Stability of Bimetallic Reforming Catalysts

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The catalytic activity, selectivity, and stability of catalysts whose metallic functions were Pt-, Pt–Re-, and Pt–Re–S-supported on the same γ-Al_2O_3 were measured in the reforming of *n*-hexane and methylcyclopentane. The coke deposition was measured with a microbalance and was studied by TPO, analysis of C and H/C ratio. The introduction of Re and S to Pt increases the selectivity similarly to, but more effectively than, coke formation on Pt during the run. The deactivation during the first hours of the run is due to coke deposition on the metal and at longer times to deposition on the support, which produces very small deactivation. Comparison of the coking of the presulfided bimetallic catalysts with that of the monometallic reveals that the main difference resides in the distribution of the coke. On the presulfided catalyst the fraction of coke on the metallic function is very small because this function was predeactivated for coke formation. The deactivation of the metallic function controls all the catalyst deactivation. © 1988 Academic Press, Inc.

INTRODUCTION

The introduction of the bifunctional metal–acid catalyst in 1949 (*1*) was a revolutionary event for the naphtha reforming process. The catalyst was platinum supported on γ-alumina whose acidity was promoted by the addition of chlorine. Another great advance occurred in 1968 (*2*) with the addition of Re to promote Pt, opening the era of the bimetallic catalysts. These catalysts are more stable than the monometallic, allowing work at lower pressures (for instance 15 kg cm^{-2} instead of 30 kg cm^{-2}) for a similar cycle length (period between regenerations by burning the coke). The lower pressure increases the selectivity to aromatics and decreases the gas formation. Because of these improvements in stability and selectivity the monometallic catalyst was displaced by the bimetallics. In the last decade many bimetallic and multimetallic catalysts such as Pt–Sn, Pt–Ge, Pt–Ir, and Pt–Re–Ir, were patented and some of them are used commercially. Still Pt–Re is the catalyst more widely used today in commercial plants. This catalyst is sulfided before use to decrease its great hydrogenolytic activity.

Coke is deposited on both functions of the catalysts, as was shown by temperature-programmed oxidation (TPO) (*3–11*). The references showed that at the beginning of the run coke is mainly deposited on the metallic function and later mainly on the acidic one (*7*). This phenomenon produces changes of selectivity during the run which are different for mono- or bimetallic catalysts.

The objective of this paper is to study the coke depositions on Pt/Al_2O_3 (monometallic) and Pt–Re–S/Al_2O_3 (sulfurized bimetallic) in order to explain the improved selectivity and stability of the bimetallic catalyst. For comparative purposes the bimetallic catalyst before sulfurization was also studied.

EXPERIMENTAL

Catalysts

A high-purity γ-alumina CK-300 from Cyanamid Ketjen (Amsterdam) with a specific surface area of 200 m^2 g^{-1} and pore volume 0.48 cm^3 g^{-1} was used as support.

This support was ground and the fraction of 35–80 mesh was calcined 3 h at 650°C in a dry air stream before impregnation with the catalyst precursors. Pt/Al$_2$O$_3$ containing 0.35% Pt and 0.90% Cl was prepared by impregnation of the support with an aqueous solution of H$_2$PtCl$_6$ and HCl (6 N), which was added as a competitor to obtain uniform Pt distribution. Pt–Re/Al$_2$O$_3$ containing 0.33% Pt, 0.35% Re, and 0.93% Cl was prepared by impregnation with a solution of H$_2$PtCl$_6$, HReO$_4$, and HCl. The impregnation time was 12 h at 30°C.

The impregnated samples were dried at 120°C for 12 h and the calcination and chlorination were executed by passing first air and then a gaseous mixture of HCl–H$_2$O–air at 500°C as described in (12). The samples were reduced at 500°C and the metallic dispersions were for Pt/Al$_2$O$_3$ 75% (H$_2$ chemisorption) and for Pt–Re/Al$_2$O$_3$ 69% (O$_2$ chemisorption). In the case of Pt–Re/Al$_2$O$_3$ after reduction, the samples were sulfided with a stream of 0.06% molar H$_2$S in H$_2$ at 500°C and 1 atm during 4 h. Afterward H$_2$ flowed for 8 h at the same temperature to eliminate the reversible sulfur remaining, 0.04% S, on the catalyst.

Feed

n-Hexane and methylcyclopentane, Carlo Erba RPE, dried over molecular sieve 4A and pure H$_2$ from AGA were used.

