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Coke and Product Profiles Formed Along the Catalyst Bed during *n*-Heptane Reforming

II. Influence of S on Pt/Al_2O_3 and Pt–Re/Al_2O_3

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Studies of coke and product profiles along catalyst beds of Pt/Al_2O_3 and Pt–Re/Al_2O_3 during *n*-heptane reforming have provided insight into catalyst deactivation and reaction mechanisms. The addition of rhenium to a Pt catalyst changes coke and product profiles similar to those observed with an increase in pressure. Sulfur modifies these profiles in the opposite direction of rhenium. It affects the catalyst in a similar manner to a decrease in reactor pressure: a reduction in hydrogenolysis activity, an increase in dehydrogenation and coke-make, and a shift of the maximum in the coke profile toward the bottom of the reactor. Due to a slow stripping of sulfur during reforming reactions, an increasing sulfur concentration along the bed is observed at the end of several-days run. As a consequence, the coke profile does not match exactly with the C5-ring naphthene concentration profile, as was previously found on both unsulfided Pt and Pt–Re catalysts. The observed increase in coke-make and dehydrogenation activity, when sulfur is added to the Pt–Re catalyst, is probably due to a decrease in the hydrogen surface fugacity produced through electronic modifications of Pt by adsorbed sulfur atoms. © 1996 Academic Press, Inc.

INTRODUCTION

The effect of sulfur upon activity, selectivity, and stability of reforming catalysts has been extensively investigated. One of the first papers reported in this area appeared in the literature in 1957 (1). Sulfur modification of catalyst selectivity becomes more important with the advent of bimetallic catalysts. Pt–Re catalysts are presulfided in commercial reformers in order to decrease the high hydrogenolysis activities of fresh catalysts (2). However, Pt–Re catalysts are more sensitive to S than Pt, and, therefore, feed sulfur concentration should be <1 ppm, to obtain stable operation with Pt–Re catalysts (3).

Sulfur also affects both coke-make and coke distribution between metal and support. The total amount of coke deposited on the catalyst is higher when the catalyst is presulfided (4, 5). The role of S has been shown to selectively decrease the hydrogenation capacity of Pt–Re and the ensemble size, resulting in lower cracking and a higher amount of coke (6). However, its effect on the coke profile in a catalyst bed and catalyst stability are not clear.

Investigation of coke and product profiles along the catalyst bed has provided useful information regarding deactivation and reaction mechanisms (7, 8). In the present paper, changes of coke and product profiles along the catalyst bed for Pt and Pt–Re upon sulfidation were studied during *n*-heptane reforming. A multi-outlet reactor that allows analyses of product compositions along the bed (7) was used. Coke was characterized by a highly sensitive TPO technique (9).

EXPERIMENTAL

Activity Tests

The catalytic tests were carried out in a fixed-bed down flow stainless steel multi-outlet reactor. It has four outlet ports along its wall where gas-phase samples can be withdrawn. Numbers 1, 2, 3, and 4 will identify such outlets from the top to the bottom of the reactor. In a typical run, 20 g of catalyst are loaded above outlet 4 (exit of the reactor). At outlet 4 the weight hourly space velocity is 2 w/w/h. The amount of catalyst placed above outlet 1 is 3.7% of the total charge. Therefore, the space velocity at outlet 1 is 54 w/w/h. The catalyst mass placed above outlet 2 is 40% of the total charge. This corresponds to a space velocity of 5 w/w/h. Similarly, the space velocity at outlet 3 is 2.9, since there is 70% catalyst above outlet 3. The catalyst is discharged in discrete sections without mixing so that the coke content of each section can be analyzed. The amount of catalyst placed above outlet 1 is separated from the catalyst bed and is called section 1. The quantity of catalyst placed between outlets 1 and 2 is collected and is called section 2, and so on. Additional description of the reactor can be found elsewhere (7).

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After loading, the catalyst is reduced *in situ*, heating from room temperature to 515°C at 3°C/min, under 2000 cm^3/min of hydrogen. The catalyst is reduced at 515°C for 8 h, then the reactor temperature is lowered to 370°C in 3 h, before *n*-heptane is added to the reactor. Subsequently, the reactor temperature is increased over 3 h to the run temperature. On oil time is counted from the moment the reactor attained the pre-selected reaction temperature.

Typical reaction conditions were 499°C, 525 kPa, total hourly space velocity 2 w/w/h, and hydrogen/hydrocarbon ratio 3. No sulfur was added to the *n*-heptane during the run.

The average product concentration in each section is calculated as the mean concentration between its inlet and outlet and is expressed as a weight percent in the hydrocarbon mixture which is equivalent to the yield of the product.

Coke Analyses

Coke was characterized by a highly sensitive temperature-programmed oxidation technique, using a modified Altamira TP unit (Model AMI-1). The modified unit converts CO_2 produced during coke oxidation to CH_4, using a Ru catalyst. The CH_4 is then continuously monitored with a flame ionization detector. This improves both sensitivity and resolution when compared with a thermal conductivity detector (TCD), which also requires a GC column to separate CO_2 from oxygen. Details of the technique have been reported (9). TPO analyses are performed using 1% O_2/He flowing at 60 cm^3/min through the sample while increasing temperature at a rate of 13°C/min from room temperature to 770°C. Sample weight was generally 20 mg.

Coke content is reported as weight percent (g of coke per 100 g of catalyst). The percentage value of coke for each section is assumed to be representative of the coke content in the middle of that section.

Catalyst

The monometallic catalyst contains 0.6 wt% Pt and 0.9 wt% Cl on Al_2O_3. The bimetallic Pt–Re/Al_2O_3 contained 0.3 wt% Pt, 0.3 wt% Re, and 0.9 wt% Cl. Both catalysts display a BET specific surface area of 200 m^2/g. They were used in the form of 0.16 cm in diameter by 0.25 to 0.51 cm in length extrudate particles.

