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New materials as FCC active matrix components for maximizing diesel (light cycle oil, LCO) and minimizing its aromatic content

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Abstract

Different materials such as sepiolite (magnesiumsilicate), amorphous silico-alumino-phosphate (ASAPO) or other mixed oxides such as SiO_2–ZrO_2, or SiO_2–Al_2O_3–MgO, are studied as potential active matrix components of a FCC catalyst, with the final objective of maximizing the light cycle oil (LCO) yield while minimizing the aromatic content of this fraction. The physico-chemical characteristics of these materials as well as their hydrothermal stability play a decisive role in their catalytic behavior. The high surface area amorphous SAPO stands out presenting high selectivity to LCO while decreasing the aromatics content as compared to a commercial SiO_2–Al_2O_3 used as reference material. A formulation has been simulated using this material and, after equilibration, its catalytic behavior has been compared to that of a conventional FCC catalyst formulation.

Keywords: Catalytic cracking; FCC; Active matrix; Light cycle oil (LCO); Diesel; Aromatics in LCO

1. Introduction

More stringent environmental legislation is forcing refiners to significant changes in their plant strategies. Most of these modifications concern the quality of their liquid fuels, both gasoline and diesel. Although desulfurization is still the main issue, other restrictions have to be considered, such as lower product densities, higher cetane numbers and lower levels of polynuclear aromatics (PNAs).

The fluid catalytic cracking unit (FCC) is still a main conversion unit in many refineries. It is able to process very large amounts of heavy oil fractions, and it is flexible enough to direct production preferentially to gases (propylene, butenes), gasoline or diesel, with minor modifications of the unit or the operation conditions [1]. However, the light cycle oil (LCO) fraction obtained by FCC is high in aromatics, sulfur and has a low cetane index. This implies that hydrotreatments are always necessary before blending this fraction into the final diesel pool. By doing this, sulfur content will be decreased, and the aromatics content reduced, but converting them to naphthenes. An additional increase of the cetane may be achieved with the selective opening of the naphthenic rings obtained by hydrogenation [2–6]. Despite the low quality of the LCO, and due to the processing capacity of the FCC unit, it would be interesting, especially from an economic point of view, to improve the quality of this fraction during the process itself.

The FCC catalyst is a complex mixture containing an active zeolite, a matrix that can participate in the overall cracking process at different levels, a binder, and different additives for specific functions. Whereas the zeolite properties will affect more to the composition of gases and gasoline, the matrix will have a direct influence on the properties of the heavier LCO fraction. It is known that their chemical composition and textural properties play an important role in the final selectivity of the catalyst. Concerning the aromatics content in LCO, during the FCC process aromatic compounds may end up in the LCO fraction following two different pathways: they may be directly obtained by cracking of the heavy hydrocarbons present in the feedstock, or they may be formed by secondary reactions such as cyclation/dehydrogenation of primary cracking products. The process variables and the nature of the catalyst will have a direct influence on the extension of these two pathways.

In a first part of the work, the influence of different process variables on the LCO yield and on its aromatics content will be studied using two different reaction systems: a Microactivity

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Test unit (MAT) and a Microdowner unit (MD). In a second part, we will compare different materials as possible substitutes of more conventional matrices of a FCC catalyst, with the aim of maximizing, not only the LCO yield, but also the quality of the diesel by minimizing its polynuclear aromatics (PNAs) content.

2. Experimental

2.1. Materials

A commercial FCC catalyst (Table 1) has been used for the study carried out in the MD unit.

An amorphous silica–alumina (25% Al_2O_3, supplied by Crossfield, SiAl25) is used without further modifications as the reference material for the tests in the Microactivity unit.

A phosphorous impregnated SiO_2–Al_2O_3 (0.2 wt.% P) has been prepared here for the study of the reaction conditions in the MAT unit after steam treatment at 750 °C for 5 h in a 100% steam atmosphere.

A natural sepiolite was modified in order to introduce acidity and cracking activity as described in reference [7]. More specifically, a Na-sepiolite was obtained by exchanging a natural magnesium silicate sepiolite with a 1 M NaOH solution during 6 h at 200 °C using a liquid-to-solid ratio of 6 (w/w). Then, an aluminum substituted sample was obtained by exchange with a 0.25 M $Al(NO_3)_3$ solution at room temperature. Finally, the Al-sepiolite (SEPAL) was calcined at 550 °C during 3 h.

A non-ordered mesoporous SiO_2–ZrO_2 material was prepared following a sol–gel fluoride catalyzed procedure described in reference [8], used for the preparation of other high surface area non-ordered mesoporous silica based materials, such as SiO_2–TiO_2 and SiO_2–Al_2O_3. The Zr-containing silicas were prepared adding tetramethoxysilane (TMOS) as silica precursor to a 1-propanol solution of zirconium-ortho-propoxide ($Zr(OPr)_4$) at 36 °C in a glass beaker. Then a water solution of NH_4F was added to the former under vigorous stirring until gelation occurred. The final reaction mixture had the following molar composition:

$$1\text{TMOS} : x\text{Zr(OPr)}_4 : 4\text{PrOH} : 4\text{H}_2\text{O} : y\text{NH}_4\text{F}$$

where x and y were adjusted to reach the desired Si/Zr and $(Si + Zr)/F^-$ ratios. Then, the gel was aged at 36 °C for 24 h, and finally it was dried at 150 °C for 24 h. Four different samples were prepared. Two Si/Zr ratio (6.2 and 60) were compared at a $(Si + Zr)/F^-$ ratio of 100, and the effect of the F^- concentration was studied for the highest Zr content ($(Si + Zr)/F^-$ of 10, 100 and 200 for Si/Zr = 6.2). The final solids were calcined at 550 °C for 3 h.

Table 1
Characteristics of the commercial FCC catalyst

Rare earth (wt.%)	2.7
UCS (nm)	24.30
BET area (m^2/g)	114
Y zeolite content	11

An amorphous silico-alumino-phosphate (ASAPO) was prepared following Kearby's procedure for preparing aluminophosphates [9], but in our case a silicon source was also added. An aqueous solution was prepared containing $AlCl_3·6H_2O$, H_3PO_4 and tetraethylorthosilicate (TEOS). After hydrolyzing the TEOS during 2 h, the final gel was precipitated at 25 °C by slow addition of aqueous ammonia (10 wt.% NH_3) used as neutralizer agent. This was done under vigorous stirring in order to get a homogeneous pH through the whole solution until gelation took place. The pH value at the precipitation end point was 6.1. The obtained gel was filtered, washed with isopropyl alcohol and dried at 100 °C overnight. Finally, the sample was calcined at 650 °C for 3 h. Two samples with different silica content were prepared, with the following molar compositions of the starting solutions:

Al_2O_3: P_2O_5: $0.6SiO_2$: $20.8H_2O$

Al_2O_3: P_2O_5: $0.3SiO_2$: $20.8H_2O$

An amorphous SiO_2–Al_2O_3–MgO material was prepared by means of a neutralization-precipitation method [10]. Thus, a Si–Al–Mg aqueous acidic solution was prepared by addition of HNO_3 (63 wt.%), water glass solution, $AlCl_3·6H_2O$ and $MgCl_2·6H_2O$ to miliQ water, and neutralized with aqueous ammonia, at 25 °C and under stirring. The obtained slurry was aged at 40 °C during 20 h, dried for 24 h at 100 °C and finally calcined at 550 °C for 3 h. Starting molar ratios in the solution were Si:Al:Mg of 0.6:0.2:0.2.

The calcined samples are considered as fresh (F) and have been characterized and tested catalytically. Moreover, and to evaluate the hydrothermal stability of the different materials, they have been characterized and tested after a hydrothermal treatment of 5 h at 750 °C in a 100% steam atmosphere. These samples are named as steamed (S). In all cases, the solids have been pressed, crushed and sieved to obtain particles in the range of 0.2–0.4 mm before reaction, and tested without further dilution in the MAT unit tests. Their properties are summarized in Table 2.

2.2. Catalytic experiments

Two lab units, i.e. a transported bed MicroDowner reactor and a fixed bed micro activity test (MAT), were used to evaluate the influence of reaction conditions on LCO yield and quality during catalytic cracking of vacuum gas oil (VGO). Hardware and detailed operation of the MD have been described previously [11]. Main features of the unit comprise a catalyst preheater where the catalyst is stored before the test, a once-through tubular reactor, where the feed and the preheated catalyst are contacted continuously at a short residence time (0.3–2 s), and a disengager in which catalyst is separated from hydrocarbons before regeneration. The unit runs at a steady-state regime during the reaction step. The catalyst, separated from the reaction products, is continuously stripped during the reaction and 60 s after the reaction step. Products are recovered by known methods (cold traps for liquids and a burette for gases) and catalyst is regenerated after the stripping step with

Table 2
Characteristics of the samples tested

Sample	Characteristics	Fresh samples				Steamed
		BET (m^2/g)	External surface (m^2/g)	Micropore volume (cm^3/g)	Mean pore diameter (Å)	BET (m^2/g)
SiAl25	SiO_2–Al_2O_3, 25% Al_2O_3	287	287	–	40–45	138
0.2P/SiAl25	0.2 wt.% P on SiAl25	–	–	–	–	143
SEPAL	–	194	142	0.026	–	86
SiZr-A	Si/Zr = 60, $T/F^- = 100$	870	870	0.000	55	416
SiZr-B	Si/Zr = 6.2, $T/F^- = 100$	307	198	0.050	–	134
SiZr-C	Si/Zr = 6.2, $T/F^{a-} = 10$	349	226	0.060	–	152
SiZr-D	Si/Zr = 6.2, $T/F^- = 200$	294	205	0.040	–	145
Amorphous SAPO-1	Al_2O_3:SiO_2 = 1:0.6	427	427	–	60	287
Amorphous SAPO-2	Al_2O_3:SiO_2 = 1:0.3	275	275	–	45	271
Si–Al–Mg	Si:Al:Mg = 0.6:0.2:0.2	387	387	–	–	66

an air flow of 500 ml/min during 3 h. Nitrogen is injected for catalyst smooth transport and feed dispersion. The unit can work in a fully automatic way, and an option for testing different catalysts is available.

