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The Role of Re and S in the Pt–Re–S/Al_2O_3 Catalyst

J. M. PARERA, J. N. BELTRAMINI, C. A. QUERINI, E. E. MARTINELLI, E. J. CHURIN,
P. E. ALOE, AND N. S. FIGOLI

Instituto de Investigaciones en Catálisis y Petroquímica (INCAPE), Santiago del Estero 2654, 3000 Sante Fe, Argentina

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The modifications in catalytic activity, selectivity, and stability when a Pt/Al_2O_3 catalyst is promoted by Re and/or S is studied following several C_6 hydrocarbons reforming. A bifunctional reaction scheme, showing modifications from those previously proposed, is introduced in order to interpret the results. Even the catalyst properties of Pt–Re are not the sum of the ones of Pt and Re, Pt–Re has properties brought by Pt and by Re. The addition of Re and S modifies the hydrogenolysis-dehydrogenation capacity of Pt. Re decreases the dehydrogenating capacity of Pt, reducing coke formation (desired effect) and increasing the formation of lower molecular weight paraffins by hydrogenolysis (undesired effect). The undesired contribution of Re is partially suppressed by the addition of S, that decreases the hydrogenolytic capacity of Pt–Re and increases the production of benzene and coke. This opposite action of Re and S on Pt can be related to the opposite electronic transfers, from Re to Pt and from Pt to S. Both geometrical and electronic effects influence the changes in selectivity.

INTRODUCTION

After the Second World War the catalytic reforming of naphtha was becoming more important. A great improvement in this process was the introduction of the bifunctional catalyst—platinum supported on an acidic oxide, announced by Universal Oil Products Co. in 1949 (*1*). From that moment, the typical monometallic catalyst has been platinum supported on chlorided alumina, Pt/Al_2O_3. The metallic function of the catalyst was later improved by the addition of a second metal; and, in 1968, Chevron (*2*) obtained the patent for the addition of rhenium. The introduction of Re decreases the coke formation on the catalyst and increases the gas production, consequently the selectivity (aromatic yield) is disfavored. To decrease the gas formation, sulfurization of the catalyst is necessary; in this way, a catalyst with improved stability and selectivity is obtained. The catalyst most used today has three components in the metallic function, Pt–Re–S. During commercial operation the metallic function activity can be decreased by addition of S to the feed, and the acidic function can be either increased or decreased by the addition of chlorine or water, respectively.

Because of the commercial success of Pt–Re–S/Al_2O_3 catalyst, there are many studies of this catalyst trying to explain how it works. These studies, reviewed by Sachtler *et al.* (*3–5*), state that the combined action of sulfur and rhenium is essential to modify favorably the conversion of hydrocarbons in catalysts based on platinum. The influence of sulfur on Pt/Al_2O_3 was studied by Haensel (*6*), who, by adding sulfur to the feed, found a stabilizing effect on catalytic activity. Hayes *et al.* (*7*) suggested that a platinum–sulfur complex is formed. Kluksdahl (*2*) stated in his patent that Pt–Re/Al_2O_3 produces an excessive amount of gases caused by a high-metal hydrogenolytic activity which can be diminished by sulfiding the catalyst prior to contact with naphtha. Menon and Prasad (*8*) studied the sulfurization of Pt–Re/Al_2O_3 and Pt/Al_2O_3 during the catalyst reforming of six-carbon-atom hydrocarbons; they observed an increase in the aromatics yield upon sulfurization.

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Bertolacini and Pellet (*9*) ascribed the lower coke formation on Pt–Re/Al_2O_3 when comparing with that on Pt/Al_2O_3, to the ability of Re to destroy cyclopentane which is a coke precursor. A similar explanation is given by Margitfalvi *et al.* (*10*). Another explanation is given by Zhorov *et al.* (*11*), and Burch and Mitchell (*12*), who stated that Pt–Re is more suitable than Pt to hydrogenate cyclopentadiene, avoiding the formation of coke precursors from this diene.

Jossens and Petersen (*13*) reported that the addition of Re to a Pt/Al_2O_3 catalyst affects the metallic function but not the acidic function of the catalyst for the model reaction tested. Presulfurization of the Pt or Pt–Re catalyst altered significantly the reaction rates and deactivation characteristics of the metallic function and they concluded that there is a metal–metal interaction between Pt and Re. This state of close interaction or alloying of the metals is accepted by many authors (*5, 14–18*), although others claim that the metals act separately (*9, 10*). According to the conditions of catalyst preparation the metals can be alloyed or segregated (*19*).

Margitfalvi *et al.* (*10*) studied the influence of Re on the behavior of Pt/Al_2O_3 in *n*-hexane reaction and suggested that Re increases the amount of hydrogen available. Then, hydrogen-consuming reactions, like hydrogenolysis, are increased and coke formation and catalyst deactivation are decreased.

Regarding the degree of oxidation of Re, Charcosset (*20*) stated that reduction by dry H_2 leads to metallic rhenium, although it was shown by EXAFS (*21*) that Re on Al_2O_3 is not completely reduced. Johnson and LeRoy (*22*) suggested that Re is present as ReO_2 associated with the surface of the alumina. They also suggested that the hydrogenation activity of this oxide is the reason for the decrease in coke formation. We shall, however, assume as did Satchler (*3*) that partially oxidized and completely reduced Re atoms coexist on the catalyst surface during its steady state.

The objective of this paper is to study the modifications in catalytic activity, selectivity and stability when Re is added to a Pt/Al_2O_3 catalyst and when the catalysts are sulfurized. Since the main reforming reaction is the transformation of *n*-paraffins into aromatics (dehydrocyclization), *n*-hexane reforming is taken as a test reaction. For comparison, other C_6 hydrocarbons (methylcyclopentane, cyclohexane, and benzene) are also studied.

EXPERIMENTAL

Catalysts

Three catalysts with different metallic components were prepared and tested, sulfurized and nonsulfurized. In all cases, the support was alumina CK 300 from Ketjen Cyanamid (Amsterdam) with a specific surface area of 200 $m^2\ g^{-1}$.