The above catalysts (100 g each), after a hydrogen reduction at 500°C, were presulfided separately in another reactor (not the multi-outlet reactor) at 455°C under 0.5 vol% of H_2S in hydrogen flowing at 1000 cm^3/min. The sulfiding process was continued until H_2S broke through as indicated by the darkening of the lead acetate paper at the reactor outlet. The sulfided catalyst was purged with hydrogen at 455°C for 2 h before it was cooled to room temperature and discharged. Sulfur content was 0.03 and 0.06 wt% for Pt and Pt–Re, respectively.

RESULTS

Product Profiles

Figure 1 shows the results obtained with Pt–S/Al_2O_3 and Pt–Re–S/Al_2O_3 catalysts. *n*-Heptane (nC7) conversion, toluene, and 2-methylhexane (2MH) concentration as a function of time in each of the four positions along the bed are plotted. Label 1 refers to analyses of the samples taken from outlet 1, above which 3.7% of the catalyst mass is located. The equivalent space velocity at this point is 54 w/w/h. In a similar manner, curves 2, 3, and 4 represent samples taken at 40, 70, and 100% of the catalyst bed, at a corresponding space velocity of 5, 2.9, and 2 w/w/h, respectively.

At a space velocity of 54 h^{-1} (outlet 1), more than 40% of the *n*-heptane is converted at the start of the run. As the reaction proceeds, conversion decreases with time-on-oil in all positions of the bed with both catalysts (Figs. 1A and 1D).

Pt–S and Pt–Re–S show that toluene increases along the bed and the toluene concentrations at the four outlets are initially the same. Toluene concentration at the outlet of the reactor (number 4) decreases from an initial 50 wt% to 17 and 25 wt% for Pt–S (Fig. 1B) and Pt–Re–S (Fig. 1E), respectively, after 215 h. Sulfided Pt deactivates faster than sulfided Pt–Re. Initially, both Pt–S and Pt–Re–S show that about 90 wt% of the toluene is produced in the top 70% of the catalyst bed. Utilization of the bottom 30% of the bed for toluene production is low because not many feed molecules (*n*-heptane and iso-heptanes) remain unconverted through the top 70% bed. The contribution of the bottom 30% of the bed to toluene production increases as both catalysts deactivate. At 200 h, this section produces 28% of the toluene on Pt and 19% on Pt–Re–S.

Concentration of 2MH as a function of time is shown in Figs. 1C and 1F for Pt–S and Pt–Re–S, respectively. Both catalysts display similar 2MH time-on-oil patterns. However, not the same pattern is obtained at the four outlets. Depending upon the position in the bed, 2MH composition versus time follows different behavior. In outlet 1, composition of 2MH decreases with time on oil. In outlet 2 it goes through a maximum, while in outlets 3 and 4 there is a continuous increase in the amount of 2MH.

Figure 2 shows the total C5 naphthene (all five-member ring naphthenes) concentration profiles. Similar patterns were found for Pt–S and Pt–Re–S at 525 kPa. At high space velocity (outlet 1) there is an initial fast decay in the concentration of these compounds followed by a reduced rate of decrease. At outlets 2, 3, and 4 significant increases in the naphthene concentrations with time-on-oil are observed leading to the existence of a maximum in the C5-ring naphthene concentration profile along the bed for the most part of the run except the initial 40–60 h.

At 1225 kPa, sulfided Pt–Re shows important changes in the C5 naphthene concentration profiles in comparison to

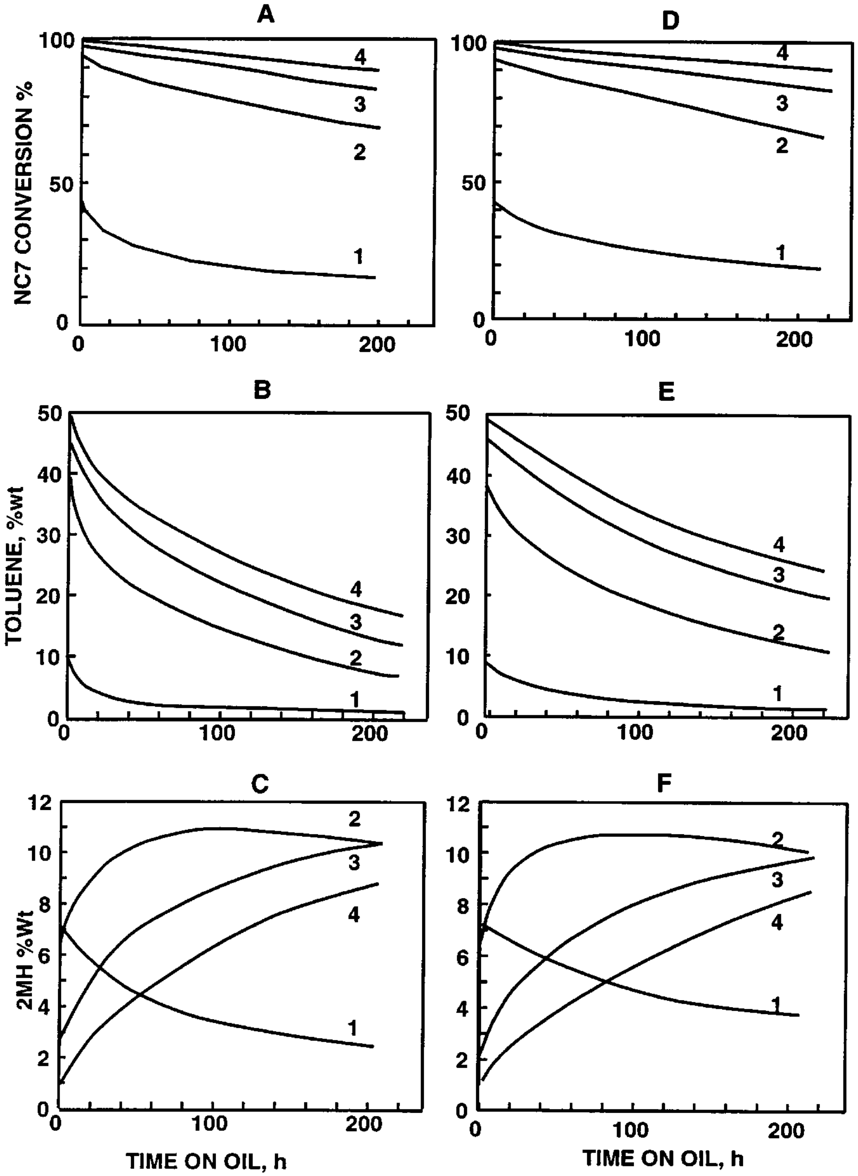

FIG. 1. Composition profiles for Pt–S, (A) nC7 conversion, (B) toluene, (C) 2MH, and for Pt–Re–S, (D) nC7 conversion, (E) toluene, (F) 2MH. Labels: 1, 3.7% bed; 2, 40.4% bed; 3, 70.7% bed; 4, 100% bed.

