

1. INTRODUCTION

In order to contribute to environmental protection, several countries seek to strengthen the legislation on the composition of transportation fuels. Among the most important changes, the increasingly lower amount of sulfur admitted in gasoline and diesel fuels is probably the most demanding issue for refineries (Marcilly, 2003). Sulfur is related to soot production in diesel fuels and is also a poison for catalytic converters, while its emissions contribute to acid rain.

Concerning gasoline, the catalytic cracking of hydrocarbons (FCC) is the process which contributes the highest amounts of sulfur to the pool through its products, up to approximately 90 % of the total (Can *et al.* 2007). FCC is in turn one of the most important conversion process in refining. Then, a number of different approaches which can be applied prior to, during, or after the FCC process have been tried in order to control the amount of sulfur in gasoline. The hydroprocessing of the FCC feeds, which usually include mercaptanes, sulfides, thiophenes, benzo or multiring thiophenes and oxidic sulfur as the sulfur impurities, is very effective, impacting on all the FCC products (Jaimes *et al.* 2008). Hydrotreating the FCC gasoline implies dealing with smaller process loads, but olefins in gasoline and aromatics can be hydrogenated to some extent, thus affecting octanes negatively. Finally, the heaviest fraction in gasoline, where most of the sulfur is present, could be removed and added to the diesel fraction; actually this means that the problem is placed into another fuel product and a loss in gasoline yield is produced. It is clear that the hydro options require extra capacity and hydrogen supply, thus becoming bottlenecks in the refinery operation. Reviews analyzing this problem have been published in the literature (Jaimes *et al.* 2008, Siddiqui *et al.* 2007).

The removal of sulfur-containing hydrocarbons during the FCC process can be achieved by means of catalyst additives (Can *et al.* 2007, Hernandez-Beltran *et al.* 2001, Siddiqui *et al.* 2006). Catalyst manufacturers offer a number of them (Wormsbecher *et al.* 1996, Albemarle 2011), which are usually based on Lewis acid materials highly dispersed on proper supports such as alumina. Zn, Ga and B oxides, or their mixtures, could perform as sulfur control additives. The catalytic mechanism could be based on the fact that sulfur-containing hydrocarbons behave as Lewis bases and would adsorb and/or react on the active sites of the additive. In the first case (adsorption), adsorbed sulfur compounds can be released oxidized in the regeneration section; in the second, (adsorption and reaction) the additive is supposed to crack them into H₂S, which can be removed with conventional technologies (Wormsbecher *et al.* 1996).

At least under certain conditions, the FCC catalysts can convert sulfur compounds in the gasoline range (e.g. thiophene, alkylthiophenes, benzothiophene), as shown by Corma *et al.* (2001) and Valla *et al.* (2006), who

also postulated simple kinetic models derived from experiments in fixed bed reactors. Alkylthiophenes may isomerize, dealkylate, and be subjected to cyclization. Moreover, before cracking, alkylthiophenes would accept hydrogen and saturate (Corma *et al.* 2001). Thiophene is less active, yielding H₂S and ending as part of coke deposits (Valla *et al.* 2006). Contaminant metals which are always present in equilibrium FCC catalysts, such as nickel and vanadium, have shown a positive effect on the reduction of sulfur compounds in gasoline (Lappas *et al.* 2004, Myrstad *et al.* 2000).

In order to develop a better control of sulfur in FCC products by means of catalyst additives, it is necessary to better understand the behavior of different types of sulfur compounds under the conditions of the process. It is the objective of this work to report the results of experiments that contacted various sulfur compounds in the gasoline boiling range, at low concentrations typical of the process, with different types of equilibrium commercial FCC catalysts under process conditions in a CREC Riser Simulator laboratory reactor. The sulfur compounds were injected dissolved into solvents which represent different hydrocarbon environments.

