aromatics is favored by small particle additives, while the effect of particle size on gasoline range hydrocarbons is clearly evident on the yields of gaseous products.

## Introduction

The ZSM-5 zeolite has long been tested<sup>1,2</sup> as a fluid catalytic cracking (FCC) catalyst additive, to increase the octane number of gasoline. Together with the utilization of the low unit cell size USY zeolite, instead of REY as the basic catalyst, the use of ZSM-5 is the main catalytic route for improving octane in an FCC unit, and it has been adopted in a large number of commercial units since the initial reports in 1983.<sup>3</sup> The performance of ZSM-5 as an FCC catalyst additive was examined in a great number of previous works and was found to be dependent not only on feedstock quality, catalyst type, and unit operating conditions but also on the chemical composition, the pretreatment of ZSM-5 zeolite, and the type of the ZSM-5 additive.<sup>1,2,4–10</sup> The microactivity test (MAT)<sup>1,6,7,9</sup> has been widely used in most of the previous works. It is the most widely used method to predict FCC catalyst activity and product selectivities, instead of performing time-consuming and costly test runs in pilot plants or commercial units.

Most previous investigations refer to commercial additives usually predeactivated and diluted in inert matrixes.<sup>4,5,7,9,10</sup> High-temperature (750–850 °C) steam

pretreatment is usually employed to simulate the deactivation of ZSM-5 occurring in the commercial unit.<sup>1,4,7,8</sup> Octane enhancement, gasoline yield loss, and  $C_3$ – $C_4$  olefins increase are the main effects when ZSM-5 is added, either “fresh” or steam deactivated, to the FCC catalyst. However, different reaction mechanisms have been proposed to predominate, depending on the ZSM-5 pretreatment. For unsteamed ZSM-5, selective cracking of gasoline range alkanes is important,<sup>5,8,11</sup> while for steamed pentasils, isomerization and monomolecular cracking of the reactive carbenium ions or olefin intermediates<sup>1,4,9</sup> are the predominant reaction pathways.

The dependence of catalyst activity and selectivity on the number and strength of the acid sites and the size of the zeolite crystallites is well established for the Y zeolite which is used as the main active component in FCC catalysts.<sup>12–15</sup> Although a small number of studies have focused on the effect of the Si/Al ratio of ZSM-5 on product yields and selectivities,<sup>6</sup> there is no direct and qualitative correlation with ZSM-5 acidity (number of acid sites) reported in the literature. The above parameter has been studied only in model reactions where the activity of ZSM-5 for the transformation of hydrocarbon molecules was related to the number of

**Table 1. Summary of Feed Properties**

		vol. (%)	
		distillation data	ASTM D-1160 (°C)
specific gravity 60/60 °F	0.9239		
sulfur (wt %) (ASTM D-4294)	2.39		
Conradson carbon (wt %)	0.38		
refractive index (20 °C)	1.5174		
K factor	11.54	IBP	208
viscosity (cSt)	67.82 (37.8 °C) to 6.20 (98.9 °C)	5	317
density (g/cm <sup>3</sup> )	0.9191 (20 °C) to 0.8926 (60 °C)	10	349
molecular weight	335	30	411
elem anal.			
C	86.35	50	447
H	12.56	70	479
N	0	90	526
S	2.67	95	554
		FBP	568

active acid centers in the zeolite, like alkane cracking<sup>16</sup> and xylene isomerization.<sup>17</sup>

Since H-ZSM-5 is a typical acid function zeolitic catalyst, the present work correlates the changes in acidity of ZSM-5 caused by either different initial Si/Al ratios, chemical dealumination, or steam deactivation with the observed changes in octane number and product yields. Several ZSM-5 samples with varying Si/Al ratios, because of synthesis or chemical dealumination and steam deactivated at different severities, were tested in an MAT unit as additives to an equilibrium RE-USY catalyst, used as the basic catalyst. Further properties such as the surface area and particle size of crystalline ZSM-5 were measured to detect any possible effect on catalytic performance as an FCC catalyst additive. From the experimental results of our work, it is shown that product yields are related to the total number of acid sites and the particle size of ZSM-5. On the basis of these findings, it is possible to classify many of the results of previous work, relative to the acid activity of the ZSM-5 additive used in each case.

## Experimental Section

**Materials Preparation and Characterization.** Zeolite ZSM-5 samples with different Si/Al ratios and various particle sizes were synthesized in the laboratory, based on the method of Argauer and Landolt.<sup>18</sup> Crystallographic purity was determined by X-ray diffraction. The as-synthesized ZSM-5 samples were calcinated to remove the organic template and treated with dilute HCl acid. Treatment of fresh samples with either an excess of 1.5 N HCl or (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> was also used for the preparation of certain samples. Fresh samples were steam deactivated for 6 h at different severities by varying the treatment temperature (660, 730, and 790 °C) in a fluidized bed, at atmospheric pressure and at 90% steam partial pressure. Two types of ZSM-5 samples were tested in this work, with different particle sizes, i.e., small particles (0.5–2 µm) and large particles (10–30 µm).

The chemical analysis of the samples was done by classical gravimetric and photometric analytical techniques. The X-ray powder diffraction patterns were taken on a Siemens D-500 automated diffractometer. The average particle (which is usually crystalline agglomerate composed of smaller crystals) size was measured by SEM with a JSM 840-A JEOL microscope. The specific surface area was determined isothermally by nitrogen adsorption at 77 K using a conventional volumetric apparatus.<sup>19</sup> Further details on the charac-

terization of the ZSM-5 samples are given in another publication.<sup>20</sup> The total number of acid sites was measured by temperature-programmed desorption (TPD) of ammonia. TPD experiments were performed in a conventional apparatus with a quartz microreactor, a vertical well-controlled high-temperature furnace, and a gas chromatograph equipped with a thermal conductivity detector (TCD). The samples (typically 0.2 g) were degassed at 520–530 °C for 3 h. The total number of ZSM-5 acid sites was calculated from the mmoles of ammonia desorbed from each sample between 100 and 700 °C, after saturation with ammonia at 100 °C.

An equilibrium RE-USY catalyst, from the FCC unit of a Greek refinery, was used as the additive-free base catalyst with the following characteristics: low percentage of Re<sub>2</sub>O<sub>3</sub>; UCS (unit cell size) 24.24 Å; total surface area, 180 m<sup>2</sup>/g; zeolite surface area, 102 m<sup>2</sup>/g. The equilibrium catalyst was calcined in dry air at 540 °C for 10 h before use. Catalyst samples containing ZSM-5 were prepared by mixing fixed preweighed amounts of pure ZSM-5 with the base catalyst to a constant weight percentage, 2 wt %, and they were designated ZM-1, ZM-2, etc.

**Catalytic Experiments.** The catalytic experiments were made in an MAT unit, method ASTM D-3907, with minor modifications. A detailed description as well as a schematic diagram of the MAT unit is given elsewhere.<sup>7</sup> The catalyst temperature was 521 °C, the weight of the catalyst was 3 g, and the duration of feed injection was 50 s. The catalyst-to-oil ratio varied between 2.5 and 3.5 to obtain product yield curves centered at about 62 wt % conversion. Both gaseous and liquid products were analyzed by gas chromatography,<sup>7,9</sup> and the weight of coke deposited on the catalyst was measured by an elemental analyzer (Leco CHN-800). Complete separation and identification of the individual components in the gasoline was made by an advanced GC technique, described elsewhere.<sup>9</sup> The model of Anderson<sup>21</sup> was used to predict research octane numbers (RON). The feedstock characteristics are shown in Table 1. A carbon balance of better than 98–99% was achieved in the experiments.