The MAT unit, described previously [12], is fully automated and can be operated in a continuous way up to eight cycles, i.e. stripping-reaction-regeneration, without operator intervention. Reactions were performed at temperatures ranging from 490 to 550 °C and times on stream (TOS) of 15, 20 and 30 s, and the catalyst to oil ratio was varied in a range of 1.5–5.0 g/g keeping the amount of catalyst constant (3 g), and changing the amount of oil fed, in order to vary the conversion. Before each experiment, the system was purged with a 30 cm^3/min N_2 flow for 30 min at the reaction temperature. After reaction, stripping of the catalyst was carried out for 15 min using a N_2 flow of 30 cm^3/min. During the reaction and stripping steps, the liquid products were collected in the corresponding glass receivers located at the exit of the reactor, kept at 283 K by means of a computer controlled bath. Meanwhile the gaseous products were collected in a gas burette by water displacement. After stripping, the catalyst was regenerated at 813 K for 3 h, in a 100 cm^3/min stream of air.

Table 3
Characteristics of the vacuum gas oil

Density (15 °C) (g/cm^3)	0.916
Aniline point (°C)	79.2
K (UOP)	11.82
Sulfur (wt.%)	1.65
Nitrogen (ppm)	1261
Na (ppm)	0.18
Cu (ppm)	<0.1
Fe (ppm)	0.3
Ni (ppm)	0.2
V (ppm)	0.4
Average molecular weight	407
Aromatic carbon (ndM)%	22.96
Naphthenic carbon (ndM)%	15.16
Paraffinic carbon (ndM)%	61.88
Aromatic rings/molecule (ndM)	1.17
Naphthenic rings/molecule (ndM)	1.01

Distillation curve ASTM D-1160 (°C)

5%	10%	30%	50%	70%	90%
319	352	414	436	459	512

The feedstock processed in both units is a heavy VGO whose properties are given in Table 3. Conversion is defined as the sum of liquid products boiling below 359 °C, gases and coke.

For the study of the different materials described in the previous section, catalytic cracking of the VGO described in Table 3 has been performed in the MAT unit using these materials fresh (F) and steamed (S). The reactions were carried out at 520 °C and with a catalyst time on stream (TOS) of 30 s.

2.3. Analysis of the products

The gases were analyzed using a Varian 3600-GC equipped with two detectors. A thermal conductivity detector (TCD) was used for analysis of H_2 and N_2, which were separated in a 15 m molecular sieve column, and a flame ionization detector (FID) for C1–C6 hydrocarbons separated in a 30 m Plot/Al_2O_3 column. Simulated distillation of the liquids was carried out on a Varian 3800-GC following the ASTM-2887-D procedure. Cuts were made at 150.8 °C for light gasoline, 216.3 °C for heavy gasoline and 359 °C for LCO. In addition to this, a Varian 3900-GC equipped with a Petrocol-100 fused silica column connected to a FID detector has been used. This equipment allows a determination of the detailed composition of the liquid products in the gasoline fraction (C5–C12) as well as the identification and quantification of some of the most important aromatic compounds present in the LCO fraction. The detailed composition of the gasoline was determined up to C12, using detailed hydrocarbon analysis (DHA) 5.0® software from VARIAN. Research octane number (RON) and motor octane number (MON) were determined by means of the correlations published by Lugo et al. [13]. Identification of aromatics in LCO was carried out with the help of commercially available standards and GC–MS. The CO_2 formed during the regeneration step is monitored and quantified by means of an IR cell (Rosemund Binos-100).

3. Results and discussion

3.1. Characterization of the catalysts

The physico-chemical characteristics of the different materials tested as potential matrices of a FCC catalyst are given in Table 2. The amorphous silica–alumina used as the reference material has 25% Al_2O_3. It can be seen that its surface after steam treatment is considerably reduced. A BET surface area reduction close to 50% is observed, independently of the starting surface area value, for all samples except for one of the amorphous SAPO, ASAPO-2. The Al-exchanged sepiolite (SEPAL) is the sample with the lowest BET surface area when fresh.

The nominal compositions and surface areas of the non-ordered mesoporous SiO_2–ZrO_2 materials are also presented in Table 2. The first thing to be noticed is the influence of the Zr content on the BET surface area of the material obtained. Sample SiZr-D, with a Si/Zr = 60 presents a very high BET value, which is more than double than the samples with higher Zr content (Si/Zr = 6.2), independently of the fluoride concentration in the synthesis media. Although steaming reduces the surface area of all the SiZr samples by more than 50%, the surface area of SiZr-D steamed is still much higher than that of any of the rest of the samples. This high surface area SiZr-D only presents external surface, and although the pore distribution is wide, an average pore diameter of 5 nm can be given. Moreover, it has to be noted that the three samples with higher Zr content present similar external surface areas, around 200 m^2/g, and the additional area is due to the presence of some microporosity. The external surface areas, together with the micropore volumes are given in Table 2. Besides Zr content, we have also studied here the influence of F^- concentration of the final characteristics of the sample. Then, the concentration of fluoride, i.e. (Si + Zr/F), was varied from 10 to 200 as shown in Table 2. F^- anion is an effective catalyst for the hydrolysis of alkoxysilanes in water containing media [14–16], and in a previous paper we have described its influence on gelation time [8]. In the case of the SiZr samples obtained here, there were no significant differences in the gelation times, and the BET surface area, as well as the micropore volume, slightly decreases when decreasing fluoride concentration. Although, it is known that hydrolysis and condensation rates of TMOS must increase as the Si/F ratio does, Zr content in these samples is significant (Si/Zr = 6.2), and the influence of F^- on the Zr alcoxide hydrolysis may be different. Steam treatment results in the loss of any microporosity present in the fresh materials, and in the broadening of the pore size distribution.

In the case of the amorphous SAPO, the silicon content greatly affects the surface area of the fresh material, and the sample with the highest Si content presents much larger BET, and a slightly wider mean pore diameter, although the pore size distribution is quite broad in both cases. However, the surface areas are equalized after steaming, as the value for ASAPO-2, with an Al_2O_3:SiO_2 ratio of 1:0.3, scarcely diminishes. Finally, the amorphous SiO_2–Al_2O_3–MgO material, with an initial surface area of 387 m^2/g, is the most affected by the hydrothermal treatment, and results in a final BET of 66 m^2/g.

With all materials used here, only SiO_2–Al_2O_3 and Al-sepiolite present weak Brönsted acidity (results not shown), since a small band assigned to the protonated pyridine appears at 1450 cm^{-1} in the IR spectrum after desorption at 150 °C and 10^{-2} Torr. However, these two samples are not able to retain pyridine at temperatures higher than 150 °C. In the case of ASAPO1, a very small band seems to appear also, but too small for quantification.

3.2. *Catalytic cracking of a VGO*

3.2.1. *Influence of process variables*

Fig. 1 shows the temperature effect on conversion and overall selectivities for catalytic cracking of a VGO at 30 s TOS in the MAT unit with a P-doped silica–alumina. As expected, when increasing temperature, conversion as well as the gas yield increase, while the LCO yield decreases, especially at the highest temperature (550 °C). Moreover, the reaction temperature increase leads to more dry gas and higher olefinicity in the LPG fraction (see Table 4). This increase in the olefin/paraffin ratio is due to the fact that the temperature effect is larger on the cracking reactions (higher activation energy) than on the hydrogen transfer reactions, responsible for conversion of olefins into their corresponding paraffins [17]. Concerning the total aromatics content of the LCO fraction, shown in Fig. 1, there is a slight increase in the LCO aromatics when increasing reaction temperature. Still, it has to be taken into account that some of the major drawbacks associated to the conventional MAT system are the long catalyst residence time in reactor and the development of temperature and coke profiles along the fixed catalytic bed [18], factors that can influence the product distribution in LCO in different ways at different temperatures, and that can prevent us from seeing a more direct effect of temperature on the aromatics content of LCO. Owing to this, we have carried out a series of experiments with the MD unit, which results are more meaningful.