Catalyst Test

The test to show catalyst activity, selectivity, and stability in n-hexane and methylcyclopentane reforming was performed using bench-scale equipment with chromatographic analysis on line as described elsewhere (13). The run length was 7 h and the operational conditions were 5 atm, 500°C, H$_2$: hydrocarbon molar ratio = 4, and weight hourly space velocity = 4.

Coke Deposition during the Run

A stainless-steel high-pressure microbalance Sartorius Model 4401 was used under the same operational conditions as those of

the catalyst test and with a catalyst sample of 0.2 g. Reaction products were not analyzed because conversion was low.

Analysis of the Carbonaceous Deposit

Carbon content was measured using combustion–volumetry equipment. Temperature-programmed oxidation was performed with a Shimadzu DT-30 thermal analyzer as described before (14). H/C ratio was calculated from the chromatographic analysis of the TPO effluent, measuring carbon dioxide formation and oxygen disappearance, according to details given in Ref. (8).

RESULTS AND DISCUSSION

Figure 1 shows the total conversion of n-hexane and its conversion to methane on the three catalysts as a function of time. As can be seen, Pt/Al$_2$O$_3$ is rapidly deactivated during the first 2 h, then the rate of deactivation decreases continuously, and the activity reaches a plateau at 6–7 h. On the other hand, the catalytic activity of Pt–Re/ Al$_2$O$_3$ at the beginning of the run is higher than that of Pt/Al$_2$O$_3$, mainly because of the very high hydrogenolytic activity that produces methane. The high initial hydrogenolytic activity of Pt–Re/Al$_2$O$_3$ is rapidly decreased and this catalyst is more stable than Pt/Al$_2$O$_3$. The catalytic activity of
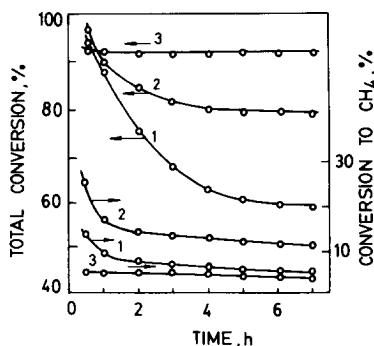

FIG. 1. n-Hexane reforming. Total conversion and conversion to methane as a function of time. 5 atm, 500°C, H$_2$: n-hexane = 4, weight space velocity = 4 h^{-1}. (1) Pt/Al$_2$O$_3$; (2) Pt–Re/Al$_2$O$_3$; (3) Pt–Re–S/Al$_2$O$_3$.

Pt–Re–S/Al$_2$O$_3$ is practically constant during the whole run, hydrogenolysis being very small.

Hydrogenolysis is a reaction catalyzed by the metallic function of the catalyst. As time goes on, methane formation on Pt/Al$_2$O$_3$ and Pt–Re/Al$_2$O$_3$ quickly drops due to the poisoning effect of the coke deposited on the metallic function. The decrease in hydrogenolysis is very rapid and this phenomenon can be interpreted according to different suppositions. According to Boudart (15) hydrogenolysis can be considered a "demanding reaction": an ensemble of several contiguous metal atoms is required to have an active site. In the case of Pt–Re/Al$_2$O$_3$ the ensemble includes atoms of both metals. During coke deposition some metal atoms (Pt and Re) are covered or blocked by coke, greatly decreasing the possibility of having ensembles of many atoms together. In the case of Pt–Re–S/Al$_2$O$_3$, Sachtler (16) stated that sulfur is bonded to the Re atoms of the alloy Pt–Re producing an inert S–Re that divides the Pt surface, decreasing the possibility of having large Pt ensembles. Then, presulfiding produces a geometrical effect similar to the one that coke deposition produces during the run. But Fig. 1 shows that on Pt–Re–S/Al$_2$O$_3$, hydrogenolysis is smaller than that on both Pt/Al$_2$O$_3$ and Pt–Re/Al$_2$O$_3$ stabilized by coke. This can be ascribed to differences in Pt ensemble destruction. According to Davis et al. (17), on coked Pt most of the surface is covered by the carbonaceous deposit and hydrocarbon conversion occurs over the bare metal islands, which form patches or ensembles of several contiguous atoms. Some of these Pt ensembles are big enough to be still active for hydrogenolysis. Meanwhile on Pt–Re–S/Al$_2$O$_3$ the Re–S diluters are more uniformly distributed on Pt than the coke, producing a greater decrease in the number of large Pt ensembles.