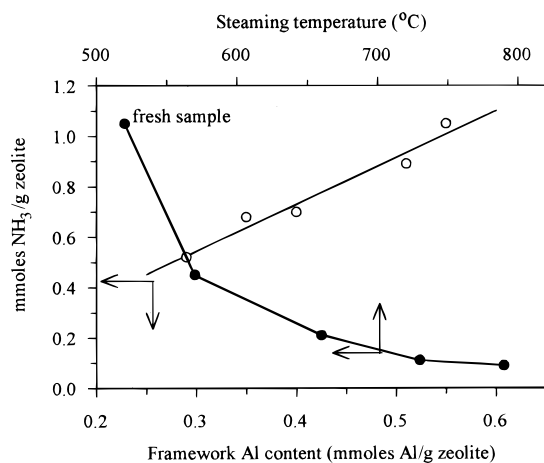
## Results and Discussion

**Physicochemical Characteristics of the ZSM-5 Additive.** The physicochemical characteristics of all of the ZSM-5 samples are listed in Table 2. The Si/Al ratio, estimated from chemical analysis, represents the framework Si/Al ratio for the fresh samples ZM-1 to ZM-6. For samples ZM-7 to ZM-12, the Si/Al ratio is for the

**Table 2. Physicochemical Characteristics of Zeolite ZSM-5 Samples**

sample	pretreatment	Si/Al ratio (C.A.) <sup>a</sup>	surface area (m <sup>2</sup> /g, SP BET) <sup>b</sup>	no. of acid sites (mmol of NH <sub>3</sub> /g of zeolite, TPD)			particle size (μm, SEM)
				total	weak	strong	
ZM-1	fresh	12.5	431	1.15	0.55	0.60	10–15
ZM-2	fresh	25	476	1.05	0.51	0.54	0.5–2
ZM-3	fresh	35	448	0.70	0.34	0.36	10–30
ZM-4	fresh	> 1000	430	0.07	0.07	0	10–15
ZM-5	fresh	28	437	0.89	0.42	0.47	0.5–2
ZM-6	fresh	41	439	0.68	0.34	0.34	0.5–2
ZM-7	steamed 660 °C	26	393	0.21	0.14	0.07	0.5–2
ZM-8	steamed 730 °C	27	395	0.11	0.07	0.04	0.5–2
ZM-9	steamed 790 °C	27	396	0.09	0.07	0.02	0.5–2
ZM-10	steamed 790 °C	42	420	0.08	0.06	0.02	0.5–2
ZM-11	steamed 790 °C	36	425	0.08	0.08	0	10–30
ZM-12	steamed 790 °C	> 1000	432	0.02	0.02	0	10–15

<sup>a</sup> Chemical analysis. <sup>b</sup> Single-point BET method.



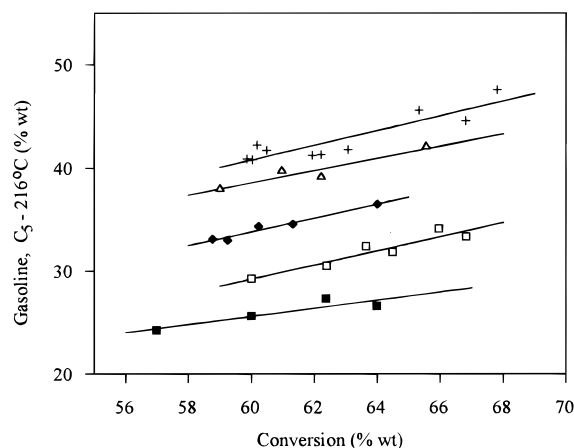
**Figure 1.** Effect of the framework Al content (○) and the steaming temperature (●) on the total number of H-ZSM-5 acid sites measured by ammonia TPD.

bulk which includes framework and nonframework aluminum, since Al is extracted from the skeleton with steaming.

The surface area measurements are nearly the same for all of the samples, fresh and steamed, indicating that the pore structure of the samples is retained, even at severe steaming conditions.

The correlation between the total number of acid sites of ZSM-5 samples and the aluminum content, in the case of fresh samples, and the temperature of the hydrothermal treatment, in the case of steamed ZSM-5 samples, is presented in Figure 1. This correlation has been used to reduce the number of the catalyst additive (ZSM-5) characterization parameters to one, the total number of acid sites, instead of using the common practice of correlating the performance of ZSM-5 with either the aluminum content, in the case of fresh samples, or the temperature of the hydrothermal treatment, in the case of steamed samples.

Briefly, the NH<sub>3</sub> TPD curves of the fresh H-ZSM-5 samples consist of two peaks with temperature maxima between 170 and 210 °C for the first peak and between 430 and 440 °C for the second peak. These correspond to weak and strong acid sites, respectively. The ratio of weak to strong acid sites was determined from the areas of the two peaks after Gaussian deconvolution of the TPD spectra. For the fresh samples, the strong acid sites have been assigned to -OH groups of skeletal aluminum and correspond to the relatively strong Bronsted acidity of H-ZSM-5. The sites of weaker strength can



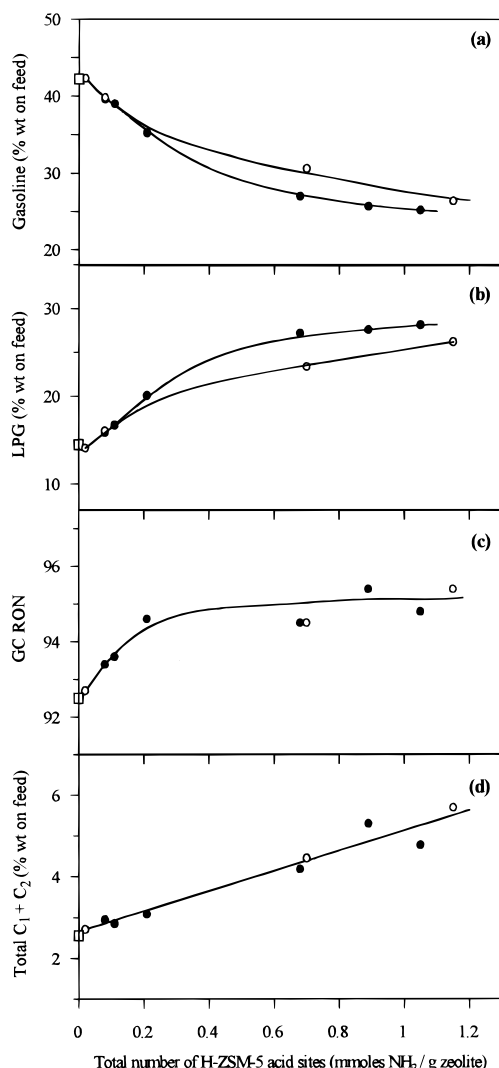
**Figure 2.** Gasoline yield vs total conversion curves: (+) base, (Δ) ZM-9, (◆) ZM-7, (□) ZM-3, (■) ZM-1.

be either Bronsted or Lewis, and their origin is not yet clear, despite the theories that have been proposed.<sup>22–24</sup> The ratio of strong to total number of acid sites in the low acidity region (steamed and Al-free samples) is less than 0.5 and decreases slightly with framework dealumination, while it remains stable at ~0.5 in the high acidity region (fresh samples).

**Effect of ZSM-5 Total Acidity on Product Yields and Gasoline RON.** Figure 2 shows gasoline yield vs conversion curves of the base catalyst as well as corresponding curves for several mixtures of the base catalyst with different ZSM-5 samples. All of the product yields presented in the next paragraphs were derived, at constant conversion, 62 wt %.

Figure 3 presents the most important product yields (gasoline, LPG, RON, and total C<sub>1</sub> + C<sub>2</sub>) as a function of the total number of ZSM-5 acid sites. The effect of particle size is also shown. Increasing the total number of additive acid sites lowers the gasoline yield (Figure 3a) and increases LPG, RON, and total C<sub>1</sub> + C<sub>2</sub> yields (Figure 3b–d). Coke yield (not shown) presents a small increase with ZSM-5 addition, in agreement with the work of Biswas and Maxwell,<sup>2</sup> and is almost stable for the whole acidity region. Hydrogen yields (not shown) remain practically unchanged. Figure 3 also indicates that small ZSM-5 particles (0.5–2 μm) result in more gasoline loss and LPG gain than those of large particles (10–30 μm), while RON and total C<sub>1</sub> + C<sub>2</sub> are unaffected.