2. MATERIAL AND METHODS

The catalysts employed were two equilibrium commercial FCC catalysts, whose properties are presented in Table 1. The catalysts, named E-cat L and E-cat R, were selected based on their differences in hydrogen transfer properties and metal content, since these parameters are expected to have a strong influence on their behavior in relation to sulfur compounds in the gasoline boiling range (Can *et al.* 2007, Hernandez-Beltran *et al.* 2001, Valla *et al.* 2006, Lappas *et al.* 2004, Myrstad *et al.* 2000). The acidity of the catalysts was determined by FTIR of pyridine adsorbed on self-supporting wafers pressed with KBr (8-10 mg/cm²). Analyses were performed in a JASCO 5300 FTIR in a thermostated cell with CaF₂ windows connected to a vacuum line. Pyridine (3 Torr) was adsorbed at room temperature and desorbed at 10⁻⁴ Torr for 1 h at different temperatures, 250, 350 and 400 °C, thus defining weak, medium and strong acidity. The numbers of Brönsted and Lewis acid sites were calculated from the maximum intensity of the adsorption bands at 1545 cm⁻¹ and 1450–1460 cm⁻¹, respectively, and quantified using the literature data of the integrated molar extinction coefficients (Emeis, 1993), which are independent of the catalysts or strength of the sites.

The sulfur compounds used in the experiments were thiophene (99 %) and alkylthiophene compounds: 2-methyl (98 %), 2-ethyl (97 %), and 2-propylthiophene (97 %). They were all purchased from Sigma-Aldrich. The sulfur species were dissolved into two solvents, n-decane and a commercial mixture of C8 aromatics, in order to generate paraffinic and aromatic hydrocarbon reaction

environments, respectively. The two solutions prepared, with individual concentrations of the sulfur compounds in the range of 150 to 400 ppm, are reported in Table 2. Both solutions were injected on E-cat R, and the paraffinic solution only on E-cat L. Some additional experiments were performed on E-cat R, with only 2-propylthiophene dissolved into n-decane (132 ppm).

Table 1. Catalyst properties.

Property	E-cat L	E-cat R
Specific surface area (m ² /g) ^a	153	178
Zeolite content ^b	18.9	18.1
Unit cell size (nm) ^c	2.424	2.426
Rare earth oxides (%)	0.64	2.50
Fe ₂ O ₃ (%)	0.81	0.66
Ni (ppm)	3250	1100
V (ppm)	175	920
Acidity (μmol pyridine/g)		
Lewis	3.8	10.3
Brönsted	8.5	13.9
Weak Lewis / Lewis	0.09	0.87
Weak Brönsted / Brönsted	0.56	0.97

Table 2. Concentrations of the sulfur compounds in the solutions (ppm).

Compound	Solvent	
	n-Decane	C8 aromatics
Thiophene	396	364
2-Methylthiophene	315	267
2-Ethylthiophene	278	283
2-Propylthiophene	212	143
Total	1201	1057

The experiments were conducted in a batch fluidized bed laboratory reactor, the CREC Riser Simulator (de Lasa, 1992). The unit was equipped with a turbine on top of a chamber that held the catalyst bed between porous metal

^a BET method with N₂ adsorption.

^b Johnson's method with N₂ adsorption (Johnson, 1978).

^c ASTM D-3942-85.

plates. The turbine rotated at 7500 rpm, thus inducing a low pressure area in the upper central zone in the reactor that made gases recirculate in an upward direction through the chamber, thus fluidizing the catalyst bed. When the reactor was at the desired experimental conditions, the reactant was fed with a syringe through an injection port and vaporized instantly, thus setting the initial time. After the desired reaction time was reached, the gaseous mixture was evacuated immediately and products could be sent to analysis. Additional descriptive details can be found in, e.g., the papers by Passamonti *et al.* (2004) and Al-Khattaf (2007). Experiments were conducted at 510 °C, with a mass of catalyst of 0.8 g and injections of 0.1 mL of the n-decane solution and 0.085 mL of the C8 aromatics solution. Reaction times ranged from 5 to 20 s. Mass balances closed to more than 94 % in all cases. The amount of coke on the catalyst particles was assessed by burning off the coke deposits and further converting the carbon oxides into methane, which was quantified by a FID detector.