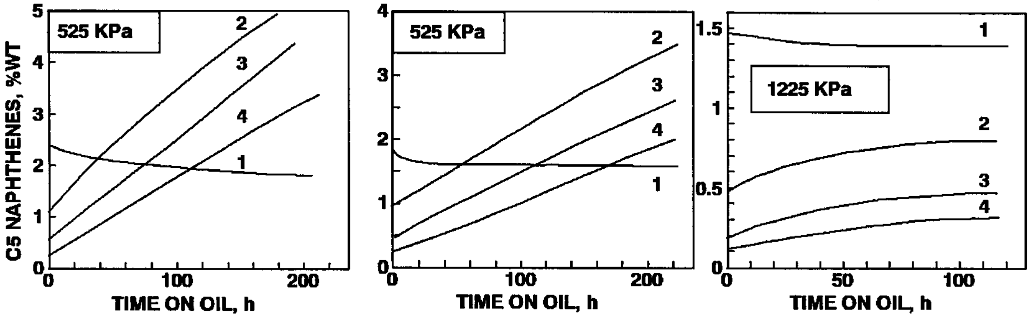

FIG. 2. C5 naphthene concentration profiles (MCP + ECP + DMCPs) for Pt–S, (A) and Pt–Re–S, (B) and (C). $T = 499°C$.

TABLE 1

C7 Olefin Production during *n*-Heptane Reforming

Time (h)	C7 olefin	Olefin concentration (wt%) catalyst			
		Pt	Pt–S	Pt–Re	Pt–Re–S
0	c3-heptene	0.654	—	0.436	0.787
	t2-heptene	0.708	0.912	0.573	0.869
50	c3-heptene	0.769	—	0.549	0.832
	t2-heptene	0.942	0.939	0.608	1.000
	Partial pressure ratio: olefins ∗ H_2/paraffin				
0	c3-heptene	0.045[a]		0.028[a]	0.053
	t2-heptene	0.052[a]	0.058	0.032[a]	0.059

Note. $P = 525$ kPa, $T = 499°C$, section 1.

[a] From Ref. (7).

those obtained at 525 kPa. C5 naphthene concentrations at all outlets are lower at 1225 kPa and C5 naphthene decreases from reactor inlet to outlet over the entire run. The increases in C5 naphthene concentrations with time-on-oil at outlets 2, 3, and 4 are much less than those observed at 525 kPa.

Table 1 shows C7 olefin composition, initially and at 50 h in outlet 1. Results for unsulfided and sulfided Pt and Pt–Re catalysts are shown. Pt–Re produces less olefins than Pt. In both catalysts, higher C7 olefin production is observed upon sulfidation. Sulfided Pt–Re produces a comparable amount of olefins to Pt–S. The concentration of C7 olefins increases as the catalysts deactivate but after 45–50 h no appreciable changes are observed. Even though initially Pt–S produces more olefins than Pt, after a few hours on oil both catalysts display similar *n*-heptane conversion to these products. In this table, the partial pressure ratio (olefin ∗ H_2/nC7) is included.

Hydrogen concentration profiles for Pt–S are shown in Fig. 3. Hydrogen weight percentage increases along the bed while hydrogen molar fraction has a maximum in outlet 2 at the beginning of the experiments, and after 120 h on oil, a decreasing profile is observed. Pt–Re–S has a very similar behavior to Pt–S regarding hydrogen concentration profiles (figure not shown).

Figures 4 and 5, respectively, show methane and total gas (C1 to C4) production with both sulfided and unsulfided Pt and Pt–Re catalysts. Sulfur strongly affects methane formation on Pt–Re and to a lesser degree the total gas production.

Coke Profiles

Figure 6 shows the coke profiles on Pt–S (Fig. 6A) and on Pt–Re–S (Fig. 6B) along the catalyst bed. The weight percentage of coke determined in each catalyst section represents an average value of coke in that catalyst section and corresponds to the coke level in the middle of the section. Pt–S shows a broad maximum in the amount of coke along the bed located somewhere between 10–30% of the bed depending on the run length. Pt–Re–S shows similar results but the maximum becomes more pronounced as time on oil increases, with a shift toward the bottom of the bed. An increase in the pressure does not produce any significant change in the profile, only a decrease in the amount of coke. A similar amount of coke is deposited on the Pt–S and Pt–Re–S catalysts.

Table 2 shows the weight percentage of coke on the reforming catalysts after 215 h on oil. More coke is deposited on sulfided Pt and Pt–Re than on unsulfided catalysts.