Pt/Al_2O_3 containing 0.3% Pt and 0.9% Cl, was prepared impregnating the support with H_2PtCl_6, according to the method of Castro *et al.* (*23*). Re/Al_2O_3, containing 0.3% Re and 0.89% Cl, was prepared impregnating the alumina with perrhenic acid and using HCl as competitor. Pt–Re/Al_2O_3, containing 0.3% Pt, 0.3% Re, and 0.92% Cl, was prepared by using chloroplatinic and perrhenic acids and HCl as competitor. Samples of the three catalysts were sulfurized up to 0.03% S, following (*24*). Sulfurization was carried out in a H_2/H_2S atmosphere (0.06 molar% H_2S) at 500°C and 1 atm. In order to eliminate reversible sulfur, catalysts were then treated in flowing H_2 at 500°C during 8 h. All the catalysts had the same support, chlorided alumina, and the metallic components were: Pt, Pt–S, Re, Re–S, Pt–Re, Pt–Re–S. There is uncertainty in the oxidation state of rhenium; nevertheless, Re was used as nomenclature for this component.

Feed

n-Hexane, benzene, cyclohexane, and methylcyclopentane, Carlo Erba RPE, were used. All these hydrocarbons were dehydrated by passing through a Molecular Sieves 4 A bed. The sulfur content of the hydrocarbons was below 10 ppm.

Catalysts' Activity and Selectivity Test

The test was performed in a bench-scale equipment described elsewhere (*25*). The equipment was operated at 5 atm, 505°C, H_2 : hydrocarbon molar ratio = 4, and WHSV = 4 h^{-1} during 7 h. For comparison, runs under commercial conditions were also carried out for each catalyst using *n*-hexane as feed. Total conversion was taken as a measure of activity, and the fraction of the converted hydrocarbon transformed into different hydrocarbons (referred to a total conversion) as a measure of selectivity. These properties were calculated from chromatographic analysis data, as previously described (*26*). The carbon content of the catalysts after the runs was determined by combustion.

RESULTS

n-Hexane Reforming

Table 1 shows the products of *n*-hexane reforming on the six catalysts tested. The nonsulfurized catalysts are not initially stable and their activities at 0.5 h are taken as representative of the initial activity. This activity is the result of the first chromatographic analysis performed at 0.5 h, but the activity at zero time could be quite different. Since the catalysts are near stabilization after about 5–6 h of operation, the activity values taken at 5 or 6 h are considered as stable values. The sulfurized catalysts show constant activity values from the beginning of the run; for this reason, only one activity value is reported.

As can be seen, under these operating conditions gases are the main products of *n*-hexane reforming. The nonsulfurized catalysts have a higher C_1 formation by hydrogenolysis which decreases with time because of coke deposition on the metallic function. Sulfurization decreases drastically C_1 formation while the formation of most of the other gases increases. Re is the greatest hydrogenolytic catalyst. As a result of successive hydrogenolysis, Re produced the lowest amount of C_5 and the highest of C_1. The formation of i-C_6 is lower

TABLE 1

n-Hexane Reforming. Products Obtained from *n*-C_6; *n*-C_6 Conversion and Carbon Deposited on the Catalyst

	Catalyst									
	Pt/Al$_2$O$_3$		Pt–S/Al$_2$O$_3$	Re/Al$_2$O$_3$		Re–S/Al$_2$O$_3$	Pt–Re/Al$_2$O$_3$		Pt–Re–S/Al$_2$O$_3$
	0.5 h	5 h		0.5 h	5 h		0.5 h	5 h	
C_1	11.47	6.21	4.96	26.66	22.95	4.54	20.47	13.22	6.35
C_2	16.34	12.20	13.59	23.09	25.28	27.79	16.23	14.12	16.19
C_3	15.72	17.29	17.46	18.24	22.21	22.05	13.14	12.26	15.82
C_4	17.06	21.90	12.60	12.56	14.67	21.92	14.41	15.34	17.36
C_5	6.57	10.02	8.40	3.02	2.26	3.28	6.55	6.13	7.97
i-C_6	22.13	19.37	13.48	7.59	4.78	9.54	13.81	21.88	22.35
MCP	1.57	1.80	1.25	2.63	1.46	3.02	1.10	1.06	1.12
Bz	3.30	6.08	24.81	0.50	0.43	0.93	11.20	10.78	12.05
ArC_7+	5.31	3.48	2.96	0	0	0	2.15	2.06	0.50
Olef. C_5	0.53	0.76	0.49	3.02	3.09	3.86	0.94	1.32	0.79
Olef. C_6	0	0.89	0	2.69	2.87	3.07	0	1.83	0
n-C_6 conv.[a]	90.62	63.00	89.70	47.00	43.50	55.00	91.00	88.00	91.50
% C[b]	—	0.97	1.01	—	0.18	0.12	—	0.45	0.44

Note. Products expressed as molar fraction percentages of the transformed *n*-C_6.

[a] Conversion as wt% of hydrocarbon fed.

[b] Carbon as wt% on catalyst after 7 h operation. $P = 5$ atm, $T = 505$°C, $H_2 : n\text{-}C_6 = 4$, WHSV = 4. $C_{1\ldots6}$, paraffins with 1 . . . 6 carbon atoms; *n*, normal; i, iso; MCP, methylcyclopentane; Bz, benzene; ArC_7+, aromatics of seven and eight carbon atoms, mainly toluene; Olef. C_5, olefins of five carbon atoms; % C, carbon on catalyst.

in Re because i-C_6 is an intermediate product easily hydrocracked. Biloen *et al.* (*5*) found similar results when adding rhenium to platinum supported on SiO_2.

Re is the less active catalyst for *n*-C_6 reforming and produces the lowest amount of benzene and coke, and the highest of MCP. Compared with Pt, Re has a greater hydrogenolytic capacity, thus producing more hydrogenated products (C_1–C_5) and less dehydrogenated ones (coke and benzene).