The analysis of the reactor effluents was performed on-line using an Agilent Technologies 6890 Plus gas chromatograph equipped with two detectors (FID for hydrocarbons and PFPD for sulfur compounds) operating simultaneously. The column used was a HP-1, 30 m length, 0.25 mm i.d., 0.25 µm phase thickness, with a splitter at the column end that produced two approximately equal-size samples. Product identifications were performed with the help of injections of the pure compounds. The simultaneous and combined use of FID and PFPD detectors improved the analysis of liquid fuels, since the sulfur analysis could be added to the standard hydrocarbon analysis (e.g. composition, simulated distillation) and the FID chromatographic areas could be used as a parameter for normalization to enhance the quality of sulfur analysis (Del Rio *et al.* 2011).

3. RESULTS AND DISCUSSION

In order to observe the possible different interactions between sulfur compounds and hydrocarbons in the gasoline boiling range, two solutions of sulfur compounds were prepared with solvents that were chosen to represent different hydrocarbon environments: paraffinic (n-decane) and aromatic (C8 aromatics). The total sulfur and particular concentrations used were in the usual process ranges (Ng *et al.* 2004). The equilibrium catalysts used represented different types of commercial catalysts, most significant differences between them being the contents of contaminant metals and the hydrogen transfer characteristics. These two are important issues concerning the observed yields of sulfur compounds in the gasoline boiling range, but the true impact of these factors is still controversial (Can *et al.* 2007, Hernandez-Beltran *et al.* 2001, Valla *et al.* 2006, Lappas *et al.* 2004, Myrstad *et al.* 2000, Pang *et al.* 2007).

The changes of the total sulfur concentration in the different reaction media as a function of contact time at 510 °C are shown in Figure 1 for both solutions on catalyst E-cat R, and for the paraffinic solution on catalyst E-cat L. It can be seen that the total amount of sulfur in the gas phase, relative to the amount injected initially to the reactor, decreased strongly as a function of contact time over both catalysts. The fact that sulfur compounds other than those in the feed were not observed in the gas phase is a clear indication that, overall, sulfur is either adsorbed on the catalyst surface or incorporated in coke deposits. The rate of change of the concentration of sulfur resulted independent of the chemical environment of the gas phase, as can be deduced from the results in the experiments with each solution, paraffinic and aromatic, at different reaction times on catalyst E-cat R, which were very similar. More than 35 % of the sulfur fed was removed from the gas phase at the longest contact time on catalyst E-cat R (20 s). However, the rate was different according to the catalyst; it can be seen in the experiments with n-decane solution over both catalysts that E-cat L exhibited a faster and more significant change, decreasing the initial amount of sulfur after 20 s contact time in about 60 %.

Commercial FCC catalysts were shown to be able to convert sulfur compounds present in VGO feedstocks, catalysts with low hydrogen transfer capacity yielding more sulfur compounds in gasoline (Gatte *et al.* 1992). However, the conditions favoring this catalytic action, and the final consequences, are still controversial; on the one hand Hernandez *et al.* (2001) suggested that the sulfur content in cracked naphtha greatly depends on the hydrogen transfer activity and on the effect of contaminant metals in the catalyst. On the other hand, Myrstad *et al.* (2000) suggested that naphtha sulfur decreases with the increase in the vanadium content, as expected from considering that the dehydrogenating action by metals leads to coke deposition, rather than associating it with the hydrogen transfer activity. The ability in different acidic catalysts to desulfurate gasoline has been reviewed by Jaimes *et al.* (2008), where even processes for selective gasoline desulfurization are described or proposed; however, temperature should not be high in order to avoid extensive hydrocarbon cracking.

In order to assess the hydrogen transfer ability of each of the catalysts under reaction conditions, the index derived from the relationship between isopentane and isoamylenes, in analogy to various other indexes (Mavrovouniotis *et al.* 1994, Cheng *et al.* 1992), can be used. The experiments performed with the n-decane solution were used, and the isopentane/isoamylenes yield relationships are shown in Figure 2 as a function of n-decane conversion. It can be seen that catalyst E-cat L showed higher hydrogen transfer capacity than catalyst E-cat R in the whole conversion range.