The MD unit, which works with a transported bed and introduces the thermal shock for the feed, gives more

Table 4
Effect of TOS and temperature on individual gases yields compared at constant total conversion of 75 wt.%

Operating conditions					
Temperature (°C)	490	490	490	520	550
TOS (s)	15	20	30	30	30
Cat/Oil	2.18	2.27	2.59	1.84	1.92
Detailed yields (wt.%)					
Hydrogen	0.06	0.07	0.06	0.05	0.08
Methane	0.34	0.35	0.39	0.51	0.79
Ethane	0.31	0.32	0.36	0.42	0.60
Ethylene	0.28	0.29	0.33	0.41	0.66
Propane	0.44	0.43	0.48	0.50	0.63
Propylene	2.94	2.82	2.87	3.06	3.88
Isobutane	2.17	2.16	2.36	1.93	1.82
n-Butane	0.35	0.34	0.36	0.35	0.39
trans-2-Butene	1.29	1.22	1.20	1.21	1.47
1-Butene	0.96	0.90	0.88	0.95	1.23
Isobutene	1.55	1.49	1.43	1.63	2.07
cis-2-Butene	0.96	0.91	0.89	0.91	1.12
Dry gas (C1 + C2)	0.927	0.954	1.075	1.346	2.044
Propylene/propane	6.741	6.516	6.026	6.145	6.195
Butene/butane	1.890	1.800	1.617	2.067	2.664
Isobutene/isobutane	0.717	0.688	0.605	0.846	1.140

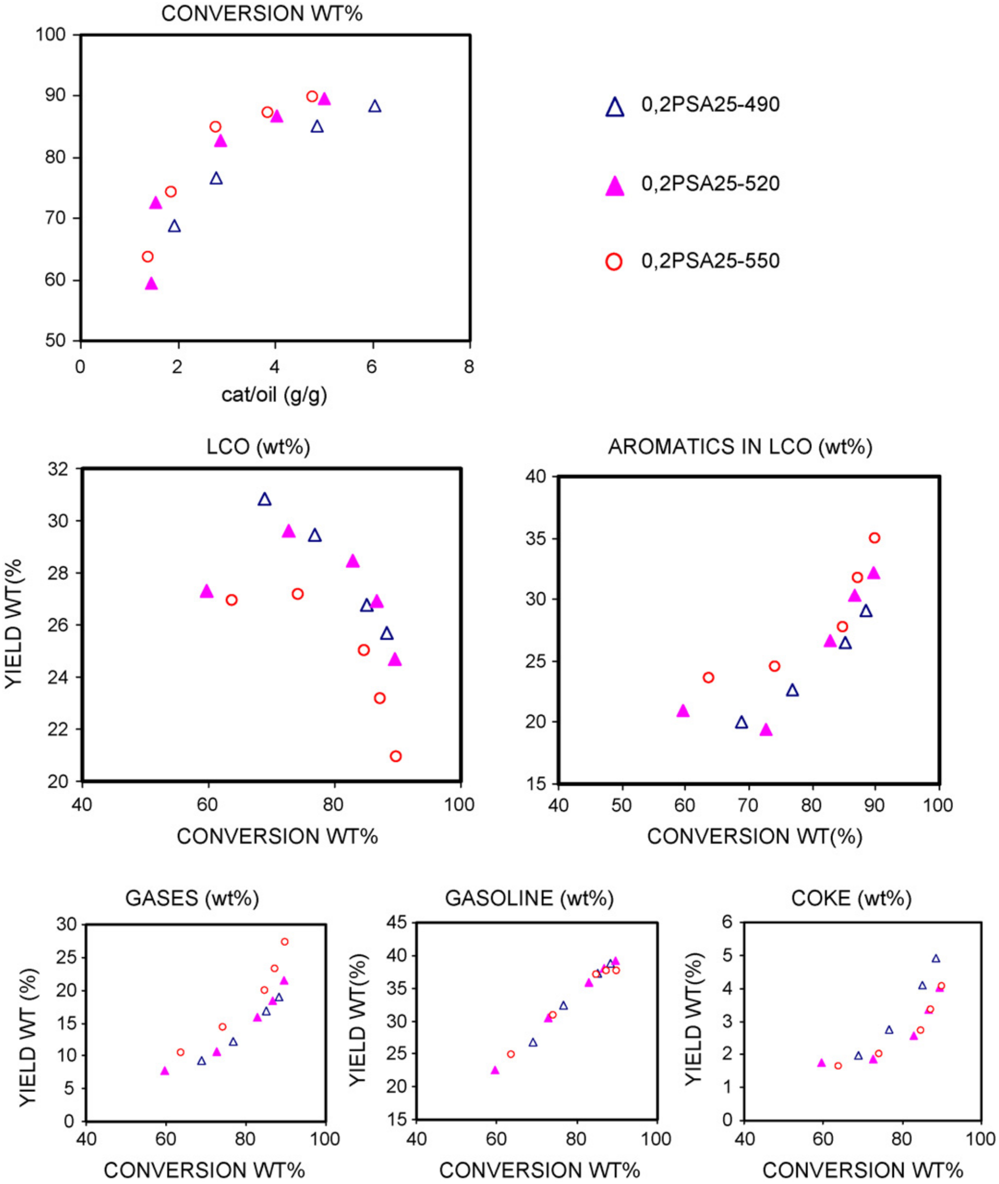

Fig. 1. Activity, overall selectivity and total aromatics in LCO (wt.%) obtained with a steamed 0.2 wt.% P impregnated SiO_2–Al_2O_3 (0.2PSA25) at 30 s TOS and temperatures ranging from 490 to 550 °C for catalytic cracking of a VGO in a MAT unit.

representative results of the behavior of an industrial unit, and has been used with a commercial catalyst and feed in order to check the effect of space velocity and temperature on LCO yield and quality. These results are presented in Figs. 2 and 3. As observed in MAT, the total conversion (including LCO) increases when decreasing space velocities and increasing temperature. The LCO selectivity decreases while gas selectivity increases when increasing conversion and temperature. Gasoline selectivity is similar at 500 and 550 °C till a conversion of 85%. Then, the gasoline selectivity is increasingly lower at 550 °C. This is due to an increase in the relative recracking rate of gasoline compared to VGO at higher temperature, as reported previously in the literature [19,20]. Coke selectivity is relatively constant with temperature, something which has also been observed previously. As for the tests in MAT unit, the LCO quality has been assessed through the content of polyaromatics in the LCO, at various space velocities that cover a wide range of VGO conversion. It has been observed that the PNA content of LCO slightly increases with the temperature at high conversion. This increase is more pronounced for methyl naphthalene, while it is nearly inexistent for trimethyl naphthalenes. As the LCO selectivity decreases with the temperature, we see that the PNA yield hardly changes with temperature, but that the PNA are more dealkylated at higher temperature, so that a higher selectivity to the smallest PNA (methyl naphthalene) is observed.

Influence of TOS in the MAT unit has been studied at 490 °C, temperature at which LCO yield was maximized. Results presented in Fig. 4 show an increase in conversion when decreasing TOS. LCO selectivity is slightly increased, although differences for 15 and 20 s TOS are small. In the fixed bed MAT unit, decreasing TOS for a given catalyst/oil (CTO) ratio

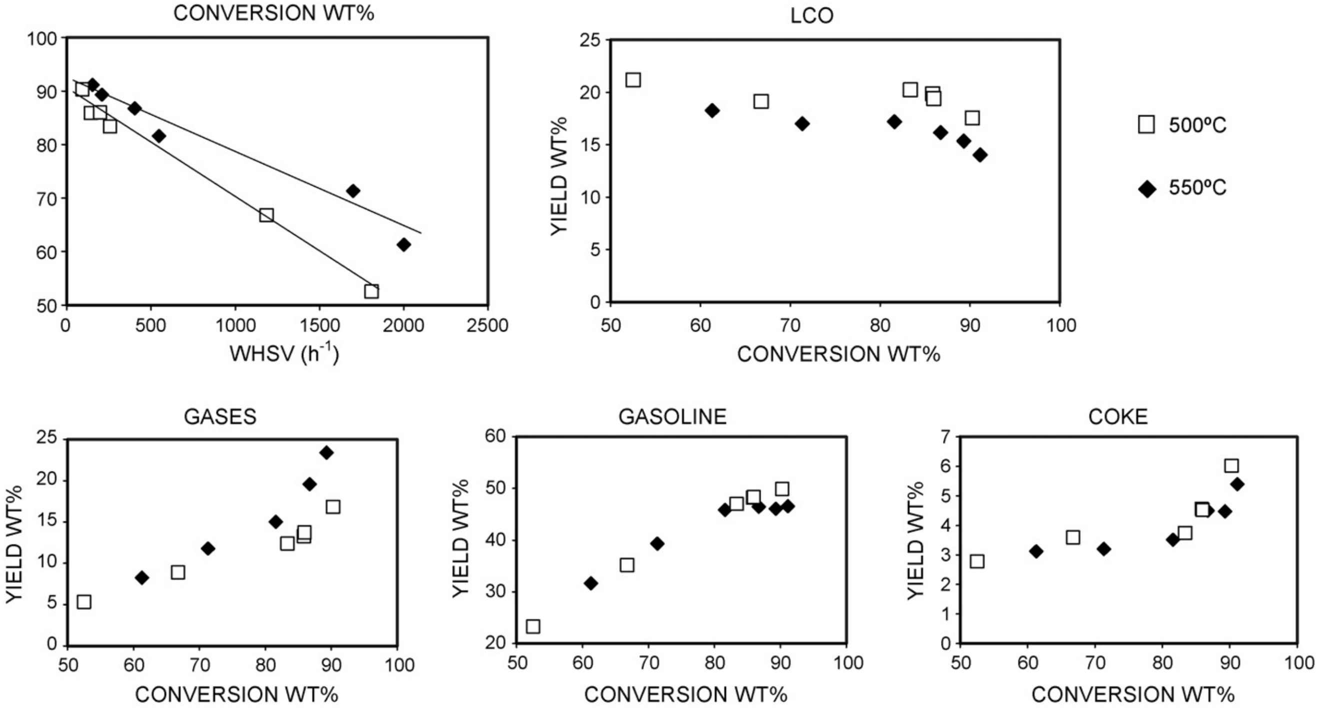

Fig. 2. Activity and overall selectivity obtained from the catalytic cracking of a VGO with a commercial catalyst based on Y zeolite at various space velocities in a MicroDowner unit, at temperatures of 500 and 550 °C.