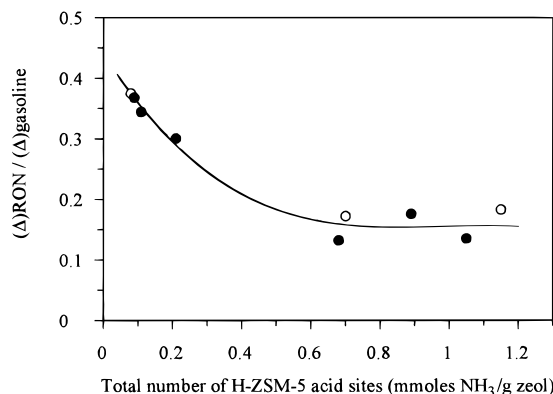
Comparing the results of this work with the results of previous investigators is not straightforward since yield vs ZSM-5 total acidity plots have not been pub-



**Figure 3.** Effect of the total number of H-ZSM-5 acid sites on product yields and RON (at constant conversion of 62% by weight): (□) base catalyst, (●) catalysts with small ZSM-5 particle additives, 0.5–2  $\mu\text{m}$ , (○) catalysts with large ZSM-5 particle additives, 10–30  $\mu\text{m}$ .

lished before. However, previous data<sup>1,2,4,6,9</sup> include a comparison of the performance of at least one HY/ZSM-5 mixture with the corresponding performance of the HY catalyst, considered as the base case. Thus, previous data represent two or more points of our yield vs total acidity curves.

The curves presented in Figure 3 show that the effect of the ZSM-5 addition in the base catalyst on product yields and RON is a monotonic function of the ZSM-5 total acidity. Differences in total acidity, depending on the Si/Al ratio or the deactivation state of ZSM-5, result only in different quantities of the effect. There are however cases, as can be seen in Figures 5 and 6 which will be discussed in the next paragraphs, where the yields are not significantly affected by the total acidity of ZSM-5 or where the less acidic ZSM-5 additives have effects different from those of the more acidic ones. In the latter cases, differences in ZSM-5 total acidity result in qualitatively different effects. In conclusion, the results of this work can be utilized for predicting the acidity range of the ZSM-5 additives tested in previous works, considering that the rest of the experimental parameters, e.g., base catalyst, feedstock type, and reaction temperature, are similar.



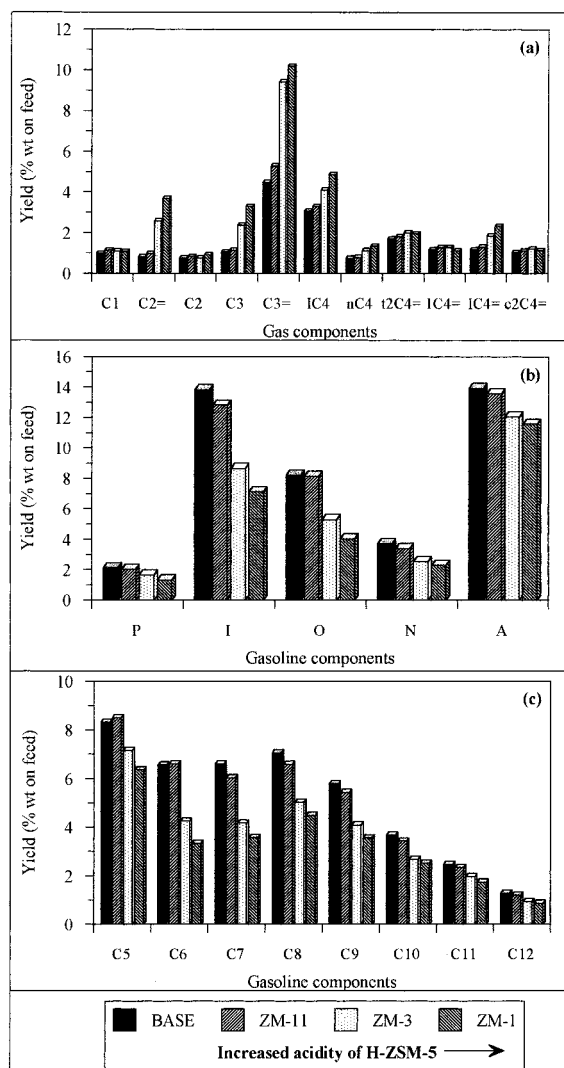
**Figure 4.** Effect of the total number of H-ZSM-5 acid sites on the  $\Delta(\text{RON})/\Delta(\text{gasoline})$  ratio: (●) catalysts with small ZSM-5 particle additives, 0.5–2  $\mu\text{m}$ , (○) catalysts with large ZSM-5 particle additives, 10–30  $\mu\text{m}$ .

Madon<sup>4</sup> and Nalbandian et al.<sup>7,9</sup> have tested a commercial additive (Z100) without any further treatment. Nalbandian et al.<sup>7</sup> found that the effect of the additive on product yields and selectivities was the same whether it was steam deactivated or not before use. By comparing the shifts in gasoline and total C<sub>3</sub> and C<sub>4</sub> yields between the above studies<sup>7,9</sup> and the results of this work, one could suggest that the performance of Z100 resembles the performance of a ZSM-5 zeolitic additive of the present work with relatively low total acidity, e.g., 0.2 mmol of NH<sub>3</sub>/g of zeolite, as shown in Figure 3. At this acidity value, which corresponds to a mildly steamed ZSM-5 sample, gasoline yield decreases by 7 wt % on feed and total C<sub>3</sub> and C<sub>4</sub> yields increase by 3.2 and 2.5 wt %, respectively. It is also clear from the graphs in Figure 3 that the effect of an increase of the acidity of ZSM-5 on gasoline and LPG yield and RON in the high acidity region is smaller compared to that of the low acidity region. Gasoline and LPG seem to stabilize above a certain acidity value with small particle additives.

The ratio  $\Delta(\text{RON})/\Delta(\text{gasoline})$ , which has been widely used to express the merits of adding ZSM-5 to the FCC catalyst, increases with a decrease in the total number of ZSM-5 acid sites in the low acidity region but remains stable when the ZSM-5 additives are relatively highly acidic, which is usually the case for the fresh additives (Figure 4). Miller and Hsieh<sup>6</sup> have found that by increasing the Si/Al ratio of the ZSM-5 additives the isomerization to H-transfer activity also increases and as a result the  $\Delta$  gasoline octane/% yield loss is higher, especially with the deactivated additives. It is thus clear that their results refer to the relatively low ZSM-5 acidity region shown in Figure 4, where a similar behavior has been observed. The RON gain observed in this study is 0.1 up to 0.35 units for every unit weight percent of gasoline loss. The RON gain is smaller compared to other similar works,<sup>2,4</sup> and it can be interpreted in terms of the base catalyst type, as well as the gas oil feed properties. In the present study, as well as in the study of Nalbandian et al.<sup>7</sup> where the effect on RON was similar to that of this work, a low Re<sub>2</sub>O<sub>3</sub> USY (equilibrium UCS: 24.24 Å) base catalyst was used in combination with an aromatic feed, and as a result the initial RON value of 92.5 was relatively high compared to those of other works.

**Effect of the ZSM-5 Total Acidity on Gas and Gasoline Compositions.** The effect on gaseous product yields and on gasoline composition of an increase of the total number of ZSM-5 acid sites is shown in Figure 5.





**Figure 5.** Effect of the total number of H-ZSM-5 acid sites on gas and gasoline composition (on a feed basis).

The catalyst samples that are presented in Figure 5 have been selected as representative of all of the samples tested in this study. This covers the whole range of the total acidity of the ZSM-5 samples, either fresh or hydrothermally dealuminated. Gasoline composition is given as both PIONA (paraffins, isoparaffins, olefins, naphthenes, and aromatics) (Figure 5b) and carbon number ( $C_5$ – $C_{12}$ ) (Figure 5c) analysis. Product yields have been calculated on a feed basis to reveal the clear effect of ZSM-5 addition.