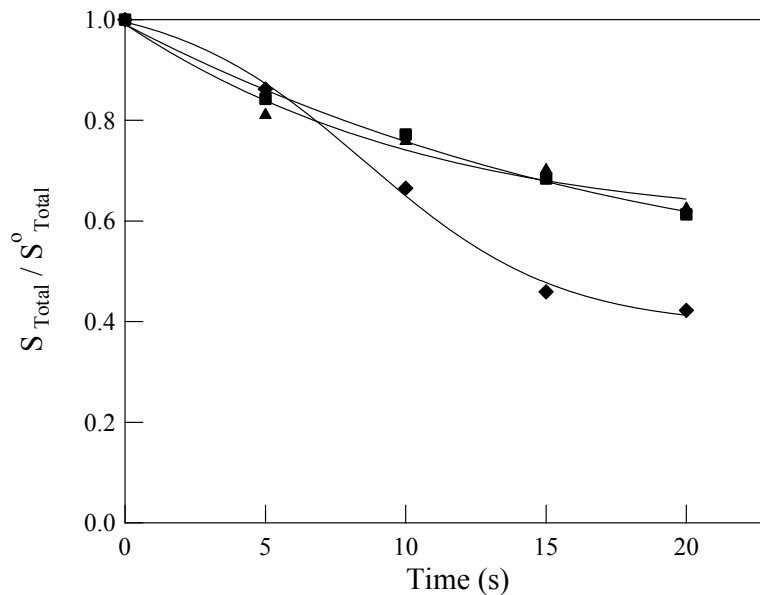


Figure 1. Total sulfur concentration, relative to the initial, as a function of contact time. Symbols: (■) n-decane solution, E-cat R; (◆) n-decane solution, E-cat L; (▲) aromatic solution, E-cat R.

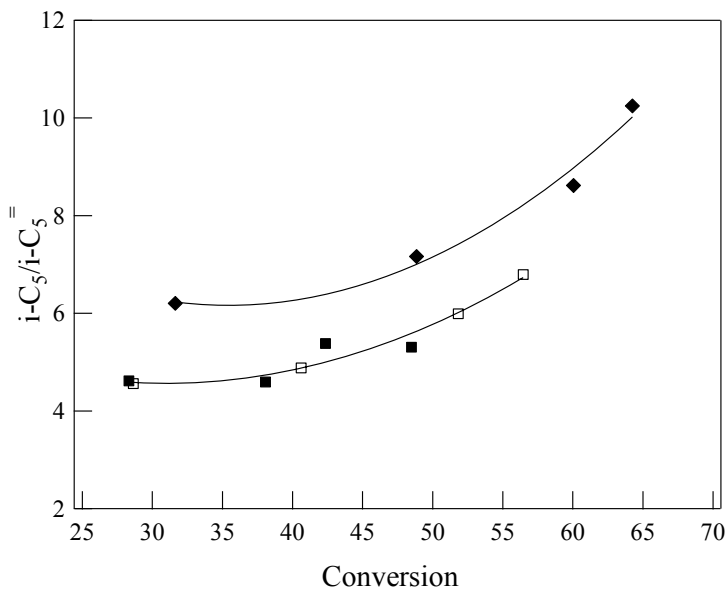


Figure 2. Relationship between the yields of isopentane and isoamylenes as a function of conversion in the experiments with n-decane solutions. Symbols: (◆) Mixture of sulfur compounds, E-Cat L; (□) 2-propylthiophene, E-Cat R; (■) Mixture of sulfur compounds, E-Cat R.

Coke deposits in the experiments performed with the paraffinic solution over both catalysts are shown in Figure 3, where it can be seen that in the case of catalyst E-cat R the values were similar in the range of contact times used, averaging a yield of 3.57 %, while in the case of catalyst E-cat L, coke yields were higher and showed a profile slightly increasing as a function of time. These profiles are in accordance with the higher hydrogen transfer ability in catalyst E-cat L and indicate a higher activity (also confirmed by acidity characterization, as shown below).