There is not a remarkable change on the coke-forming capacity of these catalysts after sulfurization. The coke formation on Pt–Re is smaller than half of the one on Pt. Pt/Al_2O_3 produces the largest amount of heavy aromatics and the smallest of olefins. Re/Al_2O_3 is the opposite for both kinds of products and Pt–Re/Al_2O_3 is intermediate. The sulfurization of the three catalysts changes the selectivity; gas formation decreases and, consequently, the aromatization (being the effect more evident on Pt/Al_2O_3) and the isomerization (mainly in Pt–Re/Al_2O_3) increases. The isomerization products are 2- and 3-methylpentane and, in smaller amounts, 2,2- and 2,3-dimethylbutane.

Methylcyclopentane Reforming

MCP reforming on the three catalysts studied is less selective to gases than *n*-C_6 reforming but more selective to benzene and coke, as shown in Table 2. Since MCP produces more coke on the catalysts than *n*-C_6, the catalytic activity is stabilized after 6 h. The comparison of product distribution at initial time (0.5 h) and after 6 h indicates that there is a high initial hydrogenolytic activity commonly associated with metal sites, and that during the run these sites are formed by ring rupture, and they can continue hydrogenolysis to C_1–C_5. Re is the less active for MCP transformations, producing the largest amount of MCPe and the smallest amount of benzene, indicating that

TABLE 2

Methylcyclopentane Reforming. Products Obtained from MCP, MCP Conversion, and Carbon Deposited on the Catalyst

	Catalyst								
	Pt/Al_2O_3		Pt–S/Al_2O_3	Re/Al_2O_3		Re–S/Al_2O_3	Pt–Re/Al_2O_3		Pt–Re–S/Al_2O_3
	0.5 h	6 h		0.5 h	6 h		0.5 h	6 h	
C_1	6.93	5.90	3.70	12.64	6.83	3.02	18.02	6.94	1.80
C_2	5.37	3.60	3.50	14.38	12.34	7.30	13.63	7.76	2.60
C_3	6.18	5.00	4.00	16.15	15.12	15.60	11.45	8.40	3.42
C_4	6.31	4.10	5.00	13.60	7.70	8.30	9.78	8.17	4.03
C_5	5.09	3.02	2.53	7.53	2.57	8.23	5.62	4.30	2.80
n- and i-C_6	17.53	16.15	15.34	18.46	25.25	23.50	12.06	17.07	13.34
MCPe	6.83	6.79	0	7.46	8.02	9.03	3.80	6.62	1.91
CH	2.15	2.20	1.37	0.63	0.84	1.09	1.06	1.64	0.27
CHe	0	0	0	0.62	0.73	1.06	0	0	0
Bz	41.36	49.55	64.36	6.38	6.13	5.43	18.96	32.78	68.61
CP	2.25	3.25	0	2.15	2.92	1.88	5.62	4.51	1.22
CPe	0	0	0	0	1.52	0.40	0	0	0
CPde	0	0	0	0	2.92	2.25	0	0	0
Olef. C_4	0	0	0	0	2.15	8.86	0	0	0
Olef. C_5	0	0.44	0	0	0.84	0.72	0	0.80	0
Olef. C_6	0	0	0	0	4.12	3.33	0	1.01	0
MCP conv.[a]	48.62	30.00	57.00	23.80	20.00	23.00	62.60	32.00	50.00
% C[b]	—	4.54	6.32	—	1.64	1.53	—	2.13	3.70

Note. Same operational conditions and symbols as Table 1. MCPe, methylcyclopentene; CH, cyclohexane; CHe, cyclohexene; CP, cyclopentane; CPe, cyclopentene; CPde, cyclopentadiene.

TABLE 3

Cyclohexane Reforming. Products Obtained from CH, CH Conversion, and Carbon Deposited on the Catalyst

	Catalyst					
	Pt/Al_2O_3	Pt–S/Al_2O_3	Re/Al_2O_3	Re–S/Al_2O_3	Pt–Re/Al_2O_3	Pt–Re–S/Al_2O_3
C_1	0.21	0.22	9.20	5.16	29.00	0.40
C_2	0.42	0.47	15.21	7.80	8.20	0.52
C_3	0	2.40	10.89	11.78	3.51	0.39
C_4	0	1.16	10.40	8.81	2.40	0.32
C_5	0	0.60	4.08	7.17	0.79	0
n-C_6	0.21	0.65	2.80	10.31	0	0.96
i-C_6 (2MP + 3MP)	0	0.79	1.26	4.74	0	0.11
MCP	0	0	26.41	12.75	0	0
MCPe	0	0	5.44	3.97	0	0
Bz	99.16	93.71	9.52	22.04	56.10	97.30
CP	0	0	3.44	4.47	0	0
CPe	0	0	0.69	0.50	0	0
Olef. C_5	0	0	0.66	0.50	0	0
CH conv.^{a}	100	100	30	32	100	100
% C^b	0.30	0.50	0.50	0.50	0.13	0.39

Note. Same operational conditions and symbols as Tables 1 and 2.

for Re/Al_2O_3 the passage of a five-carbon ring to a six-carbon ring is very difficult. Also on this catalyst, the passage from unsaturated products to more unsaturated coke precursors is difficult because in the reactor effluent there are olefins, MCPe, CPe, CPde (which are absent on the other catalysts) and less coke is produced. The sulfurization of Pt/Al_2O_3 and Pt–Re/Al_2O_3 increases greatly the productions of benzene and coke. Pt/Al_2O_3 produces more benzene than Pt–Re/Al_2O_3, but when the catalysts are sulfurized the increase in selectivity towards benzene is greater on Pt–Re/Al_2O_3. This increment corresponds to a greater decrease in hydrogenolysis.

Cyclohexane Reforming

Total conversion of CH is obtained on Pt/Al_2O_3, Pt–Re/Al_2O_3 and its sulfurized forms, being the Re/Al_2O_3 activity smaller as shown in Table 3. Since the catalysts are stable during this reaction, only one value is shown in Table 3. Pt/Al_2O_3 is a very good dehydrogenating catalyst and transforms nearly all CH into benzene. By means of sulfurization this selectivity decreases owing to the decrease in the rate of dehydrogenation of Pt. This decrease allows the cracking of CH or of some desorbed intermediates, thus increasing C_6 and C_3 formation. Maslyanskii *et al.* (*27*) have demonstrated that sulfurization of Pt/Al_2O_3 increases its stability but decreases its activity for dehydrogenation of CH, and Sterba and Haensel (*28*) quoted that sulfur poisoning of CH reaction on Pt/Al_2O_3 produces a reduction in the conversion of CH into benzene.