The selective poisoning of hydrogenolysis was also interpreted in the literature by considering the metallic surface to be heterogeneous (18, 19): certain reactions occur only on certain catalytic sites and if the poison is adsorbed only on the same particular sites, these reactions are selectively poisoned. It was shown that coke formation and hydrogenolysis occur on the same active sites (20) and that these reactions are selectively decreased by sulfiding (21, 22). This means that sulfur should be adsorbed selectively on the same active sites. To clarify this point it is interesting to analyze the changes in selectivity when changing the size of the Pt crystals because the hydrogenolysis and coking activities per exposed Pt atoms are smaller on very small Pt crystallites than on large crystals (20). This behavior could be due to the different heterogeneity of the surfaces according to the crystal size: different percentages of corner, border, or terrace atoms or different electronic states. This also could be due, on a homogeneous surface, to the different possibilities of the crystal's, according to its size, having enough Pt atoms to form the required ensembles.

If the surface is heterogeneous and sulfur is selectively adsorbed on the same active sites for coke formation and hydrogenolysis reactions, the influence of metallic dispersion on sulfur adsorption will be similar to that of the reactions. In sulfur chemisorption on Pt, it was concluded (23, 24) that there is an electron transfer from Pt to S, depending the S–Pt bond strength on the electron affinity of the metal. Cini (25) showed that a decrease in the size of the metal particles produces a decrease in the electronic affinity of the metal. On the other hand, in small metallic particles a metal–support interaction can produce an electronic transfer from the metal to the support (26), causing an increase in the electronic affinity of the metal. According to Barbier et al. (24) these opposite effects on the electronic state of very small metallic particles can neutralize each other and can explain the experimental fact that on Pt supported on alumina, sulfur coverage of Pt

is independent of the crystal size (24, 27). This conclusion disagrees with results for the adsorption of sulfur on Pt single crystals. Oudar (28) stated that the adsorption stoichiometry S–Pt is different according to the exposed Pt face. The adsorption could be stronger on smaller Pt crystallites, but in the studied Pt supported on alumina catalysts this difference is not observable. This means that the surface of different-size crystals in Pt-supported catalysts behaves homogeneously for S adsorption. Then, as S adsorption poisons selectively hydrogenolysis and coke formation, the possibility of a geometric effect due to the necessity of large Pt atom ensembles for these reactions seems to interpret the results better than the concept of surface heterogeneity.

The presence of a second element added to Pt can produce changes in the electronic state of one or several of its neighbor Pt atoms. These atoms could become inactive for hydrogenolysis, and still be active for other reactions, like hydrogenation–dehydrogenation, not requiring the same electronic configuration. In the case of Pt–Re–S/Al$_2$O$_3$, as cited before, Sachtler (16) stated that sulfur is bonded to Re atoms of the Pt–Re alloy, not being Pt affected by S. Therefore there is no electronic influence of S on Pt. For Pt alloys, Ponec (29) using different techniques (IR, electron spectros-

copy, heat of adsorption) stated that there is no noticeable difference in the electronic structure of pure or alloyed Pt atoms. This suggests that the catalytic activity of the Pt atoms would be the same, being alloyed or pure. Then, it seems that in Pt–Re–S/Al$_2$O$_3$ the electronic factor as influencing the catalytic activity of Pt could be neglected.

It seems that the geometrical effect of the ensemble theory can be an acceptable explanation to interpret the results of the selective poisoning of the hydrogenolysis and coking reactions on Pt–Re–S/Al$_2$O$_3$.

During the reforming of methylcyclopentane the catalysts are more deactivated than during that of n-hexane because of the higher coke-forming capacity of methylcyclopentane. The relative positions of the catalysts' behavior are the same with both feeds. It is interesting to analyze the ring opening of methylcyclopentane to produce C$_6$ paraffins or olefins. This ring opening is the primary hydrogenolysis and the C$_6$ hydrocarbons formed can continue hydrogenolysis, producing methane. Table 1 shows the production of C$_6$ acyclic hydrocarbons from methylcyclopentane. As Pt–Re/Al$_2$O$_3$ has a greater hydrogenolysis capacity than Pt/Al$_2$O$_3$, the amount of products of primary hydrogenolysis at the reactor outlet is smaller and the amount of methane produced by the successive hydrogenolysis is greater. Pt–Re–S/Al$_2$O$_3$ has the smallest

TABLE 1

Reforming of Methylcyclopentane: Production of C$_6$ Paraffins or Olefins in Mole Percent of the Converted Fraction