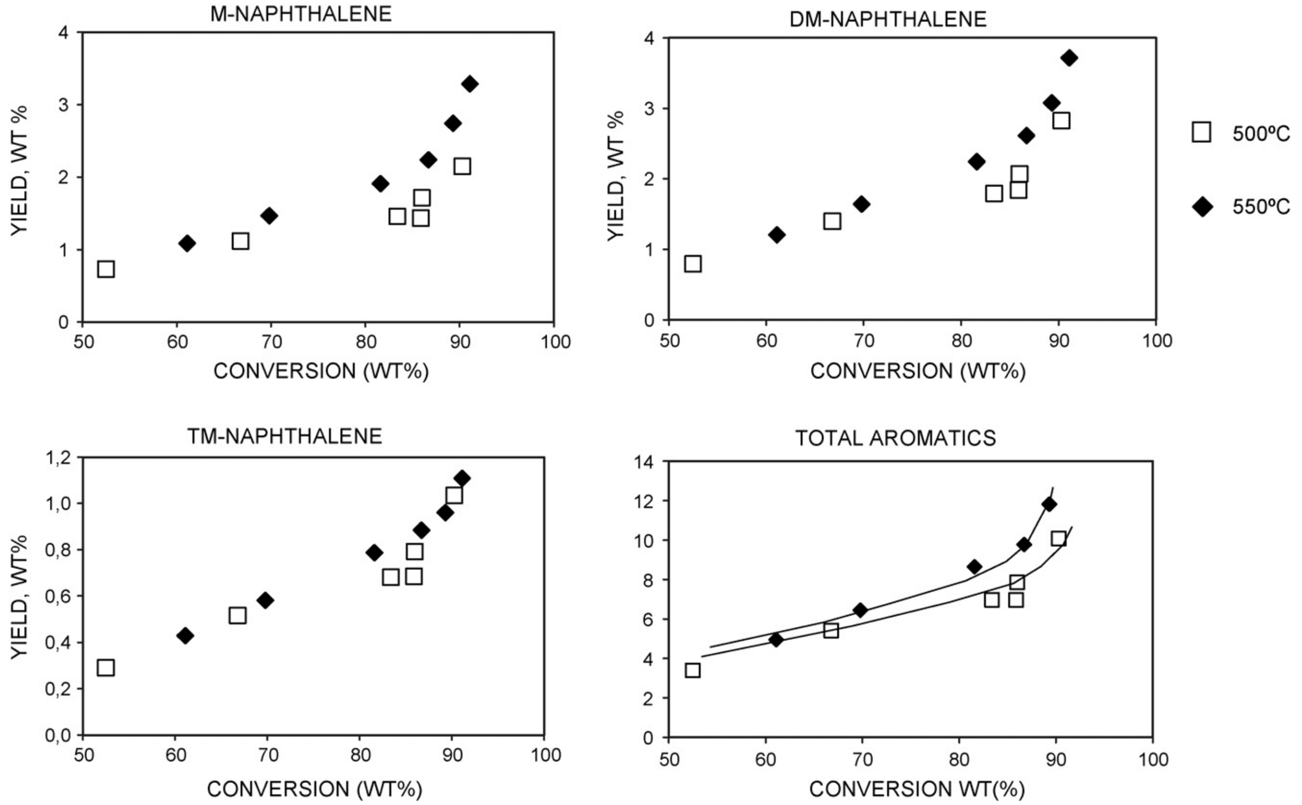

Fig. 3. Aromatic contents in LCO (wt.%) obtained from the catalytic cracking of a VGO with a commercial catalyst based on Y zeolite at various space velocities in a MicroDowner unit, at temperatures of 500 and 550 °C.

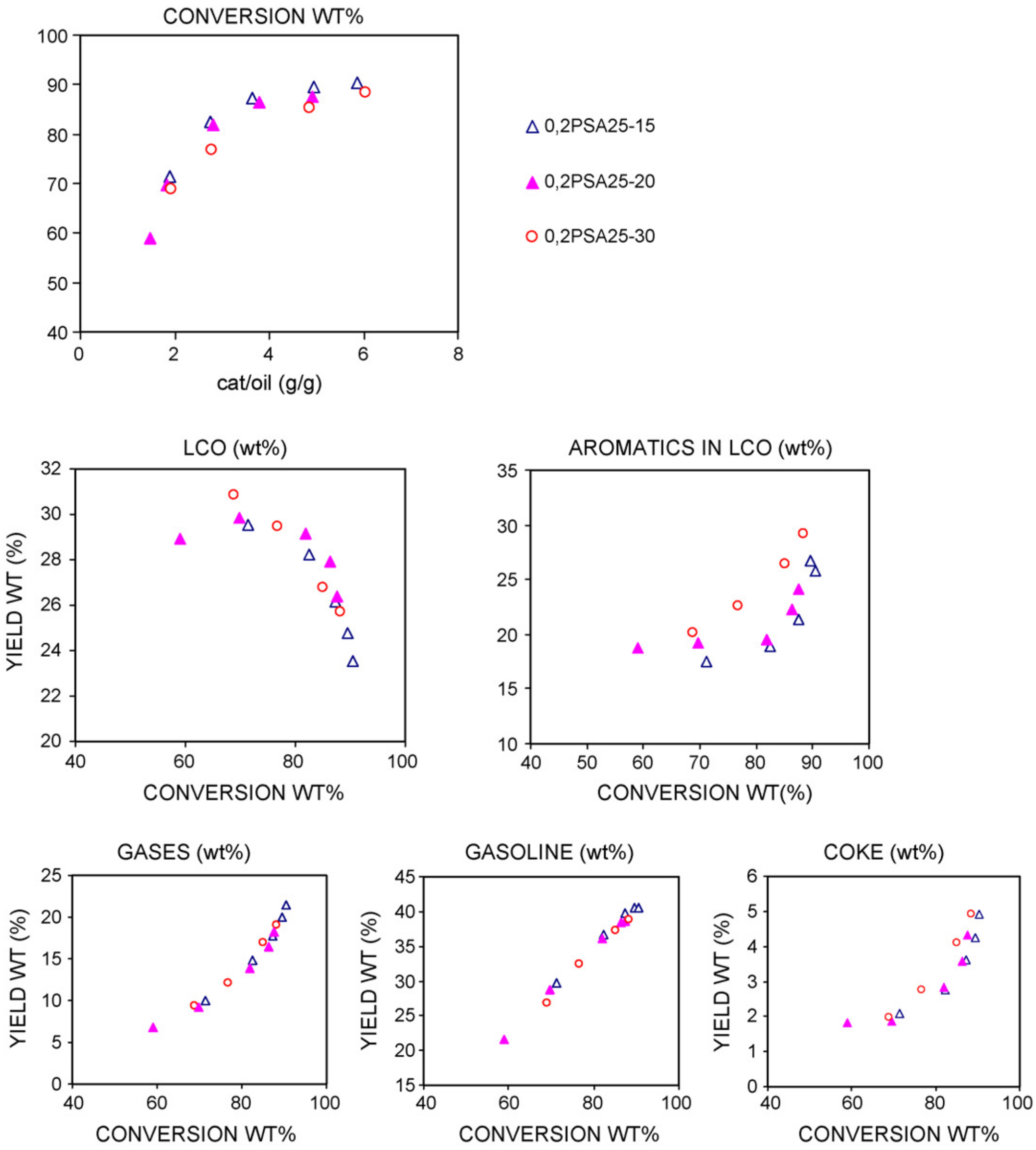

Fig. 4. Activity, overall selectivity and total aromatics in LCO (wt.%) obtained with a steamed 0.2 wt.% P impregnated SiO_2–Al_2O_3 (0.2PSA25) at 490 °C and TOS ranging from 15 to 30 s for catalytic cracking of a VGO in a MAT unit.

involves increasing the space velocity that can be defined in the MAT unit as

$$\text{WHSV}\,(\text{h}^{-1}) = \frac{3600}{\text{CTO} \times \text{TOS}},$$

where TOS is given in seconds and CTO in grams of catalyst per gram of feed.

In the MicroDowner unit the WHSV is given by:

$$\text{WHSV}\,(\text{h}^{-1}) = \frac{3600}{\text{CTO} \times t_{\text{res}}}$$

where t_{res} is the catalyst residence time in the reactor. Thus, secondary reactions such as hydrogen transfer and over-cracking take place in a lower extend, and this results in less hydrogen and dry gases, more olefins in the LPG fraction and lower coke yield (see Fig. 4; Table 4). In fact, O/P ratios clearly increase when decreasing TOS. Concerning the aromaticity of the LCO range (Fig. 4), the effect observed is very clear, and the concentration of aromatics in the LCO fraction is considerably reduced at lower TOS, especially when going from 30 to 20 s. This could indicate that, under our experimental conditions and in the MAT unit, secondary cyclation and/or hydrogen transfer reactions will have to be considered as responsible for the formation of at least a part of the aromatic compounds in LCO. This study of the TOS influence has also been performed at higher temperatures (results not shown) and the trends obtained are the same, although differences between the different series are reduced.