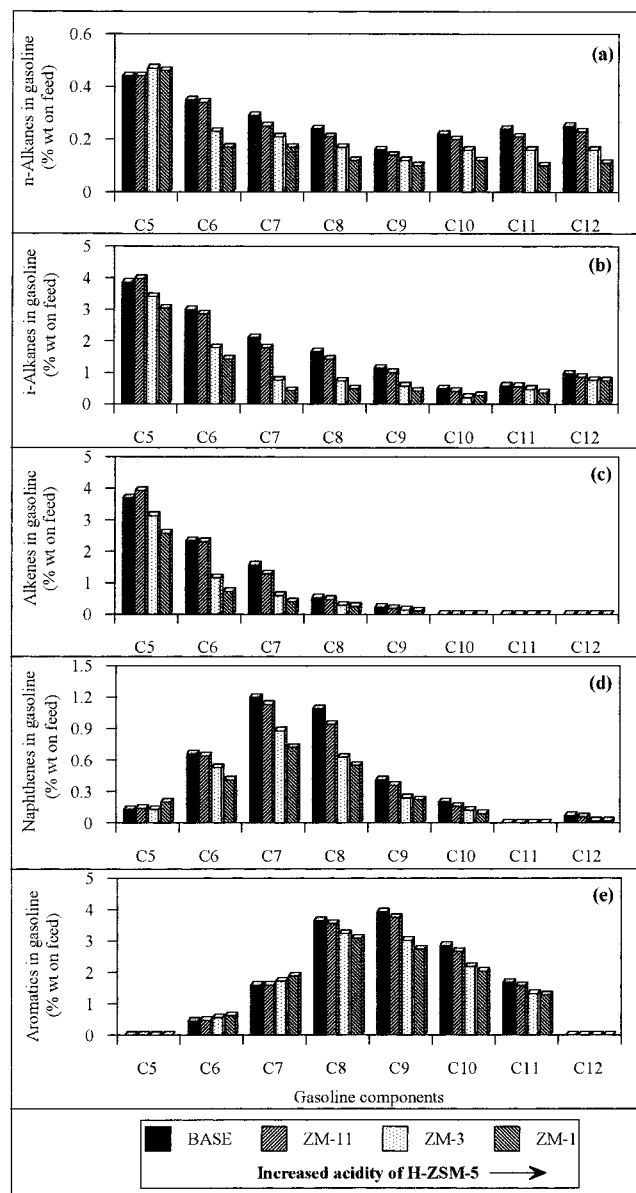
When the gaseous products (Figure 5a) are focused on the most pronounced monotonic effect of an increase of the total number of additive acid sites, it concerns ethylene, propane, propene, isobutane, *n*-butane, and isobutene, which may undergo an increase of up to 2 or even 3 times their initial yield. Such an effect of ZSM-5 on  $C_3$  and  $C_4$  is well-known and documented,<sup>1,4,7</sup> and the extent of the effect is always dependent on the deactivation state of the additive.<sup>1</sup> This is shown by the gradual increase in the yield of LPG gases with an increase of ZSM-5 acidity presented in this study. On the other hand, ethylene always undergoes a small increase in relative studies, which has been either not discussed<sup>4</sup> or attributed to the activity of the insufficiently deactivated matrix.<sup>2</sup> The ZSM-5 addition resulted also in a small increase in the yields of 1-butene and *cis*- and *trans*-2-butene, which is not a monotonic

function of ZSM-5 total acidity. The very small increase in methane and ethane formation is also not systematic with an increase of the total acidity, in accord with most of the previous works.<sup>1,4,7</sup>

Figure 5b indicates changes in the yields of the five gasoline structural groups (PIONA). *N*-Alkanes, isoalkanes, naphthenes, and aromatics undergo a clear monotonic decrease with an increase of total acidity of ZSM-5. However, alkenes seem to be relatively stable in the low acidity region, and they start decreasing at relatively high acidities. Figure 5c shows the distribution of gasoline compounds according to their carbon number. The effect of an increase of the additive acid sites is clear and monotonic for the  $C_{7+}$  gasoline compounds. The  $C_5$  and  $C_6$  compounds present a quite different behavior. In the same way as with the total alkenes, they start to decrease only after a relatively high value of acidity.

The same trend in the yield of the five gasoline groups has been found by Nalbandian et al.,<sup>9</sup> and the relatively small changes indicate that the additive used in their work was of low ZSM-5 total acidity, probably steam deactivated, as has already been discussed above. Furthermore, the significant decrease in isoalkane yield observed in this study, especially in the high acidity region, supports the opinion that both branched (mainly monomethyl) alkanes and *n*-alkanes in the gasoline pool have equivalent cracking reactivities, and conversion is determined by the concentration (availability) of molecules. Since branched alkanes are produced in an order of magnitude higher concentration than *n*-alkanes by the base RE-USY catalyst, the addition of ZSM-5 to the base catalyst results in a significant reduction of branched (monomethyl) alkanes in gasoline.<sup>1,2,4,6,9</sup> Still, the selective removal of *n*-alkanes is a point of contradictory results presented by previous workers and is related to the number of carbon atoms and the degree of branching of the hydrocarbon chain,<sup>8,31</sup> as is discussed in more detail below. A total alkene yield decrease has also been found by most of the previous workers,<sup>2,4,5</sup> while contradictory results exist for the yield of total aromatics. Rajagopalan and Young<sup>1</sup> and Anders et al.<sup>31</sup> concluded from their results that small aromatic molecules ( $C_6$ – $C_8$ ) are formed on the ZSM-5 additive, especially when it is relatively fresh. Biswas and Maxwell<sup>2</sup> observed a very small increase in the yield of total aromatics, Nalbandian et al.<sup>9</sup> reported a very small decrease, and Madon<sup>4</sup> did not observe any changes. From the results of the present study, it is clear that, in the very low ZSM-5 acidity region, the yield of total aromatics is almost unaffected, but with an increase of the additive acidity aromatics yield, it decreases because of the significant decrease of the  $C_{8+}$  aromatics overcoming the small increase of the  $C_6$ – $C_7$  aromatics, as discussed below.

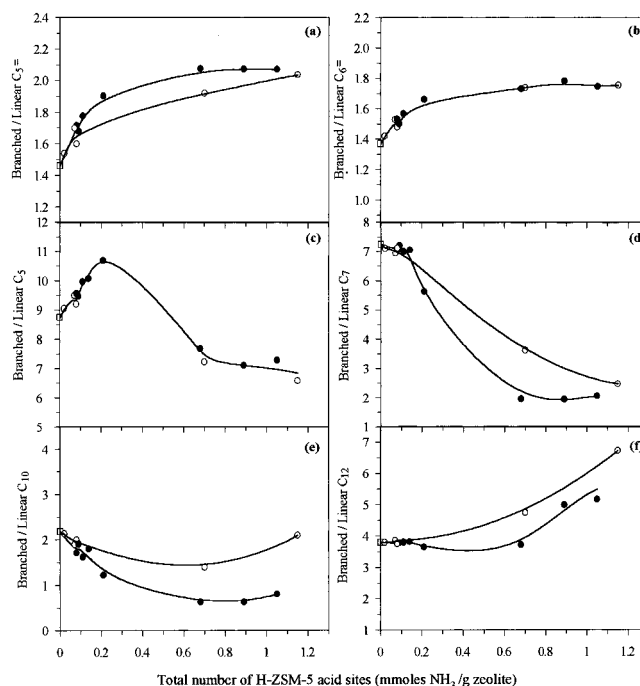
Figure 6 shows the detailed distribution of the yields of each hydrocarbon type among all gasoline range carbon numbers, with an increase of the additive acidity. Normal alkanes (Figure 6a) with six or more carbons undergo a substantial monotonic decrease with an increase of the acidity, ranging up to 55% (of the initial yield) for the highest acidity additive, except for *n*- $C_6$ , which decreases significantly only at relatively high additive acidity. *n*- $C_5$  seems to be stable or even gain a small yield increase, especially in the high acidity region. However, because the initial yield of *n*-alkanes is very low, their decreased yields contribute very little



**Figure 6.** Effect of the total number of H-ZSM-5 acid sites on the distribution of all gasoline range carbon numbers (C<sub>5</sub>–C<sub>12</sub>) among each hydrocarbon type (on a feed basis).

to the overall gasoline loss. The picture is very much the same for isoalkanes (Figure 6b). Species with six or more carbons undergo a substantial monotonic decrease with an increase of the additive acidity, reaching up to 80% (e.g., for C<sub>7</sub>), while the C<sub>5</sub> isoalkane yield starts to decrease at relatively high additive acidity. A isoalkane yield decrease contributes a lot to the overall gasoline loss, because of their relatively high initial concentration. Madon<sup>4</sup> and Nalbandian et al.<sup>9</sup> have found similar behavior for *n*-alkanes and isoalkanes, while the extent of the effect, observed in their studies, is similar to that of the low ZSM-5 acidity region.