	Pt/Al$_2$O$_3$		Pt–Re/Al$_2$O$_3$		Pt–Re–S/Al$_2$O$_3$	
	0.5 h	7 h	1 h	7 h	0.5 h	1–7 h
Olef. C$_6$	0.0	0.92	0.0	0.68	0.0	0.80
22 DMB	0.0	0.0	0.57	0.18	0.66	0.28
23 DMB	0.74	0.10	0.73	0.30	0.73	0.65
2 MP	5.63	3.59	4.61	2.56	3.83	3.29
3 MP	4.14	2.62	3.51	1.94	2.86	2.48
2 MP/3 MP	1.36	1.37	1.31	1.32	1.34	1.31
n-C$_6$	6.58	9.40	5.03	6.36	4.99	6.31
3 MP/n-C$_6$	0.63	0.28	0.70	0.31	0.57	0.39

hydrogenolysis activity from the beginning of the run, remaining nearly constant. On the three catalysts the ratio 2 MP/3 MP is nearly constant and a little higher than the thermodynamic equilibrium value (30). As the statistical selectivity of the ring opening produces a ratio 2 MP/3 MP = 2, the subsequent transformation of 2 MP to 3 MP is very rapid.

According to Gault et al. (31) on Pt/Al$_2$O$_3$ the ratio 3 MP/n-C$_6$ changes with the metallic dispersion and can be taken as a guide to infer the size of the Pt crystals: the higher the ratio the larger the crystals. This is because in large Pt crystals the ring opening of methylcyclopentane is "selective": a very small amount of n-hexane is produced. Van Senden et al. (32) using Ir/Al$_2$O$_3$ found that virgin surfaces reveal a "selective" ring opening, with a very small amount of n-hexane among the products. Surfaces with an increasing amount of carbonaceous deposits show an increasing tendency to a "nonselective" ring opening, with appreciable amounts of n-hexane among the products. These authors stated that the presence of carbon on the surface eliminates the large ensembles of contiguous sites, causing a shift in the reaction products that is equivalent to the shift in Pt when passing to smaller metallic crystals. In our catalysts, if we consider that the decrease in the number of contiguous Pt atoms that form the ensembles is equivalent to having a smaller crystal, the ratio could be a useful guide to see how the Pt surface in Pt/Al$_2$O$_3$ is covered or fractionated by carbon. In the case of alloys the dilution of Pt with inerts, such as Au, has an effect on selectivity similar to that of reducing crystal size. Our results show that on Pt–Re–S/Al$_2$O$_3$ the trend in selectivity is similar to that of dilution of Pt and we can assume that the Pt–Re alloy when sulfided is equivalent, regarding Pt ensembles, to a dilution of Pt with inert Re–S. Table 1 shows that for Pt/Al$_2$O$_3$ the ratio 3 MP/n-C$_6$ decreases from 0.63 to 0.28 during the run. The ratio values suggest that the Pt ensembles of

fresh Pt–Re–S/Al$_2$O$_3$ are smaller and decrease to a lesser extent during the run than in fresh Pt/Al$_2$O$_3$. This explains the lower activity and higher stability of Pt–Re–S/Al$_2$O$_3$ for reactions that demand a large ensemble of Pt atoms, as hydrogenolysis and coke formation.

In order to compare the catalyst deactivation with the coke deposition, coke formation in methylcyclopentane reforming was measured as a function of time with the microbalance. Methylcyclopentane was used as feed, because the small amount of coke produced from n-hexane under the experimental conditions of the runs is very difficult to quantify. The results are shown in Fig. 2. In the first few hours coke accumulates more rapidly on Pt/Al$_2$O$_3$ than on Pt–Re/Al$_2$O$_3$ and Pt–Re–S/Al$_2$O$_3$. It is accepted that at the beginning of the run, coke is mainly produced on the metal, and later on both functions, with the fraction of the support increasing with time (7, 10). Then, Fig. 2 shows that Pt will be covered by coke more rapidly than Pt–Re and Pt–Re–S. Pt–Re–S/Al$_2$O$_3$ produces the smaller amount of coke during the first 3 h but its coking rate decreases little with time. The coke deposition curve of Pt–Re–S/Al$_2$O$_3$ intersects that of Pt–Re/Al$_2$O$_3$ at about 3 h, and the sulfided catalyst produces more coke at the end of the run. Similar behavior was found previously by Coughlin et al.
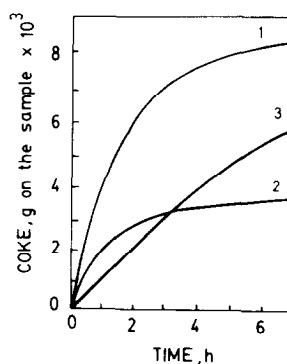

FIG. 2. Methylcyclopentane reforming. Coke formation on 0.2 g of catalyst as a function of time. Same operational conditions and numbers as in Fig. 1.