In the MD unit, and in opposition to the MAT unit, the time averaging effects due to the long residence time of the catalyst are not present, as the catalyst deactivates at the same time the products are converted. Thus, an increase in the residence time or in the CTO always implies an increase of conversion. With the MD unit, it is possible to study the effects of the residence

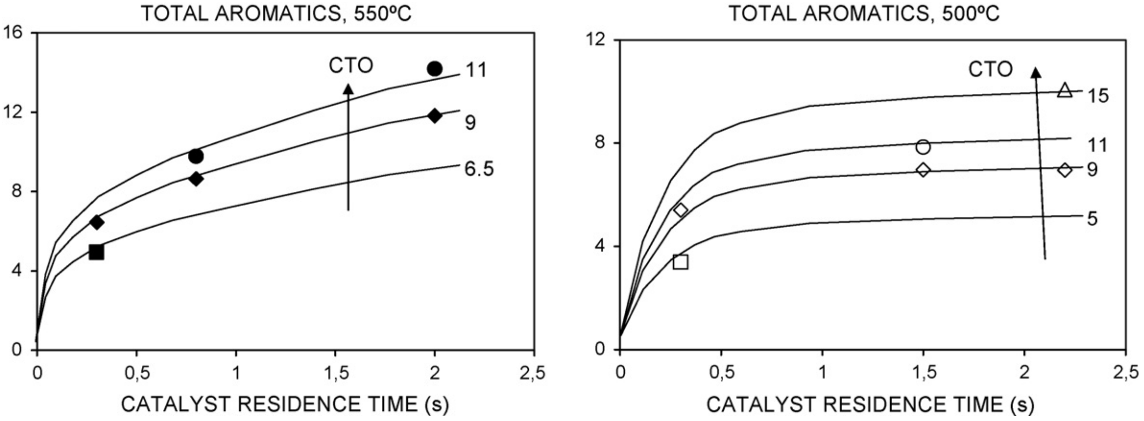

Fig. 5. Aromatic contents in LCO (wt.%) obtained from the catalytic cracking of a VGO with a commercial catalyst based on Y zeolite at various CTO and catalyst residence time in a MicroDowner unit, at temperatures of 500 and 550 °C.

time and the CTO as separate variables. The selectivity to total PNA is shown in Fig. 5 with residence time and CTO as variables, while in Fig. 6 a comparison between 500 and 550 °C temperatures at a CTO of 9 and increasing catalyst residence time is shown. In Fig. 5, the different lines in each figure represent the evolution of the PNA selectivity at a given CTO (6.5, 9 and 11 at 550 °C; and 5, 9, 11 and 15 at 500 °C). It is clear from Fig. 5 that an increase of CTO, or the residence time, always leads to an increase of the PNA selectivity. Yet, the increase at 500 and 550 °C is slightly different as shown in Fig. 6. While the PNA selectivity does not increase much at 500 °C with contact time higher than 1 s, the PNA selectivity increases steadily at 550 °C with the catalyst residence time. While in MAT the increase in PNA with TOS has been related to the hydrogen transfer, this cannot be the reason for the increase of the PNA with the temperature, as it is well known that the ratio hydrogen transfer to cracking decreases when increasing temperature. Instead, the increase of PNA may be related with a higher bottom conversion at 550 °C, which is known to be rich in polyaromatic cores, while at 500 °C the bottoms conversion is much more limited with residence time, although it can be significantly increased with CTO. Thus, the hydrogen transfer will only affect negatively the LCO quality at long contact time, while the bottoms conversion will be the main variable that

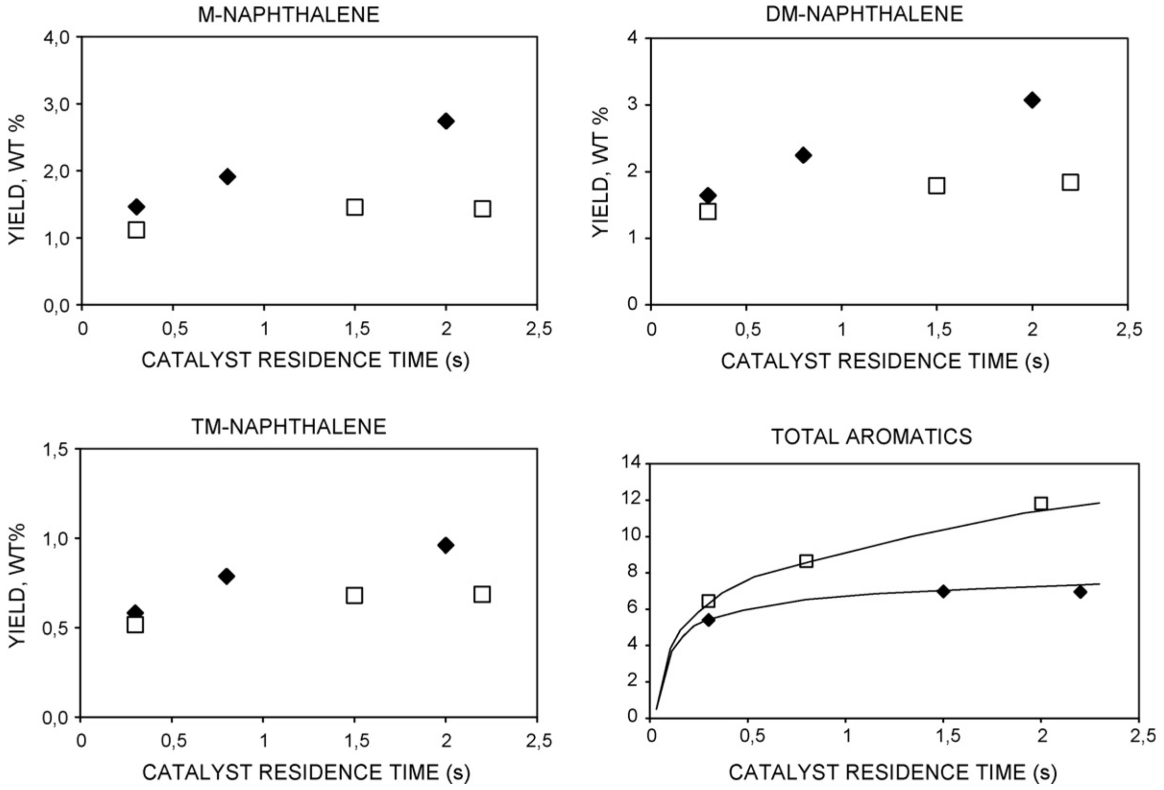

Fig. 6. Aromatic contents in LCO (wt.%) obtained from the catalytic cracking of a VGO with a commercial catalyst based on Y zeolite at CTO 9 and various catalyst residence time in a MicroDowner unit, at temperatures of 500 and 550 °C.

governs LCO quality at short contact time. Thus, it would be of great interest to be able to convert the bottoms without producing large amounts of polyaromatics with a convenient additive or a modified matrix.

3.2.2. Study of different materials

3.2.2.1. SiZr based materials. In Fig. 7, the activity and overall selectivity of the different SiZr fresh samples is compared with that of the reference $SiO_2–Al_2O_3$. Significant differences are observed in their activity. The first thing to be noted is that the conversion of VGO, defined here as the sum of gases + gasoline + LCO + coke, is considerably lower for sample SiZr-A, the one with lowest Zr content and larger BET. It has to be noted that this sample is also the only SiZr that does not present some microporosity. Samples B and D, with the higher (Si + Zr)/F ratio, present a similar activity, and SiZr-C, the high Zr content sample with highest surface area, is the most active, even more than the reference $SiO_2–Al_2O_3$. Differences in selectivity are smaller, but it is remarkable that all SiZr materials present better selectivity to diesel and gasoline, less gases and lower coke yields than SiAl. It can be seen that the most active sample SiZr-C, also presents the highest selectivity to liquid fuels. Looking into the selectivity within the gaseous products (Table 5), with the exception of SiZr-A, the rest of SiZr materials yield less dry gases (C1 + C2), and increase the olefinicity in the LPG fraction as compared to the reference case.

Despite the promising selectivity results described up to now, when the concentration of aromatics in the LCO fraction is considered (Fig. 7), it can be seen that the high activity SiZr samples maintain or decrease only slightly the total concentration of aromatics, despite the decrease in the olefinicity of the LPG.

