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The Effects of Rhenium and Sulfur on the Activity Maintenance and Selectivity of Platinum/Alumina Hydrocarbon Conversion Catalysts

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During *n*-hexane conversion at atmospheric pressure and 500°C, coimpregnated PtRe/Al_2O_3, unlike a physical mixture of Pt/Al_2O_3 and Re/Al_2O_3, displays a remarkably high selectivity for cracking which is characteristic of alloy formation. Presulfidation alters significantly the activities and selectivities of Pt/Al_2O_3 and PtRe/Al_2O_3. Hydrogenolysis is reduced for both catalysts. The rate of activity decline is also reduced for PtRe/Al_2O_3. The effects of poisoning by sulfur and deactivation by carbonaceous deposits are in competition such that after some time on stream sulfided PtRe/Al_2O_3 displays a significantly higher activity than unsulfided PtRe/Al_2O_3. Conversely, sulfided Pt/Al_2O_3 remains less active than unsulfided Pt/Al_2O_3 for the full duration (25 h) of the reaction experiments. Another remarkable effect of presulfiding PtRe/Al_2O_3 is that dehydrocyclization is enhanced for *n*-heptane conversion but not for *n*-hexane conversion. We conclude that the combined action of Re and S is responsible for the differences in performance between sulfided Pt/Al_2O_3 and PtRe/Al_2O_3. Sulfur is preferentially adsorbed on the Re atoms of PtRe alloy particles. Adsorbed sulfur on both Pt/Al_2O_3 and PtRe/Al_2O_3 causes changes in the selectivity patterns which are characteristic of a reduction in the size of Pt ensembles. The superior activity maintenance of PtRe(S)/Al_2O_3 is consistent with a tentative model which assumes that adsorbed sulfur, S_{ads}, fixed on Re impedes the reorganization of hydrocarbonaceous fragments into pseudographitic entities which cause irreversible deactivation of the Pt function by carbonaceous deposits.

INTRODUCTION

The superiority of PtRe/Al_2O_3 to Pt/Al_2O_3 for the catalytic reforming of petroleum naphtha has been well demonstrated (*1*, *2*). PtRe/Al_2O_3 catalysts show a much improved activity maintenance and a higher reformate yield under steady-state conditions of industrial reforming. Despite many reported studies, the exact role of rhenium in bringing about these advantages remains a topic of considerable discussion. The physical and chemical nature of rhenium in PtRe/Al_2O_3 has been investigated by several researchers who have arrived, however, at contradictory conclusions. It is claimed that in reduced PtRe/Al_2O_3: (a) rhenium is not completely reduced and is present as a highly dispersed oxide (Re^{4+}) which modifies the alumina support (*3*–*5*); and (b) rhenium is completely reduced to the zero-valent state and most of it intimately interacts with platinum to form an alloy or a bimetallic cluster through which the catalytic properties of platinum are modified (*6*–*15*). It has also been observed that a high degree of heterogeneity of metal states is present in the platinum–rhenium system (*16*). The degree of reduction of the rhenium on alumina depends on the conditions of drying and/or calcination and the moisture present during reduction. We prefer to avoid apodictic assumptions and accept that Re^{4+} ions, unalloyed Pt^0 atoms, unalloyed Re^0 atoms, and PtRe alloy particles exist simultaneously on the surface of a working catalyst. In this paper the term "alloy particles" is meant to also include bimetallic clusters of compositions deviating from the thermodynamically stable

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macroscopic phases. The problem to be addressed by experimental research then is which of these species contributes to the overall catalytic action and how it can affect the decline in activity.

In industrial practice, the beneficial properties of $PtRe/Al_2O_3$ are observed only in the presence of a nonnegligible fraction of adsorbed sulfur. Several studies with model compounds have shown that the reaction rates and selectivity patterns of the PtRe/support system are significantly changed by sulfidation (*17*–*22*). Therefore, it appears realistic to assume that the catalyst system of interest is actually a $PtRe(S)/Al_2O_3$ system, as suggested previously (*18*, *36*).