(*33*). Depending on the run length, we can have more coke on either Pt–Re/Al_2O_3 or Pt–Re–S/Al_2O_3. The slope of the coke vs time curve at the longest time (7 h) is much greater for Pt–Re–S/Al_2O_3 than for Pt/Al_2O_3. Therefore, the amount of coke on Pt–Re–S/Al_2O_3 will probably approach that on Pt/Al_2O_3 for longer times.

In order to see the distribution of coke on the functions of the catalysts after the 7-h run, the samples were submitted to TPO. By TPO it is possible to differentiate the burning of the coke deposited on both the metallic function and the support. Accordings to the type of support, carbon concentration, and operational conditions (O_2 concentration, rate of heating, gas flow rate), two peaks or zones, or only one great peak can be observed. In the case of two peaks, Fígoli *et al.* (*6*) suggested that the first peak (up to 370°C) corresponds to the coke deposited on the metallic function, and the second to the coke deposited on the support (acid site), which burns at higher temperatures (370–550°C). Other authors found different temperatures for the peaks; Barbier *et al.* (*8*) and Xu Zhu-sheng *et al.* (*11*) found that the limits of both zones are at 350°C. On the other hand when only one peak is observed, the first part is related to the coke that is deposited on the metal and the last to the coke on the support.

Figure 3 shows the TPO of the three catalysts after the 7 h of methylcyclopen-

tane reforming. It can be seen that the addition of Re and S produces a great decrease in coke deposition on the metal. In Fig. 3 the first peak or zone for Pt/Al_2O_3 has a maximum at about 350°C and ends at about 370°C. The coke burning up to 350°C can be taken to be representative of the coke on the metallic function because at higher temperatures most of the coke that burns is located on the support (*9*).

More coke is produced on Pt–Re–S/Al_2O_3 than on Pt–Re/Al_2O_3; nevertheless the deactivation of Pt–Re–S/Al_2O_3 is smaller. This suggests that for deactivation by coking, more important than the amount of coke is how this coke is distributed on the catalyst functions. This concept was quoted in the literature: Franck and Martino (*34*) stated that the deactivation produced by coke on different catalysts is not proportional to its amount. Sárkány *et al.* (*35*) as well as Xu Zhu-sheng (*11*) found that on Pt–Sn/Al_2O_3 the proportion of the coke deposited on the support is higher than that on Pt/Al_2O_3, Bursian *et al.* (*36*) found that the decrease in Pt surface due to coke deposition is higher on Pt/Al_2O_3 than on several bimetallic catalysts (second metal Cu, Zn, Cd, Ga, In, Ge, Sn, Pb, etc.), and Lieske *et al.* (*37*) explained the smaller coking of the metallic function of Pt–Sn/Al_2O_3 by a drain-off effect: on the bimetallic alloy the coke precursors are more easily transferred to alumina than on the Pt surface.

The data of coking on the catalyst samples after methylcyclopentane reforming (amount of carbon on catalyst at the end of the 7-h run and H/C atomic ratio of coke) and the amount of carbon according to the TPO area) that burns below 350°C are shown in Table 2. The time required in the microbalance to obtain the same amount of coke is also shown in the table and is deduced from Fig. 2. If the coke is selectively produced first on the metallic function, this coverage will be produced in a very short period of time (0.1–0.2 h); however, the decrease in hydrogenolysis
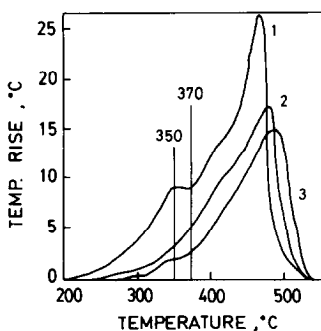

FIG. 3. TPO of coked catalysts after the 7 h of methylcyclopentane reforming (end of run in Fig. 2). Same numbers as in Fig. 1.