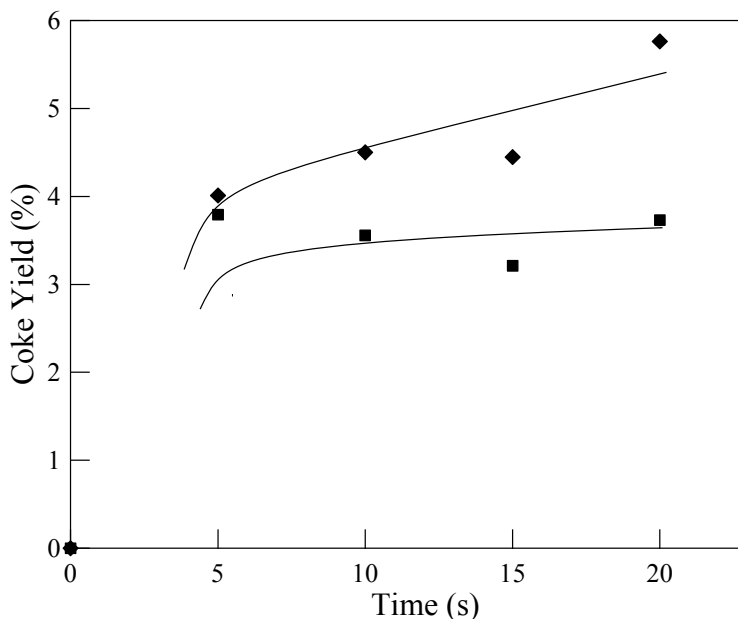


Figure 3. Coke yield as a function of contact time in the experiments with n-decane solutions. Symbols: (■) E-cat R; (◆) E-cat L.

The correlation between the hydrogen transfer properties of the catalysts and the amount of sulfur compounds removed from the gas phase (see Figure 1), together with the differences in coke yields (see Figure 3), is consistent with the view of Hernandez *et al.* (2001), who suggested that the catalysts with high hydrogen transfer capability would produce higher conversion of sulfur compounds and increase the coke formation.

Another important factor in this catalytic system is the content of contaminant Ni and V metals. It has been reported that metals contribute to decrease the amount of sulfur in FCC naphtha by catalyzing a number of reactions such as polymerization, condensation and ciclyzation (Lappas *et al.* 2004, Myrstad *et al.* 2000). Nevertheless, nickel and vanadium may have opposite effects on the amount of sulfur compounds in gasoline. Vanadium interacts with the Y zeolite in the catalyst and destroys its framework (Gallezot *et al.* 1989,

Nielsen *et al.* 1993); in this way, higher vanadium loads would decrease the catalyst hydrogen transfer ability and consequently lead to increase the amount of sulfur in naphtha (Hernandez *et al.* 2001). However, the effect of high vanadium loads observed by Myrstad *et al.* (2000) using fresh FCC catalysts doped with vanadium and nickel was the opposite and, concerning nickel, which is a strong hydrocarbon hydrogenating-dehydrogenating agent, their view was that it would contribute with additional hydrogen to diminish the concentration of sulfur compounds in gasoline by means of their hydrogenation and subsequent cracking. On the other hand, Lappas *et al.* (2004) showed that contaminant metals present in FCC catalyst may catalyze some reactions of sulfur compounds, vanadium being more effective than nickel for gasoline sulfur reduction when present at its highest oxidation state. Those results were obtained from the comparison of catalysts deactivated in a cyclic deactivation unit with different contents of both metals at different cat/oil ratios, using FCC gasoline as the feed in a SCT-MAT reactor.

The two equilibrium catalysts used can be considered as having low or intermediate overall contamination by metals, but it must be noticed that the amount of metals on the catalysts is significantly different (see Table 1). Catalyst E-cat L has three times more Ni than catalyst E-cat R, but E-cat R has five times more V than E-cat L. In this sense, catalyst E-Cat R, with a higher vanadium load, showed a lower decrease in the total sulfur concentration, as shown in Figure 1 for both types of experiments (paraffinic and aromatic solutions), which could lead to assign a negative effect to this metal on the ability to remove sulfur from the gas phase, given its impact on hydrogen transfer properties, as discussed above. However, it should be noted that in these equilibrium catalysts, both the zeolite contents (about 18 %) and the unit cell sizes (about 2.425 nm) are very similar. Thus, the properties derived from these parameters such as the amount of acid sites and, consequently, the hydrogen transfer ability resulting from the density of paired acid sites are expected to be similar (de la Puente and Sedran 2000).