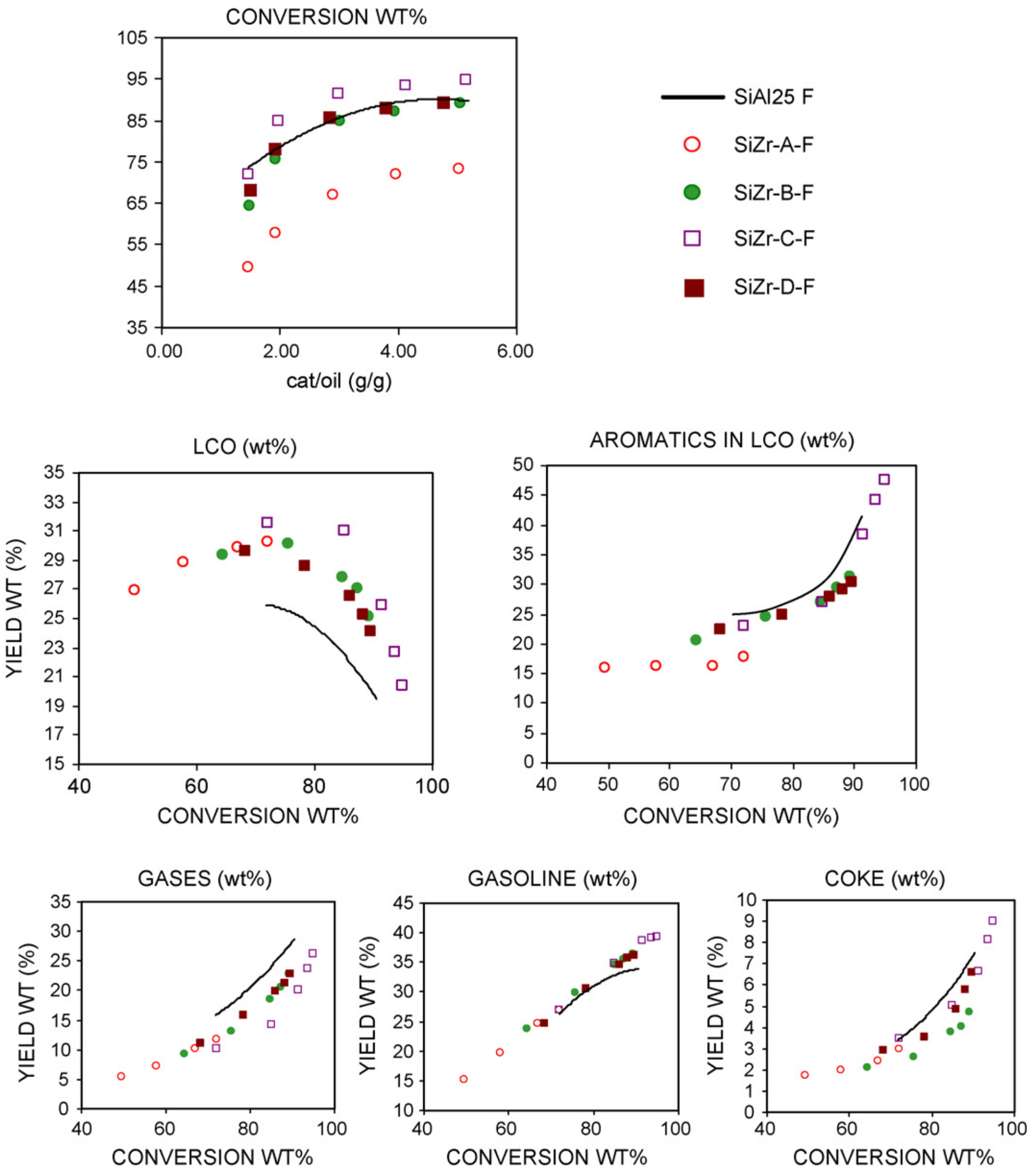

Fig. 7. Activity, overall selectivity and total aromatics in LCO (wt.%) of different SiZr materials compared to that of a reference $SiO_2–Al_2O_3$ for catalytic cracking of a VGO in a MAT unit. Fresh samples, $T = 520\ ^\circ C$, TOS = 30 s.

Table 5
SiZr materials compared with SiO_2–Al_2O_3: individual gases yields obtained in a MAT unit compared at constant total conversion of 70 wt.% for fresh samples and at constant total conversion of 60 wt.% for steamed samples

	Catalyst								
	SiAl25-F	SiZr-A-F	SiZr-B-F	SiZr-C-F	SiZr-D-F	SiAl25-V	SiZr-B-S	SiZr-C-S	SiZr-D-S
Conversion	70	70	70	70	70	60	60	60	60
Cat/oil	1.36	3.54	1.70	1.37	1.55	1.14	5.18	2.13	4.70
Hydrogen	0.08	0.06	0.02	0.03	0.04	0.02	0.06	0.04	0.05
Dry gas (C1 + C2)	1.69	2.17	1.18	1.12	1.50	0.86	1.58	1.17	1.55
LPG	12.97	8.94	9.96	8.32	10.35	4.31	5.52	5.41	5.28
Propylene/propane	2.77	3.29	5.67	4.09	4.89	5.08	3.27	4.26	3.19
Butene/butane	1.14	3.36	1.58	1.17	1.65	2.08	4.68	3.20	4.73
Isobutene/isobutane	0.46	2.10	0.56	0.30	0.56	0.87	3.13	1.64	3.24

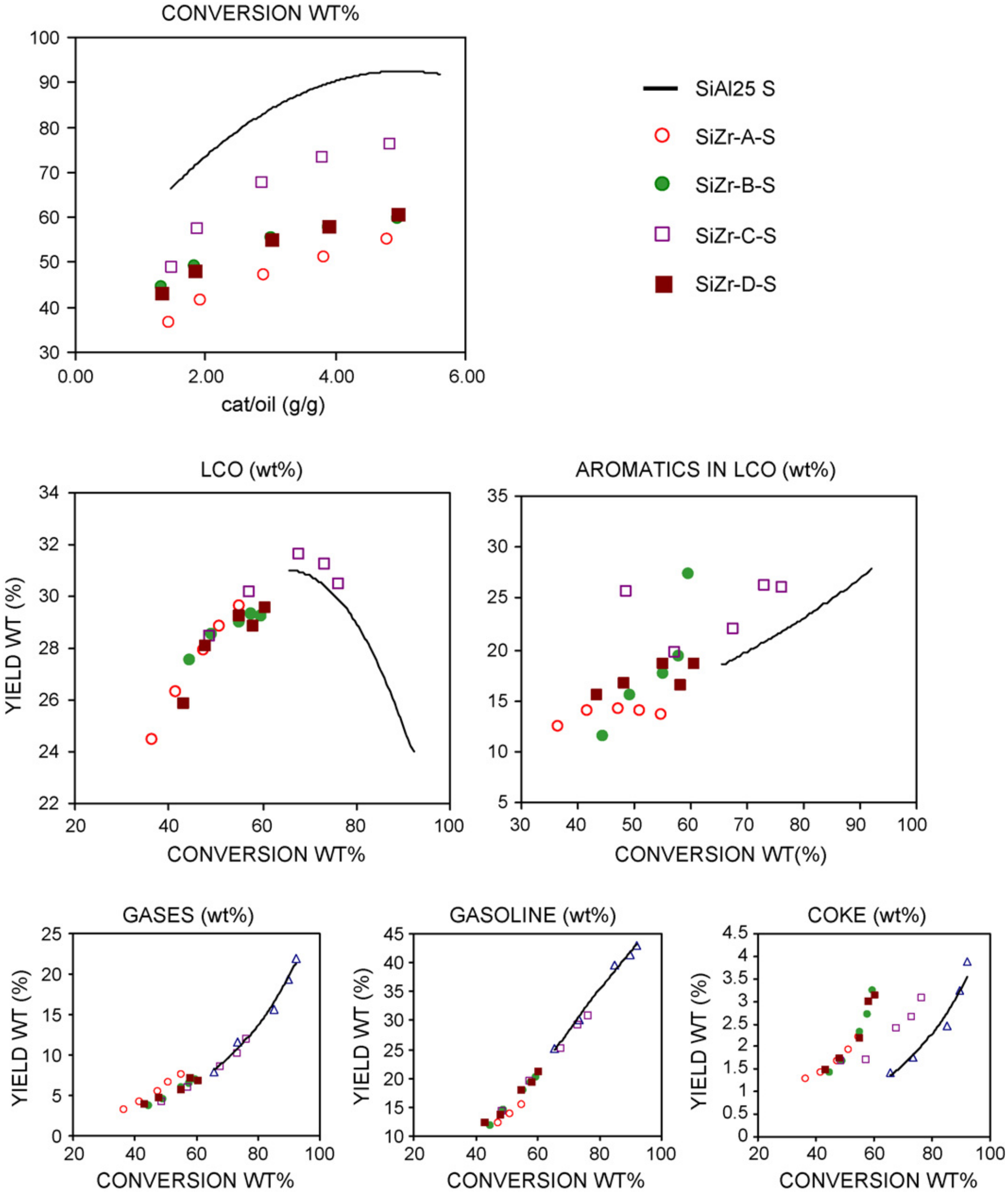

Fig. 8. Activity, overall selectivity and total aromatics in LCO (wt.%) of different SiZr materials compared to that of a reference SiO_2–Al_2O_3 for catalytic cracking of a VGO in a MAT unit. Steamed samples, $T = 520$ °C, TOS = 30 s.

After hydrotreatment, SiZr-C is still the most active of this type of materials (Fig. 8), but its activity is considerably lower than that of the steamed SiO_2–Al_2O_3, and the benefits in LCO selectivity are lost. This can be due to the loss of total surface area, or to the total loss of the microporosity. Moreover, high coke selectivities are obtained due to the almost constant coke yield combined with the lower conversions. Only sample C is able to convert the VGO above 60%, and at this higher conversion range, the aromatic content in LCO as compared to the base case (SiO_2–Al_2O_3) is increased.

In conclusion, it appears that none of the SiZr samples prepared presents any advantage over the conventional amorphous silica–alumina, at least after the samples are steamed.