TABLE 2

Reforming of Methylcyclopentane

Catalyst	Amount of carbon on catalyst (%)	H/C	Amount of C on catalyst burning below 350°C (%)	Time for depositing the coke burning below 350°C (h)
Pt/Al$_2$O$_3$	4.09	0.59	0.79	0.21
Pt–Re/Al$_2$O$_3$	1.77	0.52	0.13	0.11
Pt–Re–S/Al$_2$O$_3$	2.91	0.47	0.09	0.16

lasts about 2 h. Perhaps during the first seconds or minutes coke is only deposited on the metal and then on both functions of the catalyst, with a continuous increase in the fraction going to the support. It seems that from about 2 h the coke formation occurs only on the support.

It was found that the coke deposited on the metallic function is richer in hydrogen than that on the support (8). Then when the fraction of the total coke burning at high temperatures is higher, the H/C ratio will be smaller. For this reason on Pt–Re/Al$_2$O$_3$ and Pt–Re–S/Al$_2$O$_3$, where most of the coke is on the support, the ratio H/C is smaller than on Pt/Al$_2$O$_3$.

In order to see how coke accumulates as a function of time, runs up to 1, 3, and 7 h using Pt/Al$_2$O$_3$ and methylcyclopentane as feed were performed and the coked catalysts were analyzed by TPO. The TPO are shown in Fig. 4 and it can be seen that at 1 h coke is already formed on both functions of the catalyst. By increasing the time, the formation of coke continues on both functions but most of it is located on the support.

From the point of view of the catalyst active surface, Pt/Al$_2$O$_3$ has a BET surface area of 190 m^2 g^{-1} and a metallic surface area of 0.72 m^2 g^{-1}; this means that only 0.38% of the catalyst surface is exposed Pt and 99.62% is the support. The capacity of receiving coke of the support is enormously greater than the capacity of Pt. Considering that the places with chlorine are the more active acid sites, their number is 0.95/35.5

= 25 × 10^{-3} g at.% Cl. The Pt active sites are 0.35 × 0.75/195.09 = 1.34 × 10^{-3} g at.% Pt. The number of Cl atoms is 19 times higher than the number of Pt atoms and the Cl concentration can be changed by modifying the Cl/H$_2$O ratio of the feed. The presence of Cl generates strong acid sites but these coexist with the intrinsic acidity of alumina. Thus the acid sites are heterogeneous. During the runs there is a very slow deactivation of the acid function and this deactivation is partially compensated by chlorine addition that generates new acid sites to replace the deactivated ones.

In the case of Pt–Re–S/Al$_2$O$_3$ if, like Sachtler (16), one considers that only Re is covered by S, the numbers of exposed Pt atoms are similar to those of Pt/Al$_2$O$_3$, with the advantage that these diluted Pt atoms form smaller ensembles.

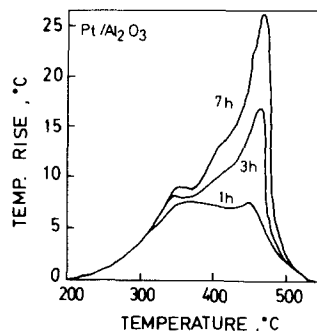It was shown that some parts of the metallic surface of Pt/Al$_2$O$_3$, Pt–Ir/Al$_2$O$_3$,

FIG. 4. TPO of Pt/Al$_2$O$_3$ coked by methylcyclopentane for 1, 3, and 7 h under the operational conditions of Fig. 1.

and Pt–Re/Al_2O_3 remain uncovered by coke, and that the active surface and catalytic activities are constant for 1 h of the run (20). According to Luck et al. (38), when the run is started, in only about 1 s, a coverage of 0.3 C atom per surface Pt atoms is produced. According to Davis et al. (17) the buildup of about the equivalent of one monolayer of strongly bound carbonaceous deposit on the Pt surface is unavoidable. This deposit is produced in only a few minutes (39). The composition and structure of this deposit are dependent upon temperature and hydrogen pressure, and under severe conditions the deposit can pass from bi- to tridimensional.