Alkenes (Figure 6c) also undergo a substantial monotonic decrease, especially for carbon numbers greater than six. The decrease can reach up to 75%. C<sub>5</sub> alkenes increase at low additive acidity, while C<sub>6</sub> alkene yield seems to be stable. Both start to decrease when the additive acidity increases beyond some certain value, and this effect is reflected in the total alkene yield, as shown in Figure 5b. These results are in accord with



**Figure 7.** Effect of the total number of H-ZSM-5 acid sites on the B/L ratio for (a) C<sub>5</sub> alkenes, (b) C<sub>6</sub> alkenes, (c) C<sub>5</sub> alkanes, (d) C<sub>7</sub> alkanes, (e) C<sub>10</sub> alkanes, and (f) C<sub>12</sub> alkanes: (□) base catalyst, (●) catalysts with small ZSM-5 particle additives, 0.5–2 μm, (○) catalysts with large ZSM-5 particle additives, 10–30 μm.

those given in previous works,<sup>4,5,9</sup> in the low additive acidity region.

The effect of an increase of the additive acidity on naphthenes (Figure 6d) is very similar to the corresponding effect on aliphatic hydrocarbons. Naphthenes with six or more carbon atoms undergo a substantial monotonic decrease, reaching up to a difference of 60%, on an increase of the additive's total number of acid sites. C<sub>5</sub> naphthene yield remains almost constant, except for the most acidic additive, where the yield shows a small increase. Aromatics (Figure 6e) are the only structural group presenting a different behavior. Aromatic components of gasoline undergo a decrease much smaller than that in the previous groups, never exceeding a difference of 40%, for carbon numbers equal to or greater than 8. On the contrary, C<sub>6</sub> and C<sub>7</sub> aromatics undergo a small but monotonic increase, with an increase of the additive acidity. The effect on aromatics is more intense in the high acidity region while it is minimized in the low acidity region, thus explaining the contradictory results presented in the literature<sup>1,2,4,9,31</sup> which depend on the deactivation state of the additive used in each case.

The branched/linear (B/L) ratio for C<sub>5</sub>= and C<sub>6</sub>= increases monotonically with ZSM-5 total acidity (Figure 7a,b). The same behavior has been observed in previous work, for both fresh and steam deactivated additives.<sup>2,4,8–10</sup> The B/L ratio for gasoline range alkanes presents a unique behavior according to the number of carbon atoms of the hydrocarbon chain (Figure 7). The B/L ratio for C<sub>5</sub> alkanes increases with an increase of the acidity in the low acidity region and starts to decrease significantly only after a certain acidity value (Figure 7c). The same holds for the B/L for C<sub>6</sub>. Similar results have been found by Miller and Hsieh<sup>6</sup> by testing additives with different Si/Al ratios and by Madon<sup>4</sup> by working in the low acidity region (deactivated additive). The decrease of the B/L ratio for C<sub>7</sub>–C<sub>9</sub> alkanes is clear

and monotonic with an increase of the ZSM-5 total acidity, as shown for  $C_7$  in Figure 7d. The B/L ratio for the  $C_{10}$  alkanes seems to decrease slightly or to be unaffected (Figure 7e), while the value of the ratio increases monotonically with the total acidity for the  $C_{11}$ – $C_{12}$  alkanes (Figure 7f). A decrease of the B/L ratio for the  $C_5$ – $C_8$  gasoline range alkanes was also observed by Guerzoni and Abbot<sup>8</sup> and Anders et al.<sup>31</sup> both working with unsteamed additives but using highly paraffinic or hydrotreated feedstocks.

From the presented results and the comparison with the results of previous works, it is evident that the increase in the total acidity of ZSM-5 induces quantitatively and qualitatively different effects to the gasoline and gaseous product yields of gas oil cracking. An effort was made to rationalize some of those effects based on the relation between the acidity of ZSM-5 and the reaction mechanisms for hydrocarbon conversion.

**Influence of the ZSM-5 Total Acidity on the Reactions of Gas Oil Cracking.** The reaction mechanisms that the addition of ZSM-5 to an FCC catalyst induces to the catalytic cracking of gas oil have been analyzed by many previous investigators. In most cases, interpretation of the results was made without considering the effect of changes in the total acidity of ZSM-5 on product yields and selectivities.

A great number of the works performed in the field was reviewed by Dwyer and Degnan,<sup>25</sup> who have tried to reconcile the seemingly contradictory results presented in the literature, concerning the performance of ZSM-5 as the FCC catalyst additive, by relating the dominant reactions catalyzed by ZSM-5 to its deactivation state. On the basis of previous works, the above authors have concluded that when the additive is fresh, the dominant reactions are cracking of  $C_{7+}$  alkanes and  $C_{6+}$  alkenes to  $C_3$  and  $C_4$  compounds via conventional classical carbenium ion chemistry, isomerization of alkenes, and some hydrogen-transfer reactions producing isoalkanes from isoalkenes.<sup>27–30</sup> When the additive is deactivated, the alkane cracking activity diminishes because of the reduction in the number of ZSM-5 acid sites, but the zeolite still has sufficient activity to catalyze alkene cracking, which is 2 or 3 orders of magnitude faster than alkane cracking under FCC conditions.<sup>11,26</sup> Alkene cracking activity diminishes when severely deactivated additives are used with a concomitant decrease in  $C_3$  and  $C_4$  production, while the faster alkene isomerization<sup>11,26</sup> becomes the predominant reaction. Guerzoni and Abbot<sup>8</sup> came to conclusions similar to those presented in the review of Dwyer and Degnan,<sup>25</sup> regarding the change in reaction mechanisms over ZSM-5 depending on the pretreatment and deactivation state of the ZSM-5 additive.

It is thus clear that the different mechanisms involved should be related to the number and strength of ZSM-5 acid sites, which reflect the dealumination or deactivation state of the ZSM-5 zeolite. The effect of the number or density and the strength of ZSM-5 acid sites on the reaction mechanisms for alkene and alkane cracking and isomerization has been studied by previous investigators, by the use of model compounds.<sup>27–30,32,33</sup> The conclusions of the above works have been taken into account in the interpretation attempted in the present study.

From the results presented in this study, it is evident that the monomolecular cracking of the  $C_{6+}$  alkenes is strongly favored by the increase in the number of ZSM-5

acid sites, while the nonfavorable, bimolecular cracking of  $C_5$  alkenes is enhanced to a lesser extent. However, it can be inferred that the increased number and density of the strong Bronsted acid sites, which are parallel with the increase of the total number of acid sites, may promote also the monomolecular cracking of the  $C_6$ –alkenes. This requires the initial formation of primary or secondary carbenium ions,<sup>30</sup> e.g.,  $C_3$ – $C_6$  carbocations, which could be stabilized on the strong Bronsted acid sites and react further to produce propylene or even ethylene, as is discussed below. This reaction route contributes to the very high decrease in the yields of  $C_5$ – $C_6$  alkenes in the higher acidity region and to the high increase of  $C_2=$ ,  $C_3=$ , and  $i-C_4=$  gases observed in our results. On the other hand, the production of the  $C_5$ – $C_6$  alkenes from the fast monomolecular cracking of  $C_{8+}$  alkenes<sup>30</sup> is not significant in the present work, since the initial yield of  $C_{8+}$  alkenes from the base catalyst is very low. On the basis of the above relation between the yield of  $C_5$ – $C_6$  alkenes and the total acidity of the ZSM-5 additive, which reflects the effect of the total acidity on the rates of formation and cracking of these two alkenes, one could reconcile the contradictory published results concerning the yield of  $C_6$  alkenes<sup>1,2,4,5,9,10</sup> as far as the performance of the catalyst additive is concerned.

Ethylene yield presents a significant monotonic increase with an increase of the ZSM-5 total acidity, being almost tripled with the most acidic additive, which is not in agreement with previous work where no or only a small increase in ethylene was recognized.<sup>2,4</sup> Ethylene can be formed only through primary carbenium ion intermediates.<sup>27–30,32,33</sup> The formation of the above unstable intermediate ions is possible only when strong Bronsted acid sites are present. Because the ZSM-5 additives with a higher total number of acid sites have a higher number and density of strong Bronsted acid sites, ethylene production is greatly enhanced, especially in the high acidity region. Primary butyl cations can be formed during the monomolecular cracking of butene,<sup>33</sup> as well as from the cracking of larger than butene alkene molecules, especially in the high acidity region where cracking continues down to the smallest fragments.<sup>30</sup> The production of ethylene from the protolytic cracking of small alkane molecules ( $C_4$ – $C_6$ ), through the pentacoordinated carbonium ion mechanism,<sup>27,29,32</sup> does not seem to be significant as is discussed below.