3.2.2.2. Al-sepiolite (SEPAL), amorphous Si–Al–Mg and amorphous SAPO based materials. Fig. 9 shows that none of the new materials compared, be SEPAL, amorphous Si–Al–Mg or ASAPOs, is able to improve the conversion obtained with the reference SiO_2–Al_2O_3, when the samples are tested fresh in the catalytic cracking of a VGO. Still, activity obtained with the Si–Al–Mg is only slightly lower than that of the base case. This ternary oxide is followed by sepiolite, and the ASAPOs are the less active, especially sample ASAPO-2. In the former section, we saw that the composition of the ASAPO materials has a great influence on their textural properties, and the results presented in Fig. 9 indicate that this also has an effect on the catalytic behavior. Thus, ASAPO-1, with the highest Si content and the highest surface area is more active and more

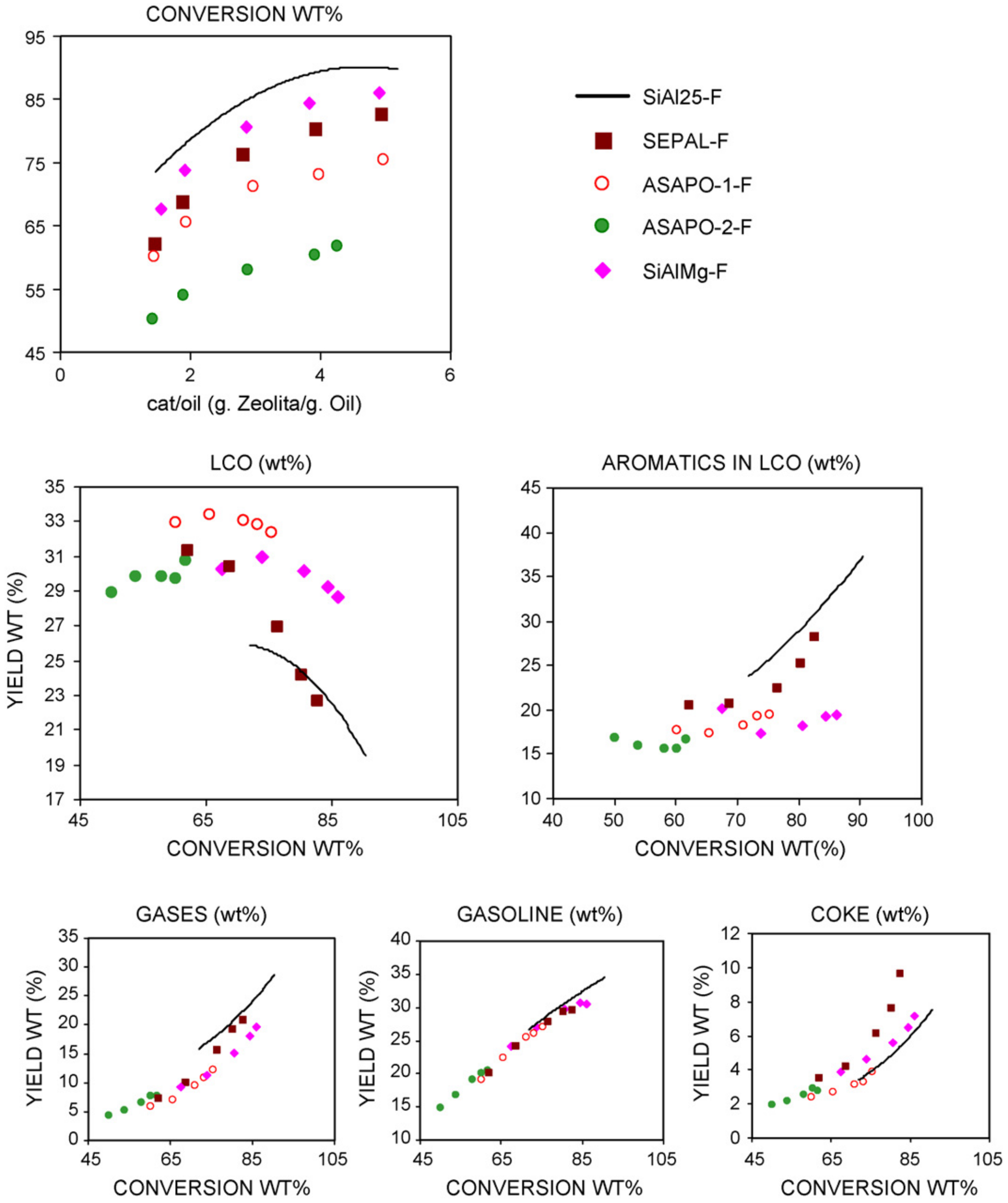

Fig. 9. Activity, overall selectivity and total aromatics in LCO (wt.%) of SEPAL, amorphous SAPO and Si–Al–Mg materials compared to that of a reference SiO_2–Al_2O_3 for catalytic cracking of a VGO in a MAT unit. Fresh samples, $T = 520\,^{\circ}C$, TOS = 30 s.

Table 6
SEPAL, amorphous Si–Al–Mg and amorphous SAPO materials compared with SiO_2–Al_2O_3: individual gases yields obtained in a MAT unit compared at constant total conversion of 70 wt.% for fresh samples and at constant total conversion of 60 wt.% for steamed samples

	Catalyst								
	SiAl25-F	SEPAL-F	ASAPO1-F	ASAPO2-F	SiAlMg-F	SiAl25-V	SEPAL-V	ASAPO1-V	ASAPO2-V
Conversion	70	70	70	70	70	60	60	60	60
Cat/oil	1.36	2.02	2.76	6.21	1.70	1.14	2.01	5.08	5.14
Hydrogen	0.08	0.12	0.13	0.15	0.07	0.02	0.06	0.10	0.14
Dry gas (C1 + C2)	1.69	1.68	2.16	2.23	1.46	0.86	1.13	2.04	2.65
LPG	12.97	9.24	6.87	5.74	8.62	4.31	3.86	4.12	5.69
Propylene/propane	2.77	4.61	3.17	3.19	5.47	5.08	3.34	1.98	2.26
Butene/butane	1.14	2.25	5.85	7.05	2.85	2.08	4.73	4.36	5.14
Isobutene/isobutane	0.46	1.10	5.75	6.32	1.40	0.87	3.45	7.61	7.92

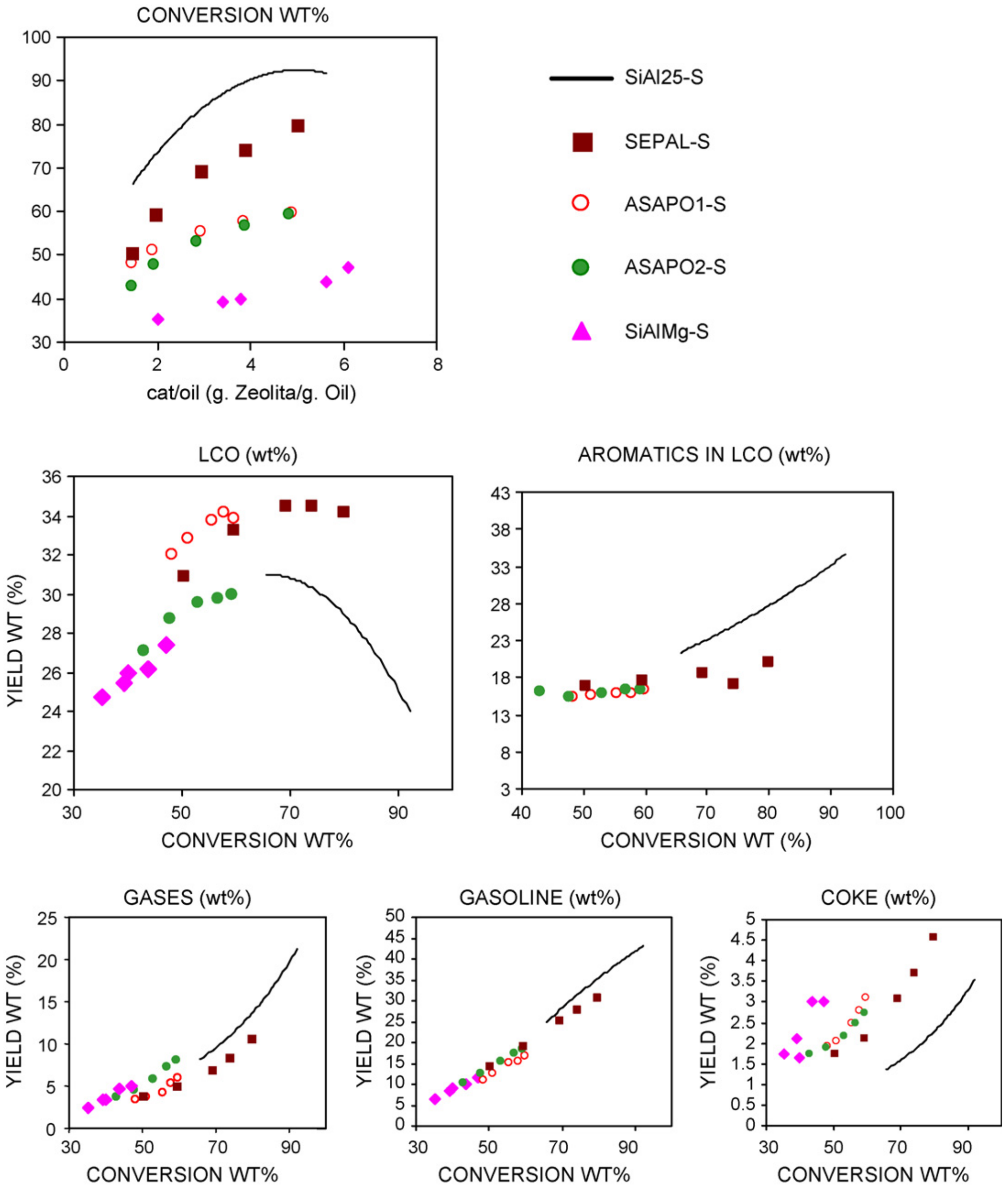

Fig. 10. Activity, overall selectivity and total aromatics in LCO (wt.%) of SEPAL, amorphous SAPO and Si–Al–Mg materials compared to that of a reference SiO_2–Al_2O_3 for catalytic cracking of a VGO in a MAT unit. Steamed samples, $T = 520$ °C, TOS = 30 s.

selective to LCO than ASAPO-2. All these materials are more selective to LCO than the reference SiO_2–Al_2O_3, and less selective to gases and gasoline, but only with ASAPO-1 there is no coke penalty. The highest coke make is obtained for the Al-exchanged sepiolite. Within the gases (Table 6), dry gases are slightly increased as compared to the reference for the amorphous SAPO materials, but on the other hand the olefins/paraffins (O/P) ratios in LPG are increased significantly in all cases. Sepiolite and Si–Al–Mg give the highest propylene/propane ratios, whereas the ASAPOs present the highest O/P ratios in the C4 fraction. Concerning the LCO aromatic content, Fig. 9 shows that the three types of new materials studied here reduce the concentration of aromatics in the LCO fraction as compared to the amorphous silica–alumina. Thus, they are promising alternatives as FCC catalyst matrices, as they are able to increase the LCO yield, while improving its quality. In these cases, the lower hydrogen transfer capacity of the ASAPOs as compared to SiO_2–Al_2O_3 can be related to the lower formation or aromatics in the LCO fraction, result that agrees with those obtained at different TOS in the previous section.