Catalytic comparisons of Pt/Al_2O_3 and $PtRe/Al_2O_3$ were carried out under industrial reforming conditions by Bertolacini and Pellet (*23*). These authors found that in the reforming of a naphtha feed, liquid products of the same octane ratings were obtained with a coimpregnated $PtRe/Al_2O_3$ catalyst and an intimate physical mixture of Pt/Al_2O_3 and Re/Al_2O_3 catalysts. As the activity decline curves were not significantly different for the coimpregnated and physically mixed catalysts, these authors reasoned that chemical interaction of Pt and Re appears not to be necessary. Their interpretation proposed that rhenium is able to intercept potential coke precursors such as cyclopentane by catalyzing their hydrogenolysis to harmless small molecules. The implication that rhenium should thus reduce the *quantity* of coke deposited is, however, at variance with the results reported by Carter *et al.* (*24*) who found that only the *quality* of coke is different. Indeed, it was observed (*25*) by IR absorption spectroscopy that substantially less carboxylic carbon was formed in the carbonaceous deposits in the presence of rhenium than in its absence. There is also ample evidence (*26*–*29*) that Re/Al_2O_3 is less active than Pt/Al_2O_3 in the ring opening and general hydrogenolysis of cyclopentanoic molecules.

In the absence of a consensus on these important issues, it appeared to us that a systematic study of the effects on catalytic performance exerted by the addition of rhenium and sulfur to Pt/Al_2O_3 would be highly desirable. The main objectives of the present work are therefore: (a) to ascertain which of the species mentioned above is dominantly responsible for the differences in catalytic performance between Pt/Al_2O_3 and $PtRe/Al_2O_3$; and (b) to identify the cause of the enhanced activity maintenance of $PtRe/Al_2O_3$. Industrial reforming catalysts contain substantial amounts of chlorine which enhances the acidity of acid sites and may also play a significant role in the metal/support interaction. In order to elucidate the effects of adding rhenium and sulfur to Pt/Al_2O_3, we decided to confine the present study to chlorine-free catalysts so that the effect of chlorination can be addressed at a later date in a separate study. We chose to use well-defined model compounds—*n*-hexane, *n*-heptane, and methylcyclopentane—for our catalytic tests carried out under standardized conditions. Pt/Al_2O_3, a physical mixture of Pt/Al_2O_3 and Re/Al_2O_3, and $PtRe/Al_2O_3$ prepared by coimpregnation were investigated. The effects of sulfidation on the performances of Pt/Al_2O_3 and $PtRe/Al_2O_3$ were compared. Hydrocarbon conversion on $PtRe/SiO_2$ of negligible acidity was also studied to ascertain the importance of monofunctionally catalyzed reactions.

EXPERIMENTAL

Materials. Catalysts were prepared using the method of incipient wetness by impregnating either SiO_2 (Davison 62, surface area 285 $m^2\ g^{-1}$, pore volume 1.2 $cm^3\ g^{-1}$, mesh size 60–80) or γ-Al_2O_3 (Cyanamid PHF, surface area 160 $m^2\ g^{-1}$, pore volume 0.5 $cm^3\ g^{-1}$, mesh size 60–80) with aqueous solutions of $Pt(NH_3)_4(NO_3)_2$ (Alfa) and NH_4ReO_4 (Aldrich). The procedures for cleaning the silica and alumina prior to impregnation followed those of Uchijima *et al.* (*30*) and Kobayashi *et al.* (*31*), respectively. After impregnation, the catalysts were dried at 100°C in an oven overnight and then calcined at 500°C in flowing tank air for 2 h. The catalysts were subsequently stored in bottles. The catalysts used in this study included 0.3 wt% Pt/Al_2O_3, 0.3 wt% Re/Al_2O_3, 0.3 wt% Pt–0.3 wt% Re/Al_2O_3, and 0.3 wt% Pt–0.3 wt% Re/SiO_2, all with a negligible halide content. The reagents included *n*-hexane (Aldrich, 99+%), *n*-heptane (Aldrich, 99+%), and methylcyclopentane (Baker, 99+%) all dried over molecular sieve before use. Hydrogen was of ultrahigh purity grade (Matheson) purified further over a Deoxo catalyst (Engelhard) and a silica trap maintained at liquid-nitrogen temperature. Helium was of ultrahigh purity grade (Linde) purified further over a silica trap maintained at liquid-nitrogen temperature.