Re/Al_2O_3 produces five-carbon-atom-ring compounds which are not produced by the other catalysts. Re/Al_2O_3 has a higher hydrogenolytic activity but its dehydrogenating activity to form benzene from CH is not high compared with the support acid activity for isomerization of six- to five-carbon rings, as was also found by Kozlov *et al.* (*29*). The catalytic activity of Re/Al_2O_3 is small and although CH dehydrogenation seems to be an easy reaction, more gases than benzene are produced. Pt–Re/Al_2O_3 produced more gases (C_1–C_4) than Pt/Al_2O_3

TABLE 4

Benzene Reforming. Percentage Molar Fraction of Products at the Outlet and Carbon Deposited on the Catalysts

	Catalyst					
	Pt/Al_2O_3	$Pt-S/Al_2O_3$	Re/Al_2O_3	$Re-S/Al_2O_3$	$Pt-Re/Al_2O_3$	$Pt-Re-S/Al_2O_3$
C_1-C_5	8.04	4.57	0.49	0.17	75.79	2.07
i- and n-C_6	0.45	0.69	0	0	0.56	0.91
Bz	91.51	94.83	99.51	99.83	23.65	97.02
% C^b	0.20	0.38	0.12	0.10	0.13	0.18

Note. Same operational conditions and symbols as Tables 1 and 2.

and, consequently, less benzene. Sulfurization increased benzene formation in Re/Al_2O_3, and in a noticeable extension in $Pt-Re/Al_2O_3$ with a great decrease in gas formation in the last catalyst.

Like a difference with n-C_6 and MCP, CH produces more coke on Re/Al_2O_3 than on Pt/Al_2O_3 and $Pt-Re/Al_2O_3$; it may be caused by the presence of five-carbon-ring compounds which are greater coke producers than the six-carbon-ring compounds (*29*).

Benzene Reforming

The results are shown in Table 4. Benzene (Bz) is very stable under reforming conditions on Pt/Al_2O_3 and Re/Al_2O_3 with the formation of hydrogenolysis and hydrocracking products. Re/Al_2O_3 is the less active catalyst in benzene transformation as well as it is the less active in Bz formation from the other hydrocarbons studied. $Pt-Re/Al_2O_3$ is the catalyst that produces the largest amount of lower molecular weight products (C_1–C_5) from Bz. This phenomenon explains why CH produces a great amount of gases on $Pt-Re/Al_2O_3$ (Table 3). These products can be formed because of hydrocracking or hydrogenolysis of CH or of its main product, benzene. Table 4 shows that Bz rupture is decreased by sulfurization of $Pt-Re/Al_2O_3$, indicating that it is mainly a hydrogenolysis on the metal sites.

Runs with n-Hexane under Normal Commercial Pressures

To verify the above mentioned results, several runs were performed feeding n-C_6 to Pt/Al_2O_3 at 30 atm (the commercial pressure for this monometallic catalyst) and $H_2 : n\text{-}C_6 = 8$, and to $Pt-Re/Al_2O_3$ at 15 atm (the commercial pressure for this bimetallic catalyst) and $H_2 : n\text{-}C_6 = 4$, and also to their sulfurized forms. The increase in pressure produces a remarkable increase in hydrogenolysis and a decrease in i-C_6, MCP and Bz formation, as can be seen by compar-

TABLE 5

n-Hexane Reforming on Monometallic Catalyst under Normal Commercial Pressure

	Catalyst		
	Pt/Al_2O_3		$Pt-S/Al_2O_3$
	0.5 h	3 h	
C_1	50.58	33.03	24.02
C_2	39.87	24.25	19.31
C_3	8.05	21.92	22.79
C_4	1.18	8.80	14.60
C_5	0.26	5.44	12.35
i-C_6	0	5.83	5.76
MCP	0	0.10	0.11
Bz	0.06	0.63	1.02
n-C_6 conv.^{a}	99.94	96.87	98.03
% C^b	—	0.17	0.20

Note. $P = 30$ atm, $T = 505°C$, WHSV = 4, $H_2 : n\text{-}C_6 = 8$. Same symbols as Tables 1 and 2.

ing Tables 5 and 6 with Table 1. Under commercial pressures and at the beginning of the run, most of the product is C_1. The n-C_6 conversion remains very high but the selectivity changes drastically during the run, decreasing C_1 and increasing the other gases, i-C_6, MCP, and Bz. The activity and selectivity of the sulfurized catalysts are more stable and the selectivity follows the same trend as the one of the nonsulfurized catalysts after some period of time.

Under the normal commercial pressures, because of the higher hydrogen pressure, heavy aromatics (ArC_7+) and olefins are not detected and coke deposition is smaller than at 5 atm. Although the hydrogen pressure is lower for Pt–Re/Al_2O_3, it produces less coke than Pt/Al_2O_3 and because of the lower operating pressure, Pt–Re/Al_2O_3 produces more Bz than Pt/Al_2O_3.

To visualize the influence of the addition of Re and S to Pt and the influence of pressure, the total transformation of n-C_6, as a function of time, is given in Fig. 1. It can be seen that because of the lower hydrogen pressure, the catalysts are less active and stable at 5 atm. In all the cases, sulfurization produces a catalyst with an initial activity similar or smaller than the one of the unsulfurized catalyst. But the activity of the sulfurized catalyst is more stable. The sulfurization produces, from the beginning, a stabilization similar to the one obtained on the unsulfurized catalysts after several hours.