The catalysts differ significantly in the content of rare earths. While it is expected that increasing amounts of rare earths will increase acidity and hydrogen transfer (Lemos *et al.* 1987), catalyst E-Cat R, with a much higher content of rare earths, indeed transferred less hydrogen than catalyst E-Cat L, as shown in Figure 2. It has to be considered that the content of rare earths in FCC catalysts may not be directly comparable, since the total amount which is reported typically does not show where the rare earths are loaded: in the zeolite, the matrix, or even the additives. Moreover, it was shown by Lemos *et al.* (1987) that rare earth ions may form OH bridges between them when the load is too high, leading to a decrease in the catalyst acidity, below that expected from the hydrolysis of the individual cations.

Catalyst E-Cat L is the one with higher nickel load and, taking into account that the dehydrogenating effect of this metal would favor coke formation, the higher loss of sulfur in the gas phase and the higher yield of coke observed with this catalyst are consistent (see Table 3 and Figures 1 and 3). Moreover, it is well known that Ni has a dehydrogenating action about four times that of V [25]. The fact that the equilibrium catalyst E-cat L, which has the highest load of contaminant Ni+V metals, showed the most significant decrease in sulfur concentration in the gas phase is in line with the observations by Valla *et al.* (2006), who reported that the effect by the contaminant metals was to convert sulfur compounds into coke deposits in their experiments with high Ni+V content in the catalysts (7130 ppm).

Table 3. Concentrations of the sulfur compounds relative to their initial concentration in the experiments with n-decane as a solvent, at 20 seconds contact time over both catalysts.

Compound	$S_{\text{total}}/S_{\text{total}}^0$	
	E-cat R	E-cat L
Thiophene	0.850	0.651
2-Methylthiophene	0.664	0.443
2-Ethylthiophene	0.438	0.274
2-Propylthiophene	0.321	0.174
Total	0.613	0.422

These overall observations were confirmed and new evidence was obtained from the analysis of the changes in the concentrations of each of the sulfur compounds. Figure 4 shows the individual time profiles for the case of the paraffinic solution over both catalysts, but it should be mentioned that the results from the aromatic solution on E-cat R were the same as those observed with the n-decane solution on the same catalyst. It can be seen that the higher the molecular weight of the alkylthiophenes, the faster the rate of change. In effect, the decrease in the relative concentration of each sulfur compound at each reaction time, as well as the total amount at the longest reaction time, led to follow the sequence thiophene < 2-methylthiophene < 2-ethylthiophene < 2-propylthiophene over both catalysts, as shown in Table 3. Consistent with the results shown in Figure 1, the faster changes over catalyst E-cat L are also apparent in the comparison of Figures 4.a and 4.b.