TPO Analyses

Figure 7 shows the TPO spectra of Pt–S and Pt–Re–S catalysts, at various times on oil, for sections 1 and 4. At a

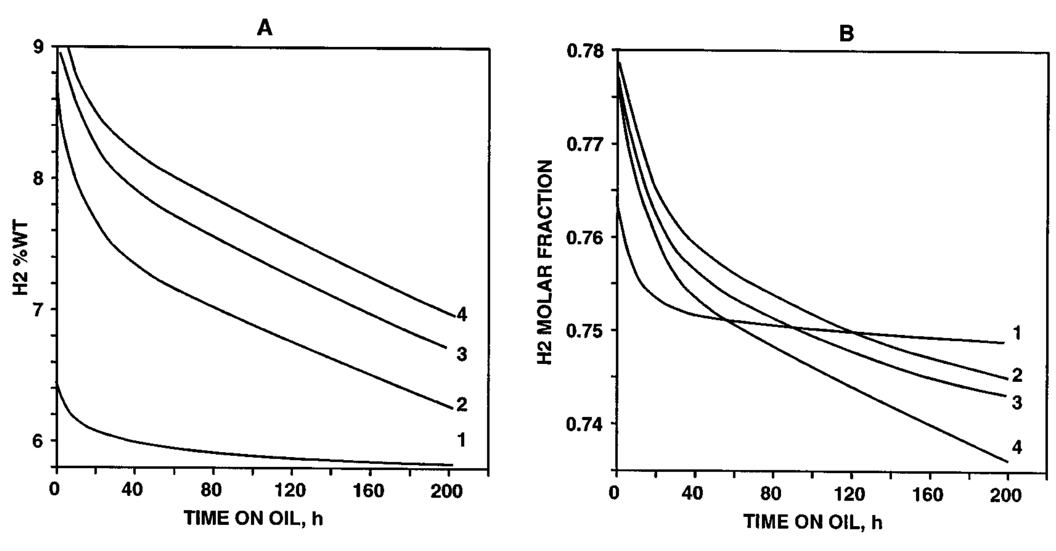

FIG. 3. Hydrogen concentration profiles for Pt–S: (A) weight percentage, (B) molar fraction.

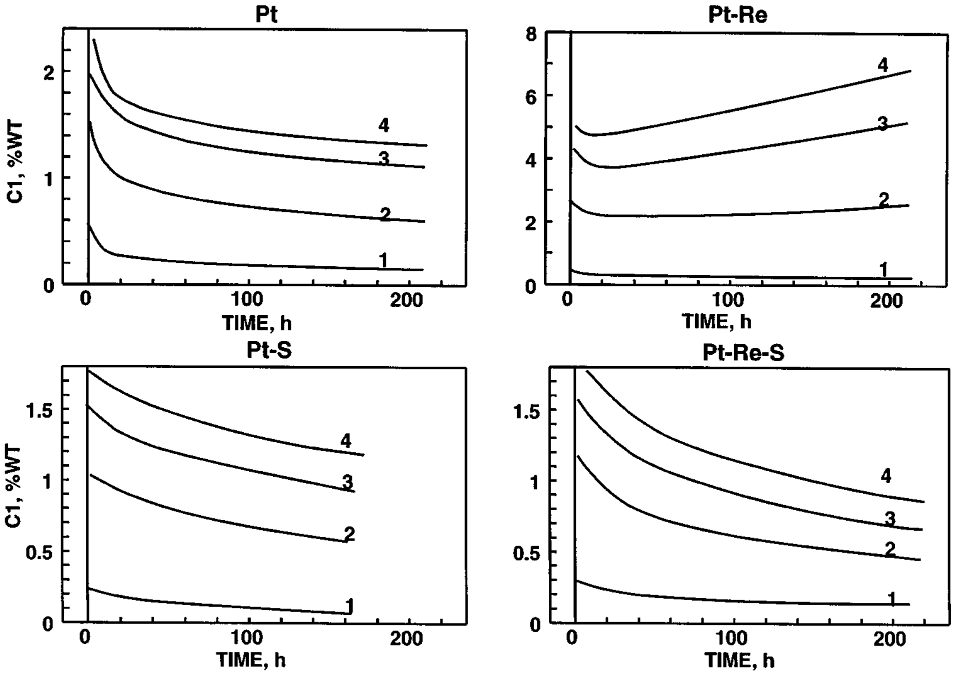

FIG. 4. Methane concentration profiles. Feed: *n*-heptane, $P = 525$ kPa, $T = 499°C$.

short time on oil, e.g., 2.5 h, a low temperature peak (below 400°C) is observed in both catalysts. As time increases, this peak cannot be resolved as the coke level on the catalyst is increased. TPO spectra for Pt–S are different from those of Pt–Re–S. The monometallic catalyst displays a peak at about 500°C that is not present on Pt–Re–S catalyst.

Coke on the unsulfided Pt–Re was also analyzed by TPO after a partial burning experiment. The partial burn was carried out by temperature-programmed burning from room temperature up to 450°C, and staying at this temperature for 30 min. The TPO profile of the partially burned catalyst is shown in Fig. 8.

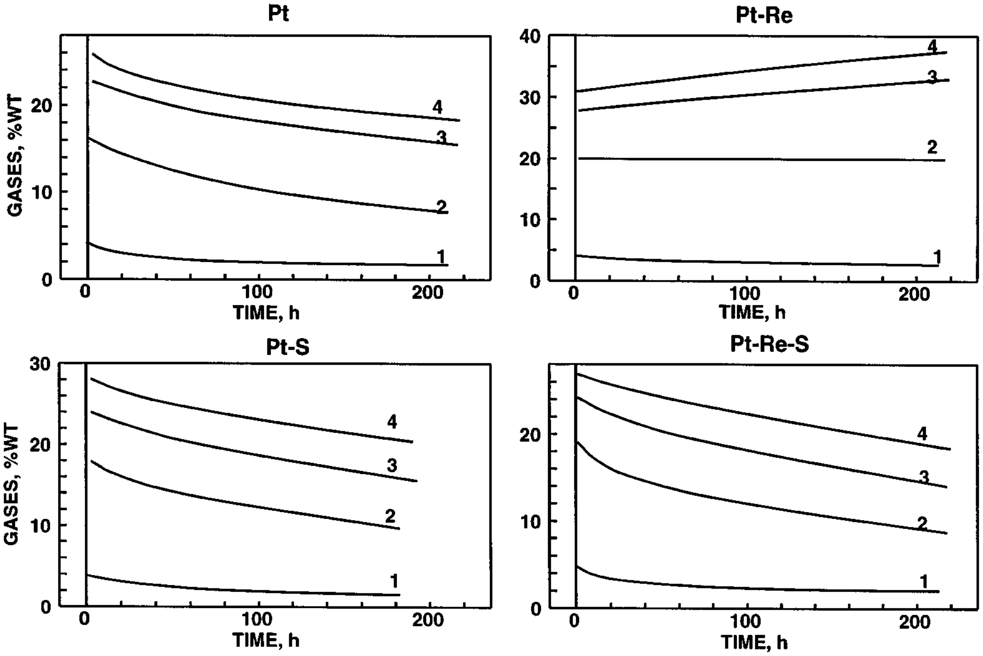

FIG. 5. Gases concentration profiles. Feed: *n*-heptane, $P = 525$ kPa, $T = 499°C$.