TABLE 6

n-Hexane Reforming on Bimetallic Catalyst under Normal Commercial Pressure

	Catalyst		
	Pt–Re/Al_2O_3		Pt–Re–S/Al_2O_3
	0.5 h	3 h	
C_1	77.81	67.44	18.07
C_2	10.02	15.27	20.16
C_3	4.41	6.98	18.52
C_4	3.32	4.32	16.51
C_5	2.10	2.91	11.16
i-C_6	1.06	1.35	9.70
MCP	0.04	0.05	0.24
Bz	1.24	1.68	5.64
n-C_6 conv.[a]	98.21	94.00	98.32
% C[b]	—	0.10	0.12

Note. P = 15 atm, T = 505°C, WHSV = 4, $H_2 : n\text{-}C_6$ = 4. Same symbols as Tables 1 and 2.

DISCUSSION

Different reaction paths have been proposed to explain the transformation of the six-carbon-atom hydrocarbons in reforming. The classical reaction scheme for the bifunctional catalyst for Pt/Al_2O_3 was proposed by Mills *et al.* (*30*) in 1953. The same mechanism was extended to Pt–Re/Al_2O_3 by Selman and Voorhies (*31*). In this mechanism, the passage of n-C_6 to Bz includes the metal- and acid-catalyzed steps being n-hexene, MCP, MCPe, and CHe intermediate products. Some other mechanisms were proposed. Christoffel *et al.* (*32*) stated that dehydrocyclization of n-C_6 is very complicated. There are successive and parallel reactions occurring on both the metallic and the acidic functions, with different steps that can be controlling. Paál and Tetényi (*33*) described their results for the dehydrocyclization of n-C_6 over Pt, Ni, and metal oxides by analogous mechanisms via the intermediates hexene–hexadiene–hexatriene. Zabotin and Levinter (*34*) postulated that the aromatization of n-C_6 occurs on the metallic active centers of the catalyst via MCP as intermediate product. According to Maggiore *et al.* (*35*), the aromatization of n-C_6 and MCP involves different intermediates: the transformation of n-C_6 into Bz is carried out through a 1-6 ring closure, while MCP forms benzene through MCPe as an intermediary.

In order to interpret our results, a modification of the classical bifunctional reaction scheme proposed by Mills *et al.* (*30*) will be used. The dehydrocyclization and the isomerization of paraffins can be performed by this bifunctional mechanism and by another one including only the metallic function. According to Sinfelt (*36*), under commer-

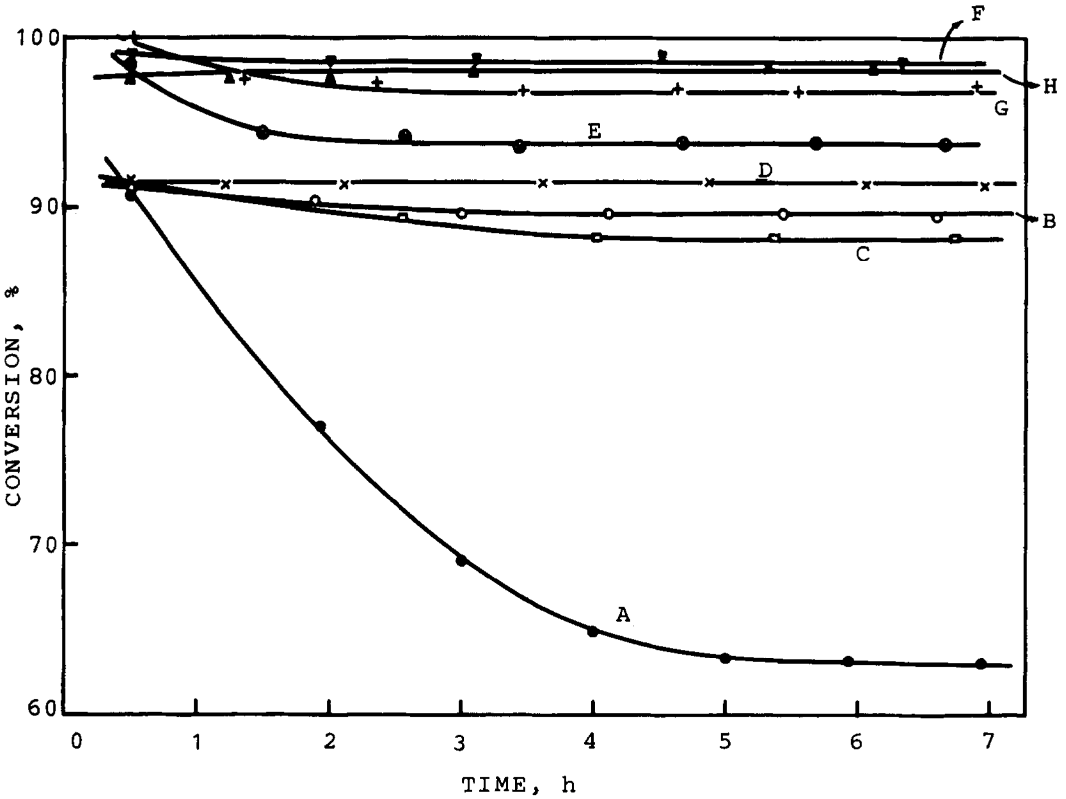

FIG. 1. Reforming of *n*-hexane. $T = 505°C$, WHSV = 4. Pressure = 5 atm, $H_2 : n\text{-}C_6 = 4$: (A) Pt/Al_2O_3; (B) $Pt\text{-}S/Al_2O_3$; (C) $Pt\text{-}Re/Al_2O_3$; (D) $Pt\text{-}Re\text{-}S/Al_2O_3$. Pressure = 15 atm, $H_2 : n\text{-}C_6 = 4$: (E) $Pt\text{-}Re/Al_2O_3$; (F) $Pt\text{-}Re\text{-}S/Al_2O_3$. Pressure = 30 atm, $H_2 : n\text{-}C_6 = 8$: (G) Pt/Al_2O_3; (H) $Pt\text{-}S/Al_2O_3$.

cial reforming conditions dehydrocyclization and isomerization on the metallic sites are negligible compared with the bifunctional mechanism. Vestiges of S are enough to poison the reaction mechanisms involving only the metal. These are the reasons why only the bifunctional mechanism will be considered here. Figure 2 shows the scheme which follows the same pattern as the one of Mills *et al.* (*30*), presenting the following differences: (a) the hydrogenolysis of n-C_6 and i-C_6 is added (reactions 1 and 4), these reactions consisting of C–C bond ruptures with hydrogenations, giving more hydrogenated products, and going upward in the scheme; (b) the hydrogenolysis of MCP to form n- and i-C_6 (reaction 7) and the following hydrogenolysis to C_1–C_5 paraffins are added; (c) the CH hydrogenolysis (reaction 14) is added; (d) the possibility of a passage from the five- to the six-carbon-atom ring by isomerization of MCPde to produce CHde (reaction 13) is introduced; (e) MCPde produces coke precursors which, by further dehydrogenations and condensations, produce coke (reactions 10 and 11). The importance of MCPde in coke formation was stated by several authors (*37–39*) and Marin and Froment (*40*) proposed very interesting condensation reactions of MCPde.