According to previous work,<sup>1,4,8,9,25</sup> the observed decrease in the yield of gasoline range alkanes is attributed mainly to the decrease in the yield of the corresponding alkenes when the additive is deactivated, since alkanes are mainly produced from alkenes via hydrogen-transfer reactions on Y zeolite<sup>4</sup> and, to a lesser extent, on the ZSM-5 zeolite additives.<sup>25</sup> Cracking of alkanes becomes significant only with fresh or mildly deactivated additives. A number of model compound studies have focused on the reaction mechanisms for alkane cracking.<sup>27–29,32,33</sup> Based on our results, the protolytic cracking of small gasoline range alkanes ( $C_5$ – $C_6$ ) through the pentacoordinated carbonium ion does not contribute significantly to the overall reaction network catalyzed by the ZSM-5 additive. The yields of hydrogen, methane, and ethane, which are typical products especially in the cracking of pentanes and hexanes, remain stable even with the highest acidity additive tested. The smallest alkane molecule that could



react through the above reaction route without producing methane and/or ethane is the  $C_7$  alkane, considering that the  $H^+$  from the surface acid site is bonded to the central carbon atom of the  $C_7$  chain, thus giving the relatively more stable carbonium ion. In this case, the main products are propane and butylene or isobutylene.<sup>27,29</sup> The formation of the initial highly unstable carbonium ion requires the presence of strong Bronsted acid sites, and as a consequence it is favored by the increased ZSM-5 total acidity, which has been shown to increase parallel to the number of strong Bronsted acid sites. On the other hand, cracking of alkanes via the classical carbenium ion intermediate does not produce methane and ethane, while the mechanism through the nonclassical protonated cyclopropyl ion intermediate requires alkanes with seven or more carbon atoms in order to be favored energetically.<sup>27</sup> Both of these reaction pathways, which are bimolecular when it comes to the hydrogen-transfer step, are mainly favored by the increase in the total number or density of ZSM-5 acid sites, thus contributing significantly to the very strong decrease of the  $C_{7+}$  alkanes observed especially in the high acidity region. This rationalizes the significant increase in the  $C_3$ – $C_4$  alkane yields and contributes also to the yield of  $C_3$ – $C_4$  alkenes.

The small increase of the  $C_5$  alkenes in the low ZSM-5 acidity region is clearly depicted on the yield of both branched and normal  $C_5$  alkane, due to the hydrogen-transfer reaction of alkenes on the Y zeolite, as explained above. However, the yield of  $n$ - $C_5$  alkane has been shown to increase further with an increase of the acidity, in contrast to the yields of  $i$ - $C_5$  alkanes and  $C_5$  alkenes. This finding is closely related not only to the increased cracking activity of alkanes with highly acidic ZSM-5 additives but also to the relative cracking between branched and normal gasoline range alkanes.

On the basis of the results of the present work, the B/L ratio of  $C_{11}$ – $C_{12}$  alkanes increases with an increase of the ZSM-5 total acidity, indicating a preferential cracking of heavier ( $C_{11}$ – $C_{12}$ ) gasoline range  $n$ -alkanes, relative to the corresponding isoalkanes, producing smaller alkanes. Furthermore, the strong decrease in the yields of  $C_6$ – $C_9$  isoalkanes with an increase of the ZSM-5 acidity is not compensated for by the cracking of the  $C_{10+}$  isoalkanes to smaller isoalkanes, thus resulting in the observed decrease of the B/L ratio for the  $C_5$ – $C_9$  alkanes.

In this study, changes in the yields of the  $C_4$  compounds with an increase of the total number of ZSM-5 acid sites indicate the presence of certain reaction pathways for gasoline range alkanes and alkenes. The small increase in the yield of  $n$ -butenes observed in our results, in relation to the very strong increase of  $i$ - $C_4$  with an increase in the number of ZSM-5 acid sites, shows that the formation of the tertiary isobutyl ion in the intermediate reaction step is favored as the total acidity increases. This effect is evident on the yields of  $n$ - $C_4$  and  $i$ - $C_4$ . Furthermore, according to the experimental results, the abstraction of  $H^+$  (toward alkenes) and the hydride transfer (toward alkanes) on the isobutyl cation take place at approximately the same rate as the acidity of ZSM-5 increases, since the relative increase for both  $i$ - $C_4$  and  $i$ - $C_4$  is similar.

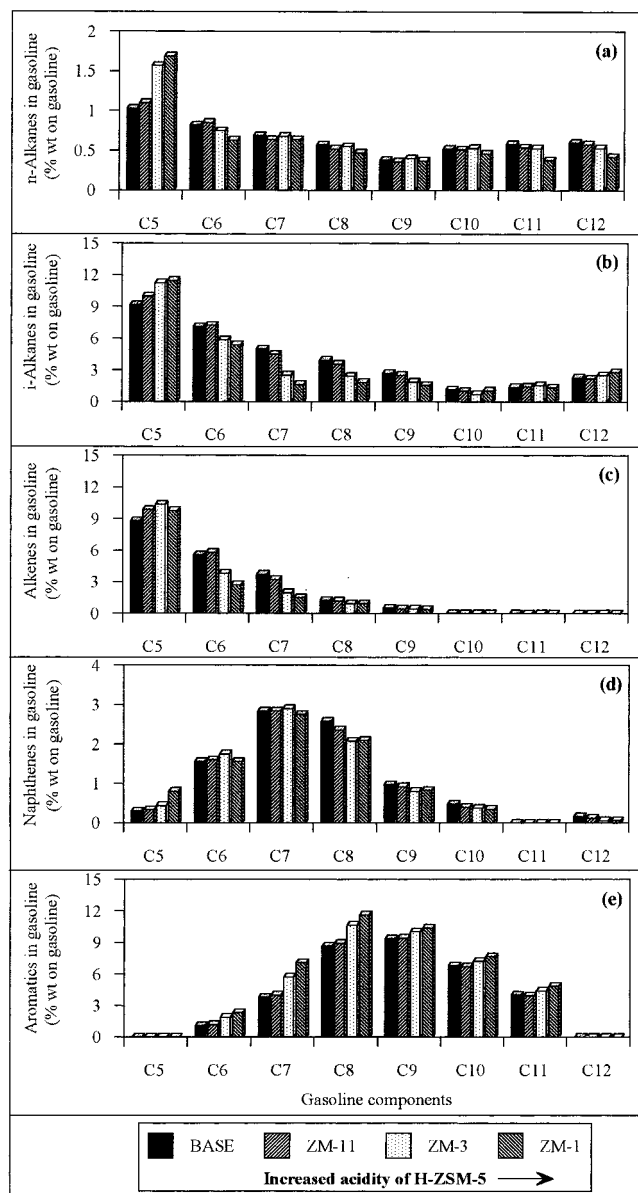
The main route for the production of gasoline range naphthenes and aromatics, the primary cracking of large feed molecules on the Y zeolitic catalyst, is not affected by the presence of ZSM-5; thus, the yields of

naphthenes and aromatics are much less affected. On the basis of the cyclization mechanisms and from the changes in the yields of gasoline range aliphatic and cyclic hydrocarbons observed in this study, it seems that three reaction routes are affected by the additive acidity and influence the final yield of cyclic hydrocarbons. The cracking of the side chains of large cyclic molecules is a reaction path which is favored by the increased ZSM-5 acidity and contributes to the production of  $C_6$ – $C_7$  cyclic hydrocarbons and  $C_3$ – $C_4$  alkenes, at the expense of  $C_{10+}$  cyclic hydrocarbons.<sup>8</sup> Naphthenes and aromatics formed through cyclization of alkenes on the Y zeolite are reduced<sup>28</sup> because of the very strong decrease in the available alkenes, at the proper boiling point range, with an increase of the ZSM-5 total acidity. Finally, the formation of cyclic hydrocarbons, through condensation of small alkenes ( $C_2$ – $C_4$ ) and dehydrocyclization of the produced intermediates on ZSM-5,<sup>34</sup> which is favored by the higher total acidity, may account for the observed increased production of  $C_6$ – $C_7$  aromatics since more  $C_2$ – $C_4$  alkenes are available with an increase of the ZSM-5 acidity. Contradictory results have been reported by previous investigators concerning the formation of small aromatic molecules on ZSM-5 as an FCC catalyst additive.<sup>1,4,11,31</sup> It is thus suggested that the formation of small aromatics by this way could not be excluded, until more elucidating experimental evidence is presented.