Apparatus and procedure. The catalysts were tested for the conversion of hydrocarbons in hydrogen in a conventional continuous-flow fixed-bed microreactor operated at a total pressure of 1 bar, a temperature of 500°C, H_2/hydrocarbon molar ratios of 8 (*n*-heptane) and 11 (*n*-hexane and methylcyclopentane), and gas space velocities of 6–15 liters (NTP) h^{-1} g cat^{-1}. The reaction products were analyzed by on-line GLC using a HP 5790A gas chromatograph (50-m crosslinked methyl silicone capillary fused silica column, FID), and peak areas were determined using a HP 3390A integrator.

Prior to reaction, all catalysts were dried in flowing He at 500°C for 1 h and then reduced in flowing H_2 at 500°C for 2 h *in situ* in the reactor. Where applicable, the catalysts were presulfided *in situ* after the standard pretreatment described above by flowing a stream of 10 ppm H_2S in H_2 at 1 bar pressure and 500°C through the catalyst bed for 20 h. These catalysts were then purged of loosely bound sulfur by flowing H_2 through the bed at 500°C until no H_2S was detected at the reactor outlet by means of wet lead acetate paper. This simple test is sensitive to <1 ppm of H_2S (*32*).

RESULTS

Experiments Investigating the Effect of Rhenium

In order to decide whether interaction of Pt with Re is essential for the catalytic performance of $PtRe/Al_2O_3$, we compared two intimate physical mixtures of catalysts for the conversion of *n*-hexane:

(a) 50 mg 0.3 wt% Pt/Al_2O_3
+ 50 mg 0.3 wt% Re/Al_2O_3
(short notation: Pt + Re)

(b) 50 mg 0.3 wt% Pt–0.3 wt% Re/Al_2O_3
+ 50 mg γ-Al_2O_3
(short notation: PtRe)

The platinum, rhenium, and alumina contents were identical in both catalyst systems. Results are presented in Table 1. The selectivity patterns of the two catalyst systems show striking differences and remain essentially unchanged throughout 25 h of reaction. The cosupported PtRe catalyst displays an extraordinarily high selectivity for the cracking of *n*-hexane, in sharp contrast to the physically mixed Pt + Re catalyst. Conversely, the concomitant selectivity for isomerization and cyclization is much higher for the Pt + Re catalyst. The two catalyst systems do not differ much in

TABLE 1

n-Hexane Conversion[a] on Pt + Re and PtRe Catalysts

Catalyst[b]	Time (h)	Conv. (%)	Selectivity[c] (%)		
			S_{cr}	S_{is+cy}	S_{dhc}
Pt + Re	1	25	28	46	26
	25	8	30	46	24
PtRe	1	25	47	28	25
	25	12	50	29	21

[a] Reaction conditions: P = 1 bar, T = 500°C, H_2/HC = 11, SV = 15 liters (NTP) h^{-1} g cat^{-1}.

[b] Abbreviations: see text.

[c] Abbreviations: cr, cracking; is + cy, isomerization and cyclization; dhc, dehydrocyclization.