There are other reactions that can be added; for instance, the dehydrogenation of *n*-hexene to *n*-hexadiene on the metallic site, which can then produce MCPe on the acid sites, as proposed by Sinfelt (*41*).

As mentioned in the Introduction, it is accepted that part of the Pt and Re species are in a state of close interaction or alloyed. Then the catalytic activity of the bimetallic catalyst should not be the addition of the activities of both monometallics. Nevertheless, according to our results, Re contributes with its great hydrogenolytic activity, and Pt with its great aromatizing and coke-forming capacity. The main difference between Pt and Re is the greater dehydrogenating activity of Pt.

Introducing the results of the reforming of *n*-C_6 and MCP in the scheme of Fig. 2, it can be seen that Pt is more suitable than Re to produce deeper dehydrogenations, going down in the scheme and producing more coke and Bz. Meanwhile, Re is more adequate to form gases. The C_1–C_5 distribution shows that Re forms lighter gases, which are products of successive hydrogenolysis and richer in hydrogen. In some cases, the C_5 concentration is higher than the C_1 concentration, and this cannot be explained if C_1 and C_5 were only produced by C_6 rupture; consequently, other sources of C_1 and C_5 could be important. According to Sterba and Haensel (*28*), a propyl carbenium ion produced by acidic cracking of *n*-C_6 can react with *n*-C_6 to form a nine-carbon chain that can produce C_5 and C_4 by hydrocracking. According to Margitfalvi *et al.* (*42*), C_1 and other paraffins can be produced by hydrogenolytic depolymerization of the carbonaceous deposit. These reactions make it impossible to establish a simple relationship between C_1–C_5 products.

Re has a lower dehydrogenating capacity than Pt. Re/Al_2O_3 produces a higher amount of MCP in the *n*-C_6 reforming, indicating the difficulty of Re to transform MCP into more dehydrogenated products. Because of this low dehydrogenation capacity of Re, its MCP reforming product contains

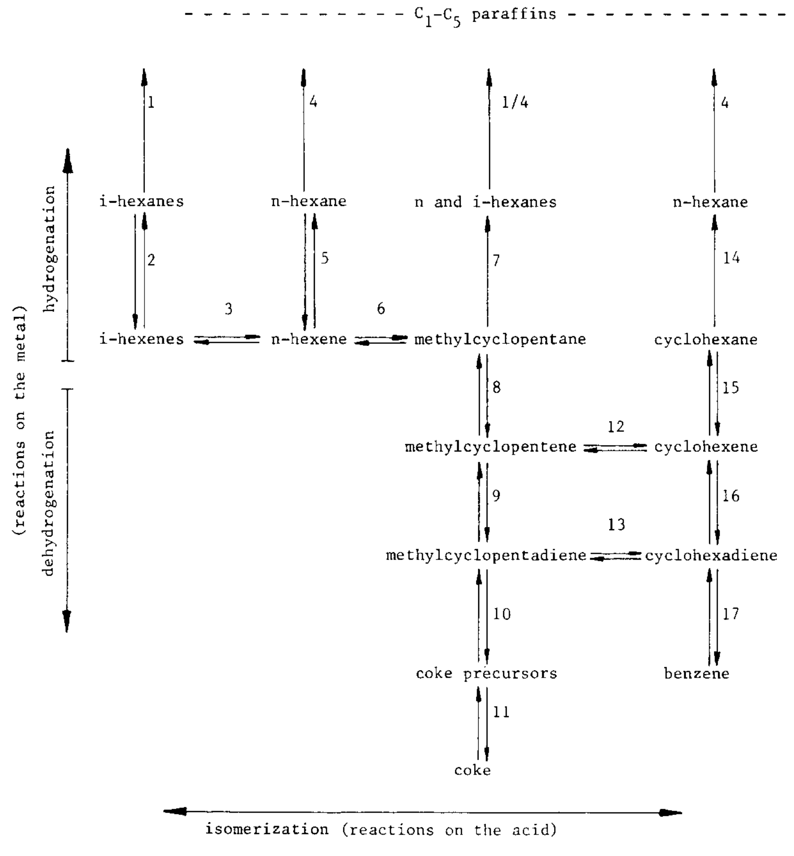

FIG. 2. Bifunctional reaction scheme for reforming of six-carbon-atom hydrocarbons.

a larger proportion of MCPe than Bz, a result similar to the one of Jossens and Petersen (*13*). The product also contains CHe, and this is different than the cases of Pt and Pt–Re where CHe is not detected because it is rapidly dehydrogenated to Bz. When Re is poisoned by coke (5-h run) or by S (sulfurization), the hydrogenolysis-dehydrogenation capacity is decreased. The formation of the lighter and more hydrogenated products of hydrogenolysis, C_1–C_5, is decreased and the formation of the intermediate products of hydrogenolysis, *n*-C_6 and i-C_6, is increased. At the same time, there are more products of intermediate unsaturation; MCPe and CHe increase, CPe, CPde, and olefins appear, and there is no increase of Bz formation. The behavior is different with Pt/Al_2O_3 and Pt–Re/Al_2O_3: the poisoning by coke or S decreases hydrogenolysis and the dehydrogenation capacity allows to increase the selectivity to Bz. The low transformation of MCP into Bz on Re/Al_2O_3 indicates that the passage from a five- to a six-carbon-atom ring is difficult on this catalyst. The reaction is an isomerization controlled by the acid function of the catalyst that, in our case, is the same for all the catalysts. Then, the difficulty must be due to the metallic function.