On Pt/Al_2O_3 the number of exposed g atoms of Pt on 100 g of catalyst is 1.34×10^{-3}. If one considers that only the metal is coked and one carbon atom is deposited on one Pt atom, the amount of carbon will be $1.34 \times 10^{-3} \times 12 = 0.016\%$ of the catalyst. The initial 0.3 C/Pt corresponds to 0.005%. But as the surface carbon is forming aromatic rings leading to a graphitic structure where 1.8 Å^2 corresponds to each carbon atom, and as the surface of one Pt atom is 8.9 Å^2, about five C atoms or a carbon concentration on the catalyst of 0.08% should correspond in a monolayer to each Pt. In our case, except for Pt–Re–S/Al_2O_3, these concentrations are smaller than the amount burning below 350°C. If all the coke that burns below 350°C corresponds to the coke on the metal, this deposit should be in a multilayer, but more probably, the coke that burns on the first part of the TPO corresponds to deposits on the metal and on the support near the metal. The carbonaceous matter on the support could migrate to the metal crystals to be burnt or could be burned by the activated oxygen that migrates from Pt (oxygen spillover) (9). Xu Zhu-sheng et al. (11) stated that on the Pt surface some carbon deposition is in the form of multilayers, some exists as a monolayer, and there are Pt sites free of deposition.

A comparison of Fig. 3 and Table 2 is made between catalysts which had the same manipulation but where different amounts of coke were deposited. To obtain Pt–Re–S/Al_2O_3 containing an amount of coke similar to that of Pt/Al_2O_3, a run of 30 h duration was performed. The amount of coke deposited on Pt–Re–S/Al_2O_3 was 4.16%, similar to that on Pt/Al_2O_3 at 7 h (4.09%). But the decrease in total activity of Pt–Re–S/Al_2O_3 was smaller, 4%, than the decrease of more than 20% in the 7 h run with Pt/Al_2O_3. The same amount of coke on both catalysts is distributed quite differently. On Pt–Re–S/Al_2O_3 there is less coke on the metallic function than on Pt/Al_2O_3 and more coke on the support. For this reason the H/C ratio is smaller, 0.44, than the 0.58 of the coke on Pt/Al_2O_3.

CONCLUSIONS

The deactivation of the bifunctional reforming catalysts is mainly due to deposition of coke on the catalyst surface. The addition of Re and S to Pt produces, compared to the monometallic catalyst, a decrease in coke formation, a great decrease in the fraction of this coke that is deposited on the metallic function, and a lower deactivation for a similar amount of total coke. The coking of the metallic function is the main reason for the rapid Pt/Al_2O_3 deactivation during the first few hours of the run. On Pt–Re–S/Al_2O_3, Pt is stabilized by "dilution" with inert Re–S, which decreases the Pt atomic ensemble sizes and decreases the demanding reactions of hydrogenolysis and coke formation on the metal. The effect of Pt dilution by Re–S on selectivity is similar to the effect produced by coke deposition on Pt, but it is more effective because Re–S is uniformly distributed; while coke leaves great islands of free Pt where hydrogenolysis selectivity is little decreased. Pt/Al_2O_3 and Pt–Re–S/Al_2O_3 have different distributions of the deposited coke, and this could be the reason for the higher stability of Pt–Re–S/Al_2O_3.

The metallic function regulates the amount of coke over itself and the amount

of coke precursors that migrate from the metal to the support. This migration of coke precursors produces the slow deactivation of the acidic function of the catalyst which follows to the rapid deactivation and equilibration of the metallic function. The metallic function of the presulfided catalyst is partially predeactivated and changes little during the run, producing a small and constant amount of coke precursors that migrate to the support, as shown in Fig. 2.