In conclusion, it is clear that most of the contradictory results among the several workers are due to the different predominant reactions imposed either by the different deactivation state, in the case of steamed or commercially deactivated additives, or by the different Si/Al ratios of the fresh additives used in each separate case, assuming that the operating conditions, the base catalyst, and the feedstock type are similar in general. The results of the present study are in agreement with nearly all of the results in the literature, contradictory or not, since all of the changes in product yields are explained on the basis of the different ZSM-5 total number of acid sites, for a broad acidity region, covering most of the current presented cases.

**Effect of the ZSM-5 Total Acidity on Product Yields Responsible for the Changes in Research Octane Number of Gasoline.** To interpret changes in gasoline RON, product yields have been presented on a gasoline basis, as weight percent on total gasoline. The distribution of the changes of each hydrocarbon type among all gasoline range carbon numbers is presented in Figure 8. All of the normal alkanes (Figure 8a) decrease slightly or do not change, with the exception of  $C_5$ , which increases monotonically with the total acidity of the additive. The  $C_5$  isoalkanes also increase, while the  $C_6+$  isoalkanes and alkenes show a distinct loss, except for  $C_{11}$  isoalkanes which are stable and  $C_{12}$  isoalkanes which increase slightly (Figure 8b,c). The  $C_5$  alkene concentration is always higher than that with the base catalyst but is almost stable in the whole acidity region. The  $C_5$  naphthenes increase monotonically while  $C_6$ – $C_7$  seem to be almost unaffected. The rest of the naphthenes show a small decrease with an increase of the ZSM-5 total acidity, especially  $C_8$  (Figure 8d). All aromatics have increased concentrations, especially the  $C_6$ – $C_8$  aromatics (Figure 8e). When these results are summarized, it has been found that gasoline  $n$ -alkanes and naphthenes remain practically unchanged, the isoalkanes decrease monotonically with an





**Figure 8.** Effect of the total number of H-ZSM-5 acid sites on the distribution of all gasoline range carbon numbers (C<sub>5</sub>–C<sub>12</sub>) among each hydrocarbon type (on a total gasoline basis).

increase of the total number of ZSM-5 acid sites, and alkenes start to decrease at relatively higher additive acidity values and to a lower extent. The concentration of aromatics in gasoline increases continuously with an increase of the ZSM-5 total number of acid sites in the whole acidity region tested. The total C<sub>5</sub>'s concentration increases while the total C<sub>6</sub>–C<sub>7</sub> decrease, mainly in the high acidity region. The total C<sub>8</sub>–C<sub>9</sub> and C<sub>12</sub> do not change significantly with ZSM-5 acidity, while C<sub>10</sub>–C<sub>11</sub> show a very small increase.

Based on the above results, an interpretation will be attempted concerning the origin of the increased RON values of the produced gasoline. Considering the data from Elia et al.<sup>5</sup> and Scherzer<sup>14</sup> on actual and blend octane numbers of individual gasoline range hydrocarbons and on the basis of our experimental results, the RON increase with a higher total number of ZSM-5 acid sites (Figure 3c) could be attributed to the following:

- Increased concentration of all aromatics (production

of "heavier" gasoline), especially of the higher octane C<sub>7</sub>–C<sub>9</sub> aromatics.

- Decreased concentration of the C<sub>6</sub>–C<sub>8</sub> and C<sub>11</sub>–C<sub>12</sub> *n*-alkanes resulting in RON gain since the C<sub>6</sub>+*n*-alkanes have low octane numbers.

- Increased concentration of C<sub>5</sub> and decreased concentration of C<sub>6</sub>–C<sub>9</sub> isoalkanes, while heavier isoalkanes are almost unaffected. The changes in isoalkane concentration have contradictory effects on RON. A decrease in monomethyl compounds results in RON gain while a similar decrease in multibranched compounds reduces gasoline RON, since these hydrocarbons have very high octane numbers (e.g., >100 for the 2,2,3-trimethylbutane).

- Increased B/L ratio for the C<sub>5</sub> and C<sub>6</sub> alkenes, with a parallel increase in the total concentration of C<sub>5</sub> alkenes, which have very high octane numbers (>150).

- Decreased concentration of the C<sub>7</sub>+ naphthenes, having relatively low octane numbers (<75).

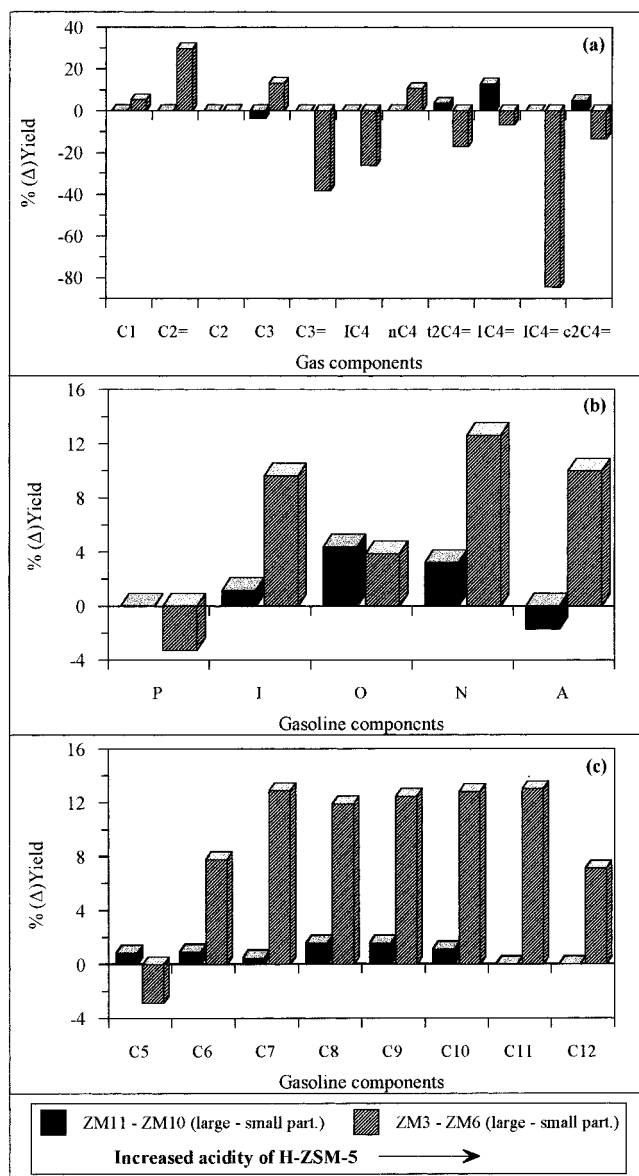
It has also been shown from our results that one can obtain the same RON increase by using two ZSM-5 samples having different acidities. It is worthwhile, at this point, to compare the performance of two such samples ZM-7 and ZM-2 (ZM-7 has 1/5 of the ZM-2 total acidity) which give the same increase in RON (2.1–2.3 units). However, the product yields, obtained by the use of the two samples, are completely different. The high acidity sample (ZM-2) gives almost 8 wt % more LPG than the low acidity sample (ZM-7) and 10 wt % less gasoline. The different composition is due to the progressive changes caused by an increase of the ZSM-5 total acidity. The high acidity additive gives higher C<sub>6</sub>–C<sub>8</sub> aromatics concentration and a higher value of the B/L ratio for C<sub>5</sub>–C<sub>6</sub> alkenes. The low acidity additive produces gasoline with higher C<sub>6</sub>–C<sub>7</sub> isoalkane and alkene concentrations and a higher B/L ratio for the C<sub>5</sub>–C<sub>9</sub> alkanes. This behavior of RON relative to the additive total acidity was also identified in previously published works which are reviewed by Dwyer and Degnan<sup>25</sup> and refer to specific cases with additives at different deactivation states.

#### Effect of ZSM-5 Particle Size on Product Yields.

As shown in Figure 3, there is a significant effect of the particle (usually being a crystalline agglomerate composed of smaller crystals) size of the ZSM-5 additive on most product yields. The limited amount of experimental data of this work, and especially the lack of crystal characterization data, does not support a complete interpretation; however, the above effect is clear and cannot be ignored.