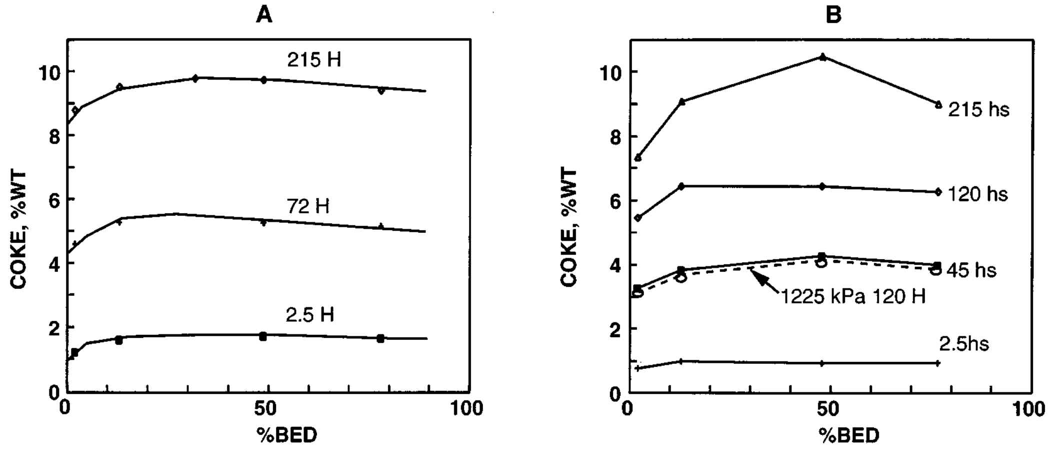

FIG. 6. %Coke as a function of %Bed for Pt–S (A) and for Pt–Re–S (B).

Sulfur Analyses

Table 3 shows sulfur content on catalysts at the end of the run. Both Pt–S and Pt–Re–S lose S during the run. The monometallic catalyst suffers the greatest loss of S. After 215 h on oil, Pt retained about 10% of the initial amount of S. In the case of Pt–Re, after 215 h about 50% of the initial 607 ppm of S was lost. An increasing profile of S along the bed is found on Pt–Re–S, both at 525 kPa and at 1225 kPa.

Chlorine concentration on Pt–Re–S/Al_2O_3 also increases along the bed at the end of a 120-h run at 1225 kPa (Table 3).

DISCUSSION

Product Profiles

Sulfur has little effect on the performance of the Pt/Al_2O_3 catalyst. The most significant change for this catalyst is the decrease in hydrogenolysis, mainly observed at short times on oil. However, a significant change in catalyst performance of the Pt–Re catalyst is observed when it is sulfided. Sulfidation lowers the methane-make and reduces toluene yield stability of the bimetallic catalyst. However, Pt–Re–S catalysts still show better toluene yield and stability than both the unsulfided and sulfided Pt catalysts (Fig. 1, this paper and Fig. 3, Ref. (7)). Final toluene concentrations on Pt–Re–S and Pt–S (after 215 h) are 25 and 17 wt%, respectively, corresponding to 50 and 35% of their initial toluene concentrations.

When the Pt–Re catalyst is presulfided, the sulfur atoms can modify the catalyst by electronic and geometric effects. Since S is preferentially bonded to Re (10), inert S–Re decorates the surface, decreasing the possibility of having large Pt ensembles. The geometrical effect of S on Pt–Re is therefore similar to that of coke deposition during the run. Adsorbed S and C, the alloy of Sn and Au in Pt, and many other "catalytically inert" modifiers act essentially in the same way as Re–S. They reduce hydrogenolysis due to the division of large ensembles into small ensembles of Pt (11).

Electronic effects are complex and involve not only the nature of the metal but also the nature of the support and

TABLE 2

Coke Content on Catalysts after 215-h Run

	Coke content (wt%) catalyst			
Section	Pt	Pt–S	Pt–Re	Pt–Re–S
1	6.70	8.78	4.16	7.35
2	7.55	9.60	2.81	9.07
3	7.08	9.73	1.44	10.48
4	6.80	9.40	1.12	9.00

Note. Feed: *n*-heptane; $P = 525$ kPa; $T = 499°C$.

TABLE 3

Sulfur and Chlorine Content on Catalyst, at the End of the Run

	Catalyst sulfur content (ppm) section			
	1	2	3	4
Pt–Re–S 215 h 525 kPa	241		285	291
Pt–Re–S 120 h 1225 kPa	275		306	304
Pt–S 215 h 525 kPa	44		27	27
	Catalyst chlorine content (wt%)			
Pt–Re–S 120 h 1225 kPa	0.532		0.747	0.749