According to Brandenberger *et al.* (*43*), the MCP ring opening can be catalyzed by the metal and by the acid sites; but during the reaction, the acid sites are inhibited by MCPe, acting only the metal sites. Similarly, Sterba and Haensel (*28*) stated that this hydrogenolysis to *n*- and i-C_6, and from them to C_1–C_5, is mainly catalyzed by the metal and less catalyzed by the acid sites. This point was verified by Martins and Nogueira (*44*), and we interpret it by the introduction of reactions 7, 1, and 4 in the scheme of Fig. 2.

The products of reforming depend on a combination of thermodynamics and kinetics (catalysts) influenced by the operational conditions. Some thermodynamic equilibrium constants at 500°C, a typical temperature in catalytic reforming, calculated by the method of Van Krevelen (*45*), are given in Table 7. Values correspond to the different interconversions of hydrocarbons presented in Fig. 2, taken under standard conditions of 1 atm.

If all the passage from the five- to the six-carbon-atom ring were produced by means of reaction 12, in the case of Pt/Al_2O_3 and Pt–Re/Al_2O_3, the acidic function would transform a great amount of MCPe in CHe, which is not detected because it is immediately dehydrogenated producing high Bz concentrations. Meanwhile, the same acidic function in Re/Al_2O_3 should be able to transform little MCPe, even when a higher concentration of MCPe is present and there is no thermodynamic limitation. In order to explain this problem we suppose that most of the passage from a five- to a six-carbon ring occurs according to reaction 13. Since Re has a low dehydrogenating capacity, a very small amount of MCPe is transformed into MCPde (reaction 9), and then reactions 13 and 10 are not important. Also the small amount of CHe produced on Re/Al_2O_3 is not easily dehydrogenated to Bz and it can be detected (Table 2).

TABLE 7

Thermodynamic Equilibrium Constants at 500°C for Reactions of the Bifunctional Scheme Calculated According to (*45*)

Reaction	*K*
n-Hexane $\leftrightarrows$ *n*-hexene + H_2	8.40×10^{-2}
n-Hexene $\leftrightarrows$ i-hexene	3.85
i-Hexene + H_2 $\leftrightarrows$ i-hexane	2.05
n-Hexane + H_2 $\leftrightarrows$ C_1 + C_5	4.44×10^{3}
n-Hexane + H_2 $\leftrightarrows$ 2 C_3	6.86×10^{3}
n-Hexene $\leftrightarrows$ MCP	11.87
MCP $\leftrightarrows$ CH	1.66×10^{-1}
MCP + H_2 $\leftrightarrows$ *n*-hexane	1.00
CH + H_2 $\leftrightarrows$ *n*-hexane	6.03
MCP $\leftrightarrows$ MCPe + H_2	1.27×10^{-1}
MCPe $\leftrightarrows$ CHe	3.33×10^{-1}
MCPe $\leftrightarrows$ MCPde + H_2	4.20×10^{-2}
MCPde $\leftrightarrows$ CHde	3.31×10^{-1}
CH $\leftrightarrows$ CHe + H_2	2.55×10^{-1}
CHe $\leftrightarrows$ CHde + H_2	4.20×10^{-2}
CHde $\leftrightarrows$ Bz + H_2	6.36×10^{7}

On the other hand, on Pt/Al_2O_3 and Pt–Re/Al_2O_3, MCPe is not detected because it is dehydrogenated into MCPde which is immediately transformed without desorption into CHde and Bz or into coke. Christoffel *et al.* (*32*), reforming MCP on Pt(0.6%)/Al_2O_3, found MCPe and stated that reaction 12 is rate controlling because CHe and CHde do not appear and Bz is produced. But similarly MCPe will be accumulated if reaction 9 is the rate controlling one.

Thermodynamically, reactions 12 and 13 have the same possibility. MCPde is more reactive than MCPe because of the great reactivity of the two conjugate double bonds; then, it is possible to suppose that reaction 13 is more rapid than 12. This means that isomerization from the five- to the six-carbon-ring occurs mainly by means of reaction 13, and that the low dehydroisomerization of MCP on Re/Al_2O_3 is not due to a low isomerization, but to a low dehydrogenation activity. The controlling step is not 12, but 9.

Regarding the reforming of CH, owing to the great dehydrogenation capacity of Pt, CH is adsorbed and rapidly dehydrogenated into Bz; the intermediates CHe and CHde are not detected, as cited by Germain (*46*). When the hydrogenolysis-dehydrogenation capacity of Pt is decreased by sulfurization, some intermediates can be desorbed and hydrogenolyzed to C_1–C_6 paraffins, as shown in Table 3. Re/Al_2O_3 is not very active for CH aromatization; Re is better for hydrogenolysis (reactions 14 and 4) than for dehydrogenation (Bz formation). The low dehydrogenation activity allows the desorption of CHe and CHde and its hydrocracking and isomerization to MCPe and MCPde, respectively. The MCPde produced is not desorbed; it is hydrogenated to MCPe and then to MCP. When Re is sulfurized, the hydrogenolysis reactions, as the production of C_1–C_5 and of MCPe and MCP, are decreased, thus producing a change in selectivity that favors the dehydrogenation of CH to Bz.

The transformation of a six-carbon ring into a five-carbon ring on Re is easier than the transformation of a five-carbon ring into a six-carbon ring. This is so because CH can be dehydrogenated to CHe and CHde and CHde can be transformed into five-carbon-ring compounds, whereas MCP is difficult to be dehydrogenated to MCPe and MCPde. Dehydrogenation on Re advances more on the six-carbon ring than on the five-carbon ring.

The best catalyst for *n*-C_6 reforming will be the one with the highest values in the rates of the reactions 5, 6, 8, 9, 13, and 17, the other reactions being negligible. The formation of coke and Bz depends on the availability of MCPe and mainly, of MCPde, and on the relative rates of reactions 9, 10, 16, and 17 on the metallic sites, and of reactions 12 and 13 on the acid sites. Promoting Pt with Re and/or S, reactions 9, 10, 16, and 17 and the availabilities of MCPe and MCPde can be modified, but reactions 12 and 13 are not altered.