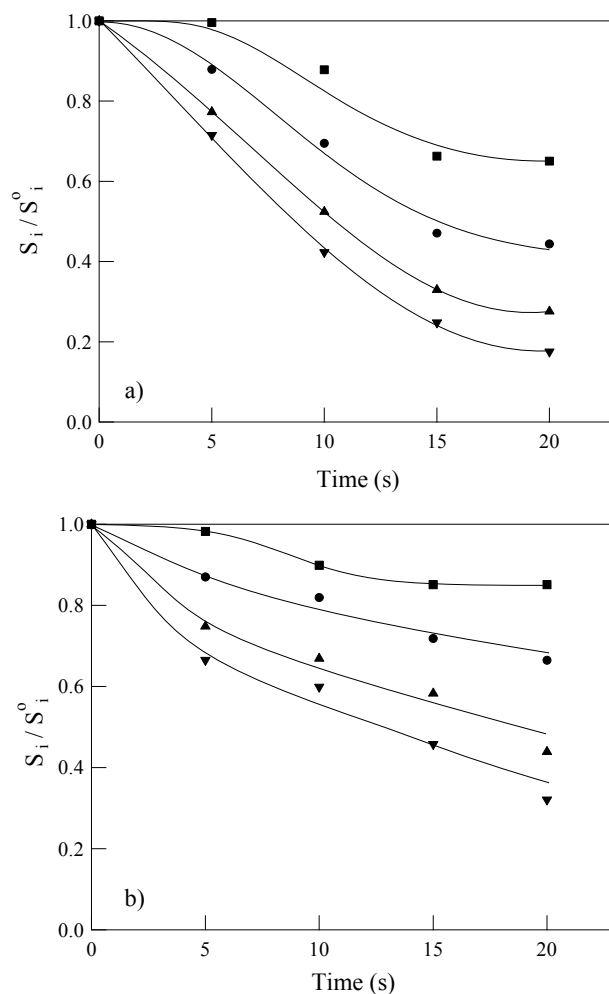


Figure 4. Concentrations of sulfur compounds, relative to the initial, as a function of contact time. Experiments with n-decane solutions. a) E-cat L, b) E-cat R. Symbols: (■) Thiophene; (●) Methylthiophene; (▲) Ethylthiophene; (▼) Propylthiophene.

It is interesting to see that the time profiles of thiophene over both catalysts showed a lower initial negative slope, indicating that this could be due to the contribution from the cracking of alkylthiophenes into thiophene, as suggested by Corma *et al.* (2001) among other authors. It should be noticed that the only sulfur species observed in the gas phase were those of the alkylthiophenes injected as reactants, thiophene and very small quantities of the corresponding isomers. For example, no saturated sulfur species, which were suggested as intermediates in the conversion of “aromatic” sulfur compounds (Corma *et al.* 2001, Valla *et al.* 2006, Lappas *et al.* 2004), could be observed. It must be pointed

out that it was not possible to verify the formation of C1-C3 hydrocarbons from the cracking of these alkylated sulfur compounds in the experiments of this work, due to both the very low concentrations used and the fact that when n-decane was the solvent it was also subjected to cracking reactions.

Concerning thiophene, the results reported in the literature depend on the experimental approach used. For example, Corma *et al.* (2001) reported high conversions of thiophene of about 60 %, with 40 % coke yield, but thiophene was used pure on a high unit cell size, fresh zeolite with high activity. Valla *et al.* (2006) reported that 1800 ppm of thiophene in hexadecane converted at about 25 % on a 2.440 nm unit cell size steamed zeolite, and at about 28 % on equilibrium catalyst (7130 ppm Ni+V), mainly to coke and H₂S. These two studies were performed in MAT fixed bed reactors. Dupain *et al.* (2003) found thiophene to be uncrackable under conditions close to those of the commercial process in a fluidized bed reactor. Gatte *et al.* (1992) observed thiophene conversions from a 5000 ppm solution in hexadecane to be lower than 13 % at 500 °C in a fixed bed reactor. Since the results in the experiments in this work were obtained with very low concentrations of each of the sulfur compounds and with very short effective contact time in a fluidized bed reactor, thiophene conversion, if any, is expected to be very low. Moreover, this could also be expected in riser units, because the conditions in the CREC Riser Simulator mimic those of commercial reactors.

In order to confirm some of the above inferences, the alkylthiophene with the highest molecular weight in these experiments, 2-propylthiophene, was diluted in n-decane and converted over catalyst E-cat R. The only sulfur species observed in the gas phase, besides the reactant 2-propylthiophene, were thiophene and a very small amount of the isomers of the alkylthiophene. This confirms that when put into contact with an equilibrium FCC catalyst, the alkylthiophenes would yield essentially only thiophene, while the rest of the sulfur hydrocarbon is adsorbed or forms coke. The results shown in Figure 5 clearly indicate that while the concentration of 2-propylthiophene in the gas phase decreased as long as reaction time increased, that of thiophene increased.

It was possible to estimate that about 40 % to 60% of the total amount of sulfur injected into the reactor was adsorbed or took part of the coke deposits on the catalyst surface, depending on the catalyst properties. For the type of sulfur compound considered (alkylthiophenes), this adsorption increased with the molecular weight, being as high as 83 % in the case of 2-propylthiophene over catalyst E-cat L. These amounts are similar to those reported by other authors (Corma *et al.* 2001, Valla *et al.* 2006). The conversion of alkylthiophenes into thiophene over acidic catalysts was also reported by Shan *et al.* (2002), who found that it increased with the length of the substituting alkyl chain. But they observed an increase in the amount of thiophene after catalytic desulfurization at 410°C over a USY-ZnO/Al₂O₃ catalyst, and explained such a change considering

that alkyl-substituted thiophenes in the gasoline cut can produce mainly thiophene via dealkylation.