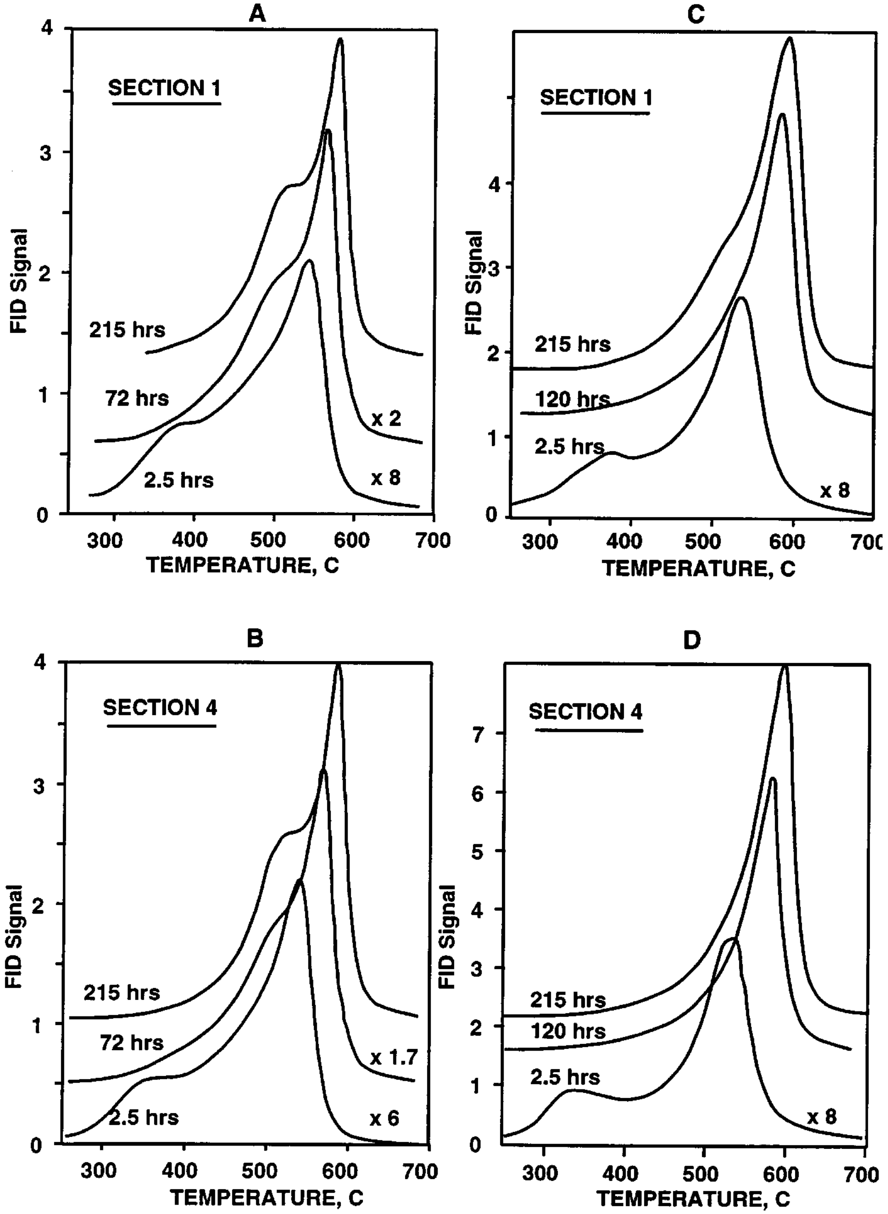

FIG. 7. TPO spectra of coked Pt–S (A) and (B) and for Pt–Re–S (C) and (D). Catalysts coked at 499°C, 525 kPa.

metal dispersion (12). Infrared spectroscopy studies of CO adsorbed on Pt suggested that the electron acceptor properties of sulfur decrease the electron density of the metal (13). Sulfur weakens the CO–metal bond. The strong chemical bond formed between Pt and sulfur modifies the chemical bonding of Pt with other co-adsorbates. It has been reported that S modifies the ratio of reversible chemisorbed hydrogen/total chemisorbed hydrogen from 0.41 to 0.63 (13). Sulfur affects the dehydrogenating activity of the catalyst and results in higher olefin concentrations. The amount of C7 olefins produced in section 1 is related to the dehydrogenating activity of the catalyst. This section contains only 3.7% of the catalyst. The residence time in this section is 0.03 s. Table 1 shows that initially there is an increase in the amount of olefins produced on both Pt and Pt–Re catalysts upon sulfidation. This change is more noticeable on Pt–Re. Unsulfided Pt–Re shows a lower dehydrogenation rate than unsulfided Pt. When S is introduced to Pt–Re its dehydrogenation rate increases, becoming similar or greater than that of Pt and Pt–S. The role of S has been shown to selectively decrease the hydrogenation capacity of Pt–Re and the ensemble size, resulting in lower cracking and a higher amount of coke (6).

Table 3 shows that the Pt–S catalyst lost most of its sulfur at the end of a 215-h run with a final S content of 0.004% on section 1, and about 0.003% on section 4. The initial

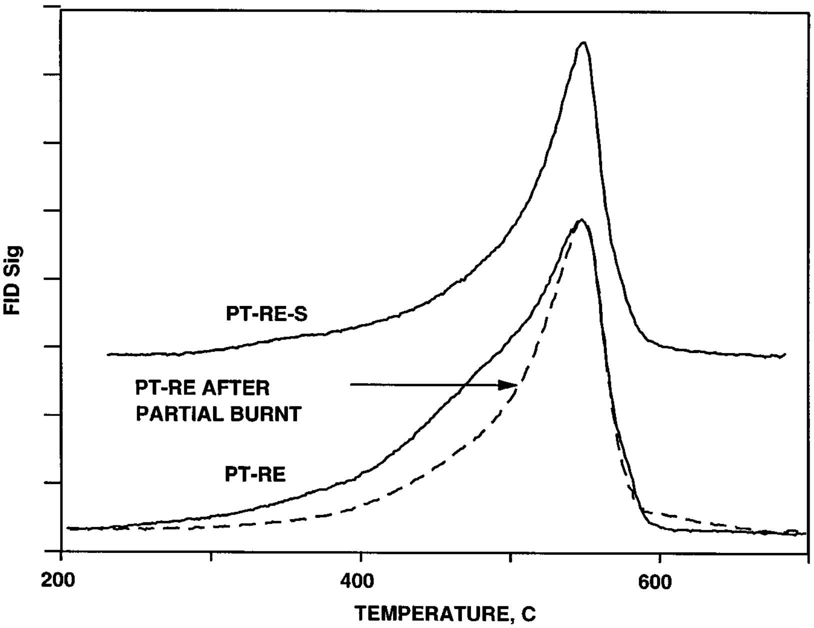

FIG. 8. TPO spectra of Pt–Re–S preburned at 450°C.

sulfur content on the Pt catalyst was 0.03 wt%. Therefore, a tenfold decrease in S content is found after 215 h on oil. It has been established that most of the S on Pt/Al_2O_3 can be removed by H_2 treatment in conditions similar to those used in this study (14, 15). It is necessary to have a continuous S introduction into the reactor, e.g., spiking the feed with an organic sulfur compound, in order to keep Pt sulfided during the run.