REFERENCES

1. Haensel, V., U.S. Patents 2,479,109 and 2,479,110 (1949).
2. Kluksdahl, H. E., U.S. Patent 3,415,737 (1968).
3. Barbier, J., Marecot, P., Martin, N., Elassal, L., and Maurel, R., in "Catalyst Deactivation" (B. Delmon and G. F. Froment, Eds.), p. 53. Elsevier, Amsterdam, 1980.
4. Fígoli, N. S., Beltramini, J. N., Barra, A. F., Martinelli, E. E., Sad, M. R., and Parera J. M., "Petrol. Chem. Div., ACS Meeting, New York, August 1981"; ACS Symp. Ser. 202, 239 (1982).
5. Bacaud, R., Charcosset, H., Guenin, M., Torrellas-Hidalgo, R., and Tournayan, L., Appl. Catal. 1, 81 (1981).
6. Fígoli, N. S., Beltramini, J. N., Martinelli, E. E., Sad, M. R., and Parera, J. M., Appl. Catal. 5, 19 (1983).
7. Parera, J. M., Fígoli, N. S., Traffano, E. M., Beltramini, J. N., and Martinelli, E. E., Appl. Catal. 5, 33 (1983).
8. Barbier, J. Churín, E. J., Parera, J. M., and Riviere, J., React. Kinet. Catal. Lett. 29, 332 (1985).
9. Beltramini, J. N., Churín, E. J., Traffano, E. M., and Parera, J. M., Appl. Catal. 19, 203 (1985).
10. Zharkov, B. B., Klimenko, T. M., Fedianin, N. P., Krasilnikov, A. N., and Zhuzina, R. Z., Zh. Prikl. Khim. 57, 2555 (1984).
11. Xu Zhu-sheng, Zang Jing-ling, and Zhang Tao, J. Catal. (China) 7, 230 (1986).
12. Castro, A. A., Scelza, O. A., Benvenuto, E. R., Baronetti, G. T., and Parera, J. M., J. Catal. 69, 222 (1981).
13. Sad, M. R., Fígoli, N. S., Beltramini, J. N., Jablonski, E. L., Lazzaroni, R. A., and Parera, J. M., J. Chem. Technol. Biotechnol. 30, 374 (1980).
14. Parera, J. M., Verderone, R. J., Pieck, C. L., and Traffano, E. M., Appl. Catal. 23, 15 (1986).
15. Boudart, M., Aldag, A., Benson, J. E., Dougharty, N. A., and Harkins, C. G., J. Catal. 6, 92 (1966).
16. Sachtler, W. M. H., J. Mol. Catal. 25, 1 (1984).
17. Davis, S. M., Zaera, F., and Somorjai, G. A., J. Catal. 77, 439 (1982).
18. Barbier, J., Morales, A., Marecot, P., and Maurel, R., Bull. Soc. Chim. Belg. 88, 569 (1979).
19. Blakely, D. W., and Somorjai, G. A., J. Catal. 42, 181 (1976).
20. Barbier, J., Corro, G., Zhang, Y., Bournville, J. P., and Franck, J. P., Appl. Catal. 16, 169 (1985).
21. Parera, J. M., Verderone, R. J., Pieck, C. L., and Traffano, E. M., Appl. Catal. 23, 15 (1986).
22. Barbier, J., and Marecot, P., J. Catal. 102, 21 (1986).
23. Apesteguía, C. R., Brema, C. E., Garetto, T. F., Borgna, A., and Parera, J. M., J. Catal. 85, 52 (1984).
24. Barbier, J., Marecot, P., Tifouti, L., Guenin, M., and Frety, R., Appl. Catal. 19, 375 (1985).
25. Cini, M., J. Catal. 37, 187 (1975).
26. Foger, K. E., and Anderson, J. R., J. Catal. 54, 318 (1978).
27. Apesteguía, C. R., Garetto, T. F., Brema, C. E., and Parera, J. M., Appl. Catal. 10, 291 (1984).
28. Oudar, J., Catal. Rev. Sci. Eng. 22, 171 (1980).
29. Ponec, V., Prepr. Div. Pet. Chem. Amer. Chem. Soc. 29, 774 (1984).
30. Surjo, I., and Christoffel, E., J. Catal. 60, 133 (1979).
31. Gault, F. G., Amir-Ebrahimi, V., Garin, F., Parayre, P., and Weisang, F., Bull. Soc. Chim. Belg. 88, 475 (1977).
32. Van Senden, J. C., van Broekhoven, E. H., Wriesman, C. T., and Ponec, V., J. Catal. 87, 468 (1984).
33. Coughlin, R. W., Hasan, A., and Kawakami, K., J. Catal. 88, 163 (1984).
34. Franck, J. R., and Martino, G., in "Deactivation and Poisoning of Catalysts" (J. Oudar, and H. Wise, Eds.). Dekker, New York, 1985.
35. Sárkány, A., Lieske, H., Szilágyi, T., and Tóth, L., "Proceedings, 8th International Congress on Catalysis, Berlin, 1984," Vol. 2, p. 613. Dechema, Frankfurt-am-Main, 1984.
36. Bursian, N. R., Zharkov, B. B., Kogan, S. B., Lartovkin, G. A., and Padkletnova, N. M., "Proceedings, 8th International Congress on Catalysis, Berlin, 1984," Vol. 2, p. 481. Dechema, Frankfurt-am-Main, 1984.
37. Lieske, H., Sárkány, A., and Völter, J., Appl. Catal. 30, 69 (1987).
38. Luck, F., Aeiyach, S., and Maire, G., "Proceedings, 8th International Congress on Catalysis, Berlin, 1984," Vol. 2, p. 695. Dechema, Frankfurt-am-Main, 1984.
39. Davis, S. M., and Somorjai, G. A., J. Catal. 65, 78 (1980).