Among all these materials, only sepiolite presents an acceptable activity after hydrothermal treatment (Fig. 10), despite the fact that the ASAPOs maintained a considerable surface area, higher than that of the SEPAL. Still, a maximum activity of 60 is obtained with the amorphous SAPO at the highest CTO of 5 g/g, and the Si–Al–Mg sample is the less stable hydrothermally, with a drastic reduction in its surface

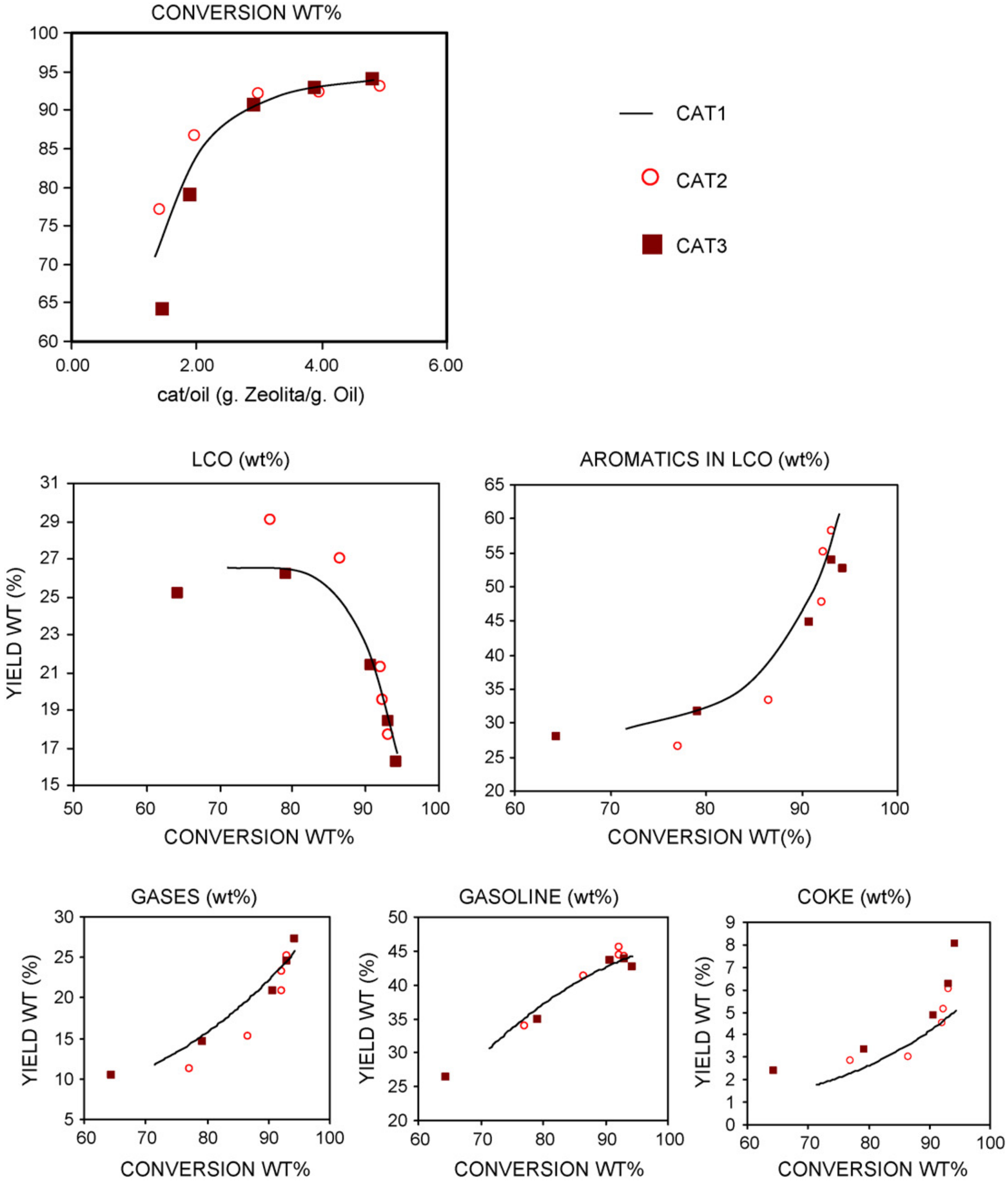

Fig. 11. Activity, overall selectivity and total aromatics in LCO (wt.%) of ASAPO1 (CAT2) and SEPAL (CAT3) as matrices in simulated FCC catalyst formulations compared to that of a reference SiO_2–Al_2O_3 (CAT1) as matrix, for catalytic cracking of a VGO in a MAT unit. Steamed samples, $T = 520\ ^\circ C$, TOS = 30 s.

area (from 387 to 66 m^2/g) and conversions below 50 wt.% in the CTO range studied. Due to the low activity this sample will not be considered in the following discussion.

Comparing the selectivity obtained with the two ASAPOs it can be seen that despite their similar activity, ASAPO1 is much more selective to LCO, with diesel yields comparable to those obtained by the SEPAL. The coke make is high for all the samples. The O/P ratios in the gases (isobutene/isobutane is the most representative ratio) indicate that the hydrogen transfer capacity of these samples is very low (Table 6). If we look into the total aromatic content in LCO (Fig. 10), we can see that the lowest concentrations are obtained with the ASAPO materials, although a considerable reduction is already obtained with the SEPAL. Thus both, SEPAL and ASAPO1 would be interesting candidates for being part of an FCC catalyst formulation.

Therefore, a commercial formulation was simulated with these two materials, ASAPO1 and SEPAL (CAT2 and CAT3, respectively), as matrices, and compared with a catalyst containing a P impregnated SiO_2–Al_2O_3 as reference (CAT1). The matrix (50 wt.%) was mechanically mixed with a USY zeolite (CBV-500 from Zeolyst International, UCS = 2.2450 nm, 25 wt.%), kaolin (20 wt.%) and silica (5 wt.%) and the final mixture was steam treated at 750 °C, 5 h, 100% steam. Results are given in Fig. 11, and it can be seen that CAT2 with an ASAPO matrix gives very interesting results, being more active than the reference CAT1, more selective to LCO and gasoline, less to gases, and with no coke penalty. Differences in LPG olefinicity are not big, but higher olefin/paraffin ratios are obtained with the ASAPO based catalyst. Concerning the LCO aromaticity (Fig. 11), CAT2 gives lower content of total aromatics. However, the sepiolite based catalyst, is also able to decrease the aromatics content in the LCO at the highest CTO ratios. Up to this point, all the discussion has been focused on the LCO yields and quality. Still, gasoline is the other main product, and it would be interesting to see how these new matrix materials affect the gasoline composition. This is shown in Table 7, where the PIONA results are enclosed. It can be seen that the ASAPO based catalyst also decreases the aromaticity of the gasoline fraction, but at the same time the proportion of isoparaffins is increased, compensating in this way most of the octane loss. CAT3, based on the SEPAL, improves gasoline quality as compared to the base CAT1, and both, CAT2 and CAT3 present gasoline selectivities close or even higher than the reference case. It is possible that a combination of ASAPO and SEPAL would be able to combine their benefits, yielding more LCO with lower aromaticity, with no penalty on gasoline yield or its quality.

Table 7
PIONA analysis and detailed composition of the gasoline fraction obtained obtained in a MAT unit with ASAPO1 (CAT2) and SEPAL (CAT3) as matrices in simulated FCC catalyst formulations compared to that of a reference SiO_2–Al_2O_3 (CAT1) as matrix

Experiment	CAT1	CAT2	CAT3
Conversion	75	75	75
Cat/oil	1.56	1.30	1.75
Aromatics	49.67	43.61	51.98
i-Paraffins	26.24	29.59	26.16
Naphthenes	12.39	15.00	11.93
Olefins	8.26	7.96	6.76
n-Paraffins	3.45	3.84	3.18
RON	82.07	81.74	82.37
MON	78.83	78.05	79.22

Steamed samples, T = 520 °C, TOS = 30 s.

4. Conclusions

We have shown that the use of a fixed bed cracking unit is not convenient when exploring FCC catalysts for maximizing diesel (LCO) and minimizing aromatics in LCO. However, a microdowner unit can give more meaningful results.

The comparative study of the cracking behavior of a series of materials including SiZr, Si–Al–Mg, amorphous silicoaluminophosphate, aluminum substituted sepiolites (SEPAL) and a high Al_2O_3 content amorphous silica–alumina has been carried out. We have found that optimized amorphous silicoaluminophosphate and Al-sepiolites can be interesting matrices (or even catalysts) for maximizing LCO and diminishing the aromatics content in this fraction.

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