The intermediate 2-methylhexane (2MH) concentration profiles show even more clearly the differences in stability between sulfided and unsulfided Pt–Re. Unsulfided Pt–Re displays the same 2MH concentration at the reactor outlet (outlet 4 in Fig. 3, Ref. (7)) at 215 h as that at the start of the run; within this time period there is a slight maximum. On the other hand, with the Pt–Re–S catalyst, 2MH concentration increases from 1 wt% at the start of the run to about 8 wt% at 215 h on oil; within this time period, 2MH in outlet 2 exhibits a maximum with the sulfided bimetallic, while an increasing profile is present with the unsulfided catalyst (Fig. 3, Ref. (7)). As has been previously discussed (7), this maximum is due to the change in the effective contact time as catalyst deactivates affecting the concentration of an intermediate in a complex kinetic mechanism as, for example, $A \rightarrow B \rightarrow C$.

C5 naphthenes play a major role in reforming catalysts deactivation. Reaction conditions and additives can have a significant impact on the C5 naphthene concentration profile in the catalyst bed. When Re is introduced to Pt/Al_2O_3, the concentration profile of C5 naphthenes changes from a profile that displays a maximum along the bed after a short on-oil time to a decreasing profile (7). When S is added to Pt–Re/Al_2O_3 its C5 naphthene profile reverses back to that of Pt/Al_2O_3. Therefore, sulfur addition to Pt–Re is acting in an opposite direction as compared to Re addition to Pt. Sulfiding Pt/Al_2O_3 has no effect on its C5 naphthene profile which also exhibits a maximum along the bed after a short on-oil time.

Coke Profiles

The monometallic Pt catalyst produces a coke profile with a maximum near the top of the bed at 525 kPa. Similar results are found when this catalyst is sulfided. Figure 6A shows that at various on-oil times, the coke profiles of Pt–S display a maximum in section 2.

Pt–Re exhibits a decreasing coke profile along the bed at this pressure (7), but when this catalyst is sulfided, its coke profile becomes similar to that found in Pt or Pt–S, i.e., with a maximum along the bed. However, the maximum seems to move downstream when it is compared with the position of the maximum in the coke profile of Pt or Pt–S.

S not only drastically changes the coke profile on Pt–Re, but also the amount of coke. At 525 kPa, Pt–Re–S makes almost double the amount of coke found on Pt–Re. Comparing Pt–Re–S and Pt–S, similar average coke content on catalyst is found at 215 h (about 9 wt%). Sulfiding Pt catalyst leads to a moderate increase in coke-make since coke-make on unsulfided Pt catalyst is 7 wt% under the same reaction conditions (7).

An increase in pressure up to 1225 kPa with Pt–Re–S does not modify the coke profile, but the amount of coke drops to half the value obtained at 525 kPa.

The coke profiles of unsulfided Pt–Re and Pt catalysts have been successfully correlated with the C5 naphthene concentration profiles under a wide range of experimental conditions. For these catalysts, only C5 naphthenes, not H_2 partial pressure, temperature, or C10+ fraction, were found to play a major role in fixing the coke profiles under a variety of experimental conditions (7). The same correlation applies to sulfided Pt catalysts. For example, from the time evolution of the mole fraction of hydrogen along the reactor (Fig. 3B) hydrogen partial pressure has either a maximum (because the molar concentration of hydrogen has a maximum) along the catalyst bed, or a decreasing profile at time-on-oil longer than 120 h. Therefore, if hydrogen partial pressure is the major variable affecting the coke deposition rate, the coke profile along the catalyst bed should display a minimum or an increasing profile according to the time-on-oil. However, at a reaction pressure of 525 kPa coke profiles along the bed at various time-on-oil all show a maximum (Fig. 6).

When one looks at the production of hydrogen along the catalyst bed in weight basis (Fig. 3A) there is always a net production of hydrogen along the catalyst bed as indicated by the increase in wt% of hydrogen from outlet 1 to outlet 4 and the hydrogen concentration at any outlet is always greater than 5.66 wt%, which is the hydrogen concentration in the feed gas.

However, a different situation occurs with the bimetallic Pt–Re–S. The maximum in the coke profile appears to be somewhere in section 3, while the maximum C5 naphthenes' average concentration seems to be in section 2 (Figs. 6B and 2). This means that the maximum in coke concentration is shifted downstream compared to the maximum in C5 naphthene concentration.

This result can be explained by considering the S profile. According to the literature (4, 5) and results reported in the present paper, S increases coke-make on Pt–Re. Table 3 shows that there is an increasing S profile along the bed at the end of the run. Therefore, even though the C5 naphthene concentration is lower in section 3, a faster coke deposition in this section compared to section 2 is observed as a consequence of the higher S content. For a given catalyst, the higher the C5 naphthene concentration, the higher the coke deposition rate. When different catalysts are compared, not only the amount of the C5 naphthene concentration plays a major role in the coking rate, but also the dehydrogenating capacity of each catalyst, since C5 naphthenes have to be dehydrogenated in order to polymerize on acid sites (16).

S has great influence on the coking rate of Pt–Re catalysts. Due to a slow stripping of sulfur during the run, with an accumulation at the bottom of the bed, S displays an increasing concentration profile. This may be the reason the coke profile does not match exactly the C5 naphthene concentration profiles. This is especially evident when the pressure is increased from 525 to 1225 kPa. At this higher pressure, the C5 naphthene concentration has a decreasing profile along the bed, but the coke profile has a smooth maximum around section 3 of the bed, indicating dehydrogenating activity overcomes the C5 naphthene concentration effect.

The chlorine concentration profile along the bed may also play a role in the amount of coke deposited on the catalyst. It has been established that the coke deposition rate depends upon catalyst chlorine concentration (17). However, this influence is smaller than that of sulfur, which greatly affects coke precursor formation, due to an increase in the dehydrogenating capacity of the catalyst (6, 11).