In Figure 9 a more detailed presentation of the particle size effect on product yields is shown. Four ZSM-5 samples have been selected comprising two pairs, one in the low total acidity region and the other in the high total acidity region. ZM-3 and ZM-6 are the high total acidity samples (0.7 mmol of NH<sub>3</sub>/g of zeolite), and ZM-11 and ZM-10 are the low total acidity samples (0.08 mmol of NH<sub>3</sub>/g of zeolite). The two later samples have been prepared from the former by hydrothermal treatment. The samples in each pair have the same total acidity but different particle sizes (e.g., 0.5–2 μm for ZM-6 and ZM-10 and 10–30 μm for ZM-3 and ZM-11).

The yields of the products have values, ranging from 0.1 wt % (methane) up to 14 wt % (total isoalkanes); thus, the differences induced by the different particle sizes of ZSM-5 samples cannot be presented clearly at a common scale. For the sake of clarity, the %Δ(yields)



**Figure 9.** Effect of the total number of H-ZSM-5 acid sites on the product yield changes caused by different ZSM-5 particle sizes.

presented in Figure 9 have been derived from the product yields after the following transformation:

$$\% \Delta(\text{yield}) = \left\{ \frac{\text{yield}_{\text{large par.}} - \text{yield}_{\text{small par.}}}{\text{yield}_{\text{BASE}}} \right\} \times 100 \quad (1)$$

$\% \Delta(\text{yield})$  values have been considered to be significant only when  $\text{yield}_{\text{large cr.}} - \text{yield}_{\text{small cr.}}$  values were higher than the estimated mean experimental error (0.03 wt %).

It is shown in Figure 3, and is more obvious from Figure 9, that at low values of total additive acidity (ZM-11 and ZM-10) the effect of ZSM-5 particle size is smaller than the corresponding effect at high acidity values (ZM-3 and ZM-6). In the high acidity region, the yields of  $C_3=$ ,  $i\text{-}C_4$ , and all of the butenes (especially of  $i\text{-}C_4=$ ) are greatly enhanced with the small particle additive, while the yields of  $C_2=$ ,  $C_3$ , and  $n\text{-}C_4$  are enhanced by the use of large particles. In the low acidity region, only the yield of  $1\text{-}C_4=$  seems to be affected, being favored by the large particle additive. In the gasoline region, where almost all of the yields decrease

with an increase of the ZSM-5 acidity, large ZSM-5 particles seem to inhibit the additive reactivity, especially in the high acidity region. The effect of particle size is more pronounced for the total isoalkanes and naphthenes, mainly due to  $C_6+$  compounds, and for the aromatics, due to  $C_7+$  compounds. In the low acidity region, aromatics yield seems to be favored by small particles mainly due to  $C_7\text{--}C_8$  aromatics. Alkenes are influenced to a lesser extent. In both acidity regions, alkene yield is favored by the large particle additive. The total  $n$ -alkane yield is only affected by ZSM-5 particle size in the high acidity region, mainly due to the yield of  $C_9\text{--}C_{11}$  species, which is favored by the small particle ZSM-5 additive.

The effect of particle size on product yields, described above, can be attributed to the differences in the rates of diffusion and mass transport, induced by the different lengths of the diffusion paths in the additive channels.<sup>26,35</sup> Thus, the size of the effect is expected to be analogous to the molecular size and shape of the reacting hydrocarbons, being more pronounced for the heavier ( $C_7+$ ) hydrocarbons and especially for naphthenes, aromatics, and multibranched isoalkanes. The results described above are in accord with these effects. It could also be suggested that the higher loss of gasoline by the use of small ZSM-5 particles is attributed not only to diffusion restrictions in the channels of large particles but also to the activity of external acid sites which is more significant in small particles.<sup>35</sup>

Although the changes in gasoline yield depend on ZSM-5 particle size, the RON value does not seem to be affected. This result can be interpreted based on the following observations. Differences in the absolute yields of certain compounds, due to ZSM-5 particle size, are in most cases not retained when expressed as concentration in gasoline and thus do not affect the gasoline RON value. Moreover, changes in the concentration of certain compounds induced by the small particle additive, which result in higher RON, are equilibrated by changes in the concentration of other compounds, which result in higher RON but are enhanced by the large particle additive. More specifically, the smaller particles result in the production of "lighter" gasoline since the concentration of  $C_5$  isoalkanes and alkenes in gasoline is higher, the B/L ratio of  $C_5$  and  $C_5=$  is also higher, and the concentration of  $C_7+$  naphthenes is lower, compared to large particles. On the other hand, large particles give a lower concentration of  $n$ -alkanes (mainly  $C_7+$ ), a higher concentration of  $C_6$  alkenes, and a higher value for the B/L ratio of  $C_7+$  alkanes.

## Conclusions

The total number of ZSM-5 acid sites, as measured by TPD of ammonia, could be used, at least on a laboratory scale, to predict the performance of ZSM-5 as the FCC catalyst additive in gas oil cracking, since it has been proven that a direct and smooth correlation exists between the product yields and the total acidity of the ZSM-5 zeolite. It has also been shown that the correlation between the ZSM-5 total number of acid sites and the aluminum content, in the case of fresh samples, or the temperature of hydrothermal deactivation in the case of steamed samples is straightforward. As a result, the number of additive characterization parameters is reduced to only 1, the total number of acid sites. Many of the contradictory results presented by previous work can be classified and explained on the basis of the

different acidity regions of the ZSM-5 additive used in each separate case.

The changes in the yields of gasoline range and gaseous products were interpreted on the basis of the present widely accepted reaction mechanisms for alkane and alkene cracking and the effect of ZSM-5's total acidity on them. The yields of *n*-C<sub>5</sub> alkane, C<sub>6</sub>–C<sub>7</sub> aromatics, and C<sub>5</sub> naphthenes increase monotonically with an increase of the ZSM-5 total acidity. In the low acidity region, the effect of ZSM-5 on alkenes through cracking and isomerization reactions is predominant and results in increased yields of all of the C<sub>5</sub> aliphatics. When the total acidity of ZSM-5 increases, cracking of alkanes and formation or cracking of aromatics become significant, and finally the yield of all of the gasoline components, except for those mentioned above, decreases significantly. Furthermore, with an increase of the ZSM-5 acidity, the B/L ratios for C<sub>5</sub> and C<sub>6</sub> alkenes increase because of increased isomerization activity of the intermediate carbenium ion in the cracking of larger alkenes. The very strong decrease in the C<sub>5</sub>–C<sub>9</sub> isoalkanes with an increase of the ZSM-5 acidity, mainly because of their increased cracking, results in a decrease of the B/L ratio for the C<sub>5</sub>–C<sub>9</sub> alkanes. The conversion of all of the gasoline range hydrocarbons, and especially that of aliphatics, resulted in a significant, monotonic increase in the yield of C<sub>2</sub>=, C<sub>3</sub>=, *i*-C<sub>4</sub>=, C<sub>3</sub>, C<sub>4</sub>, and *i*-C<sub>4</sub>, while the strong increase of ethylene has been attributed to the high number and strength of the Bronsted acid sites of ZSM-5.

The ratio Δ(ROD)/Δ(gasoline) is also a function of the total acidity, increasing when the number of total acid sites of ZSM-5 decreases. It is possible to obtain the same RON increase by using two, different in acidity, ZSM-5 samples; however, the product yields are completely different. The high acidity sample produces much more LPG and much less, rich in aromatics, "heavy" gasoline, as compared to the high C<sub>6</sub>–C<sub>7</sub> isoalkane and alkene "light" gasoline obtained with the low acidity sample.

Finally, the particle size of ZSM-5 plays a significant role in the product selectivity profile, as the small ZSM-5 particles clearly favor the gasoline loss and LPG increase. This effect is more pronounced in the high acidity region where the C<sub>7</sub><sup>+</sup> isoalkanes, naphthenes, and aromatics in the gasoline pool are mainly affected by the particle size and the decrease in their yield is favored by small particle additives. The effect of particle size on gasoline range hydrocarbons also results in changes of the gaseous products that are affected by the presence of ZSM-5. Finally, gasoline RON seems to be unaffected by the ZSM-5 particle size.

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