Pt is a great dehydrogenating catalyst and dehydrogenates MCP to MCPe. By reaction 12 some MCPe can produce CHe which immediately produces Bz. The most part of MCPe forms MCPde because 9 is more rapid than reaction 12 on this catalyst. The MCPde produced immediately disappears by means of reactions 10 and 13. Re has a less dehydrogenating activity; the rate of reaction 9 is similar to the one of reaction 12, and MCPe is accumulated. The small amount of CHe produced is similarly accumulated because reaction 16 is slow. The small formation of MCPde on Re produces little coke and Bz. On Pt–Re and Pt the availability of MCPde is increased by sulfurization, increasing the formation of coke and Bz. Reaction 10 is smaller on Pt–Re than on Pt, Pt–Re producing less coke.

In our experiments Pt–Re/Al_2O_3 produced less coke than Pt/Al_2O_3 with all the reactants. These experiments were carried out at 5 atm, but also under the commercial pressure for each catalyst (Tables 5 and 6), Pt–Re/Al_2O_3 produced less coke, in spite of the lower hydrogen pressure for this catalyst. These results are not in agreement with those of Sachtler (*3*), who stated that both catalysts produce equal amounts of coke.

Less than 1% of the catalyst surface is covered by the metallic component; nevertheless it governs the system because most of the reactions start on the metal. Then, changing the metal composition all the system is changed. The variations are somewhat obscured because the metal reaction product modifications also produce changes in the steps performed on the acid sites. Under commercial conditions, where both functions act simultaneously, it is not easy to study the differences produced by promoting the metal as it is in the case of experiments at low temperature where the metallic function acts alone. Nevertheless observing the reaction products some conclusions can be drawn.

In the promotion of Pt with Re and/or S, the more striking changes on selectivity occur in hydrogenolysis and in coke formation.

Regarding Pt, it is generally accepted that hydrogenolysis is a "demanding reaction" (*47*), i.e., an ensemble of many atoms is needed to have an active site.

The ensemble of metal atoms must be able to adsorb strongly the hydrocarbon molecule producing loss of hydrogen and the C–C bond break, giving two separate residues. A high hydrogenation capacity is also necessary to hydrogenate the two separate parts that on desorption will produce the two lighter molecules.

By sulfurization of Pt or by alloying it with inactive atoms (Au, Sn, Pb), it is accepted (*48*) that the number of large ensembles of adsorbing surface atoms is drastically reduced (geometrical effect), reducing in the same way the hydrogenolysis activity. Another possibility is the existence of an electronic effect. There is an electronic transfer from Pt to S (*49*) which should influence the chemical bonding reactants–Pt, modifying the catalytic activity of Pt. Perhaps both effects (electronic and geometrical) act together producing the great decrease of hydrogenolysis.

Regarding Pt–Re/Al_2O_3, Re and Pt can be in separate phases or alloyed. Re is very active for hydrogenolysis and, like in the case of Pt, a great ensemble of atoms could be needed for the reaction. If Re and Pt are separated each metal will behave independently and the high hydrogenolysis activity of Pt–Re, compared with the one of Pt, is due to the presence of reduced state or partially oxidized Re. If all the Pt and Re were alloyed, the poisoning of the hydrogenolysis could be due to geometrical or electronic effects. In the case of geometrical effect, as Pt and Re atoms are mixed and Re is not inert, but it is more active than Pt for hydrogenolysis, the ensemble would be a group of atoms including both metals. The hydrogenolytic capacity will be intermediate to the ones of Pt and Re. By sulfurization a strong Re–S bond is formed and the Pt–Re ensemble is destroyed because Re–S acts as an inert diluent (3). A new explanation of demanding reaction was introduced by Blakely and Somorjai (*50*). According to them, the hydrogenolytic sites on Pt are kinks, and these sites are the places preferred by the atoms of the second metal or the atoms of S, poisoning selectively the hydrogenolysis in this way.

The electronic effect can explain the opposite effects of Re and S regarding the hydrogenolysis-dehydrogenation capacity of Pt. There is an electron transfer from Re to Pt in Pt–Re/Al_2O_3 (*51*) and, on the contrary, the addition of S to Pt causes an electronic transfer from Pt to S (*49*).

Regarding coke formation, if Re and Pt were acting independently on Pt–Re/Al_2O_3, Pt would produce the same amount of coke on Pt/Al_2O_3 or on Pt–Re/Al_2O_3 because both have the same Pt concentration. But since the amount of coke on Pt–Re/Al_2O_3 is approximately half, some interaction exists.

According to Bertolacini and Pellet (*9*) the lower coke formation is due to higher destruction of MCP by Pt–Re/Al_2O_3. But by sulfurization, $Pt-Re-S/Al_2O_3$ has a smaller MCP hydrogenolysis than Pt/Al_2O_3 but also a smaller coke formation (Table 2) which is not in agreement with the idea less MCP hydrogenolysis produces more coke. Undoubtedly the high hydrogenolytic activity of Pt–Re destroys coke precursors, but it is not the only reason for coke decrease; it is a consequence of the small dehydrogenation capacity of Pt–Re. Also the destruction of MCP is not convenient because MCP is a necessary intermediate in the transformation of n-C_6 into Bz.

Platinum is the key element in the aromatic production and its hydrogenation capacity is promoted by Re and S. These promoters change the catalyst selectivity, giving different products which act on the rate of catalyst deactivation. The role of Re is to decrease the dehydrogenation capacity of Pt decreasing the coke formation (desired effect) and increasing the formation of lower molecular weight paraffins by hydrogenolysis (undesired effect). The undesired contribution of Re is partially suppressed by the addition of S. The role of S is the selective decrease of the hydrogenation capacity of Pt–Re, decreasing the production of gaseous paraffins and increasing the production of Bz and coke. But still the amount of coke in Pt–Re–S is smaller than the one on Pt/Al_2O_3. $Pt-Re-S/Al_2O_3$ is the best combination for selectivity (Bz) and stability (less coke).

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