Since S stripping is a slow process, the shorter the run, the less pronounced the effect of a S profile. This is the reason in the 2.5-h run the maximum in the coke profile correlates with the maximum in the C5 naphthene concentration profile. In this case, the coke profile displays a smooth maximum in section 2 (Fig. 6). The average C5 naphthene concentration in each section is calculated as (C5 naphthene concentration at section inlet +C5 naphthene concentration at section outlet)/2. Thus, at 2.5 h time-on-oil, the average C5 naphthene concentrations from section 1 to 4 are 0.9, 1.4, 0.7, and 0.3 wt% (Fig. 2B), respectively. Therefore, there is a correlation between the C5 naphthene concentration in the gas phase and the amount of coke deposition for the sulfided Pt–Re catalyst, for very short times-on-oil, when the sulfur profile along the bed has not developed.

It has been proposed that the higher hydrogenating activity observed in Pt–Re compared to Pt is due to a higher hydrogen surface concentration (7). As a consequence of this, Pt–Re displays lower dehydrogenating activity, higher hydrocracking activity, and lower coke-make. Upon sulfidation of Pt–Re, dehydrogenating activity increases when it is compared to Pt–Re (Table 1). This has been previously suggested in studies carried out with several hydrocarbons as feed stocks, such as cyclohexane, benzene, methylcyclopentane, and *n*-hexane (6, 18). It appears that S modifies the Pt–Re catalyst in an opposite way as Re modifies the Pt catalyst, i.e., decreasing the hydrogen surface concentration.

Since there is an electronic transfer from Pt to S, a weakening of the Pt–H bond could be expected, as has been reported in (13), where an increase in the reversible H_2/total H_2 adsorption ratio was found upon sulfidation. Also, the Co–Pt bond is weakened when the catalyst is sulfided (13). The lower hydrogen surface concentration on Pt–Re–S results in a higher dehydrogenation activity and as a consequence, a higher coke-make.

Coke TPO Spectrum

Figure 7 shows that S does not modify the TPO spectra of coke on Pt. A comparison of these spectra (Figs. 7A and 7B) with those reported in (7) (Figs. 8A and 9A in Ref. (7)) indicates that they are essentially the same. On the other hand, S does produce a change in burning characteristics of coke on Pt–Re in addition to an increase of the amount of coke on the catalyst. The shoulder of the main peak that appears on Pt–Re at about 500°C (Fig. 8B in Ref. (7)) is less defined on Pt–Re–S. For the Pt–Re–S catalyst, this peak can be seen only with the inlet section catalyst (section 1). Additionally, the main peak of the sulfided Pt–Re catalyst is about 30°C higher than the unsulfided catalyst. It appears from Fig. 7 that at short on-oil time, 2.5 h, coke produced on the catalyst is mainly the 500°C type. There is also a noticeable amount of coke burned below 400°C and it has been well characterized to be coke on metal particles (19, 20). This low temperature peak cannot be resolved as the coke on the catalyst increases because coke on metal attains a low limiting value (21, 22). At the high coke level, the relatively small signal generated by the small amount of metal coke cannot be resolved from the background signal of the large peaks.

The location of the TPO peak strongly depends on the coke amount and coke particle size (23). TPO peak temperatures can shift to a substantially higher temperature when the coke particle size increases as the amount of coke on the catalyst increases. On the other hand, if the increase in coke content can be accounted for by increasing the number of coke particles without changing the size of the coke particles, there should be little effect on the peak temperature. Without knowing the particle size of the coke, one cannot compare TPO spectra of two samples with different coke levels, i.e., to conclude that the 500°C type coke formed at 2.5 h is different from the 600°C type of coke generated at 215 h. Burning temperature differences observed within a sample indicate that there are coke deposits in the catalyst having different reactivity with oxygen. The Pt–Re–S catalyst (section 1) after 215 h on-oil has a major portion of coke burned at 600°C and a minor portion burned at 500°C. In any case, the TPO spectra show there is a change in the distribution of coke among the different types of coke present on the catalyst and their distribution depends on catalyst location in the reactor and time-on-oil. S not only affects the total amount of coke, but also its distribution on Pt–Re/Al_2O_3 catalysts.

Selective removal of the low temperature coke on Pt–Re (see Fig. 8) produces a coke with similar characteristics as that on Pt–Re–S. This also suggests that coke distribution is different on both catalysts, i.e., a larger proportion of coke is present as a high temperature burning coke on Pt–Re–S than on Pt–Re.

CONCLUSIONS

Coke and product profiles are affected by the presulfidation of Pt–Re catalysts. The effect of sulfur is opposite to that of Re. While the addition of Re to Pt/Al_2O_3 moves the maximum in coke toward the top of the bed, addition of S to Pt–Re moves this maximum in the other direction. S is slowly stripped from the Pt–Re catalysts. This generates a S concentration profile that increases along the bed. This profile in the catalyst composition influences the coke profile. Consequently, on sulfided catalysts, there is not a perfect correlation between the C5 naphthene concentration and the coke profiles. A shift toward the bottom of the reactor in the maximum of the coke profile is observed compared to the maximum in the C5 naphthene concentration.

Re increases the hydrogenating activity of Pt, but S decreases the hydrogenating activity of Pt–Re. Therefore, a higher quantity of coke is deposited on sulfided catalysts. It is proposed that the higher dehydrogenating activity of sulfided Pt–Re compared to unsulfided Pt–Re is partly due to a lower hydrogen surface concentration, because of the electronic interaction between S, Re, and Pt.

Both elements, Re and S, are needed in order to get the right balance in activity, selectivity, and stability of the catalyst. Too high of a hydrogen surface concentration leads to excessive hydrogenolysis and lower dehydrogenating activity. If hydrogen surface concentration is too low, excessive dehydrogenating activity results in a very fast coking rate. According to our results and literature, promotors of the metallic function play an important role in the dynamics of the hydrogen adsorption–desorption process, and therefore optimized catalysts would contain promotors in such a way that hydrogen surface concentration be balanced in order to achieve the best performance regarding activity, selectivity, and stability.

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