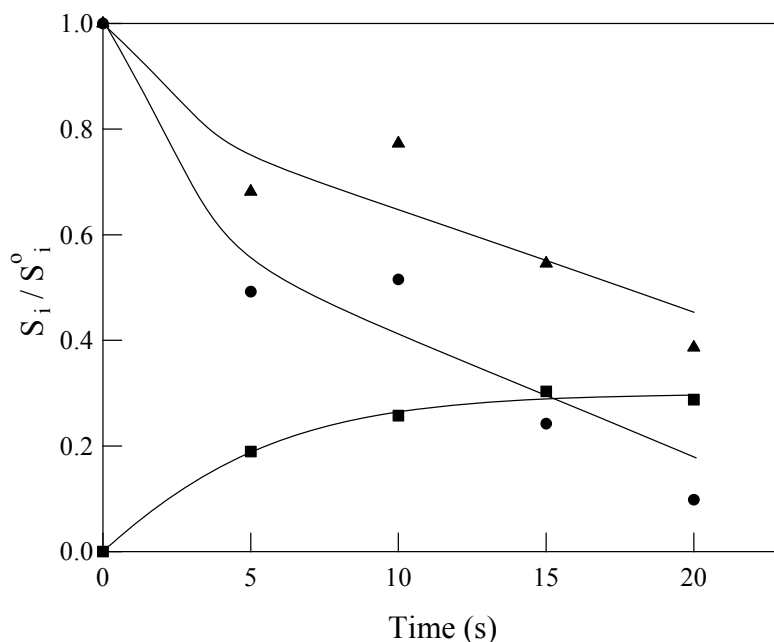


Figure 5. Concentrations of sulfur compounds, relative to the initial, as a function of contact time. Experiments with propylthiophene dissolved in n-decane. Symbols: (■) Thiophene, (●) Propylthiophene, (▲) Total sulfur.

It was shown by Pang et al. (2007) that the acidic properties of laboratory FCC catalyst have an important influence on the concentration of sulfur compounds in the gasoline boiling range. According to their experiments performed with thiophene on fixed and fixed fluidized reactors, weak Lewis sites would favor adsorption and conversion of thiophenic molecules. The subsidiary analysis of the acidic properties of the equilibrium commercial catalysts E-cat L and E-cat R (see Table 1) showed to be very different. In effect, the total amount of acid sites in catalyst E-cat R was higher than in catalyst E-cat L, but essentially all the sites in catalyst E-cat R were weak. The higher activity of catalyst E-cat L (as shown by coke yields, see Figure 3) then, can be explained based on its much higher proportion of strong Brønsted sites (Pang et al., 2007). The more significant reduction of sulfur compounds observed with catalyst E-cat L at the same contact time, however, can not be associated to the proportion of weak Lewis sites in the catalysts as deduced by Pang et al. (2007), though it must be noticed that other factors, such as contaminant metal content, have to be considered.

4. CONCLUSIONS

Sulfur compounds in the gasoline boiling range decreased their concentration in the gas phase as a function of the contact time when put in contact with equilibrium commercial FCC catalysts under process conditions. Thiophene and alkylthiophenes compounds showed a similar decreasing behavior, which is more significant with increasing molecular weights. Moreover, it was observed that alkylthiophenes can also be cracked into thiophene, thus making the variation of the concentration of this compound less pronounced; isomerization reactions were not important.

The comparison of the catalysts performance indicated that the hydrogen transfer properties impact on the reduction of the concentration of sulfur compounds in the gas phase. The higher the catalyst hydrogen transfer ability, the higher the decrease, either by adsorption or by incorporation into the carbonaceous deposits on the catalyst. In this sense, the contaminant metal content is an important factor, because nickel, with the highest dehydrogenating ability among contaminant metals, would contribute to reduce the concentration of sulfur products by increasing coke formation with incorporation of sulfur species. This evidence suggests that the contaminant metals, at least in the low to medium levels present in the equilibrium catalysts used, might have a positive effect in reducing the amount of sulfur in the gasoline boiling range.

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