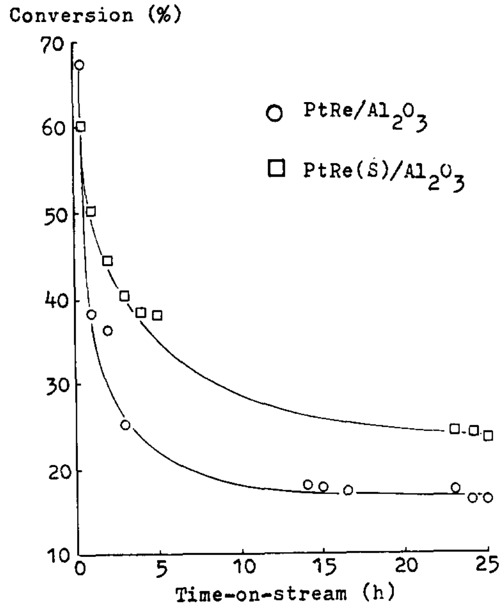

FIG. 1. Total conversion vs time-on-stream for unsulfided and presulfided PtRe/Al_2O_3. Reaction conditions: $P = 1$ bar, $T = 500°C$, $H_2/HC = 11$, $SV = 6$ liters (NTP) h^{-1} g cat^{-1}.

their selectivities for dehydrocyclization[2] or in their rates of deactivation. Since the selectivity patterns of the PtRe and Pt + Re catalysts are markedly different, we have to conclude that some interaction of Pt with Re is responsible for the characteristic performance of PtRe/Al_2O_3.

Experiments Investigating the Effect of Sulfur

In Fig. 1, the total conversion vs time-on-stream of an unsulfided PtRe/Al_2O_3 catalyst is compared with that of a presulfided PtRe/Al_2O_3 catalyst for the conversion of *n*-hexane. The initial activity of the sulfided catalyst is lower than that of the unsulfided catalyst, as should be expected, because of the poisoning effect of sulfur. It is most remarkable, however, that the sulfided catalyst displays a much smaller activity decline so that this catalyst shows a higher total conversion after several hours of reaction and retains this superior activity for the duration of our experiments. As shown in Fig. 2, sulfidation also causes very dramatic changes in selectivities. It reduces drastically the selectivity for cracking, and it reduces moderately the selectivity for the dehydrocyclization of *n*-hexane. The concomitant selectivity for isomerization and cyclization is found to be increased very significantly. Such changes in selectivities were previously observed for sulfiding PtRe/SiO_2 (*18*). The fraction of methylcyclopentane in the isomerization and cyclization products remains essentially constant at 20% for both unsulfided and sulfided PtRe/Al_2O_3. From Table 2, it can be seen that even though the selectivity for the dehydrocyclization of *n*-hexane is reduced by sulfidation, the yield of benzene at 25 h-on-stream remains essentially unchanged, as the sulfided catalyst is much less deactivated than the unsulfided catalyst at this point. These effects of sulfidation are markedly different from those observed with the monometallic Pt/Al_2O_3 catalyst, shown for comparison in Fig. 3. The total conversion vs time-on-stream curve of sulfided Pt/Al_2O_3 remains below that of unsulfided Pt/Al_2O_3 over the full period of 25 h; no tendency for the crossing of curves is visible. The data in Table 2 show that sulfidation of Pt/Al_2O_3 causes changes in selectivities in the same direction as those observed for sulfidation of PtRe/Al_2O_3. For both catalysts, isomerization becomes the dominant reaction after sulfidation. These results are in agreement with observations on industrial reforming catalysts, viz. while the addition of Re enhances activity maintenance, the product distributions are similar for catalysts with and without Re in the presence of adsorbed sulfur.

In Table 2, the effect of sulfidation on PtRe/Al_2O_3 for the conversion of *n*-heptane is also shown. As with *n*-hexane, the total conversion of the sulfided catalyst in the steady state is higher than that of the unsul-

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[2] Throughout this paper, dehydrocyclization refers to the formation of aromatics from *n*-alkanes whereas cyclization refers to the formation of saturated (cycloalkane) rings from *n*-alkanes.

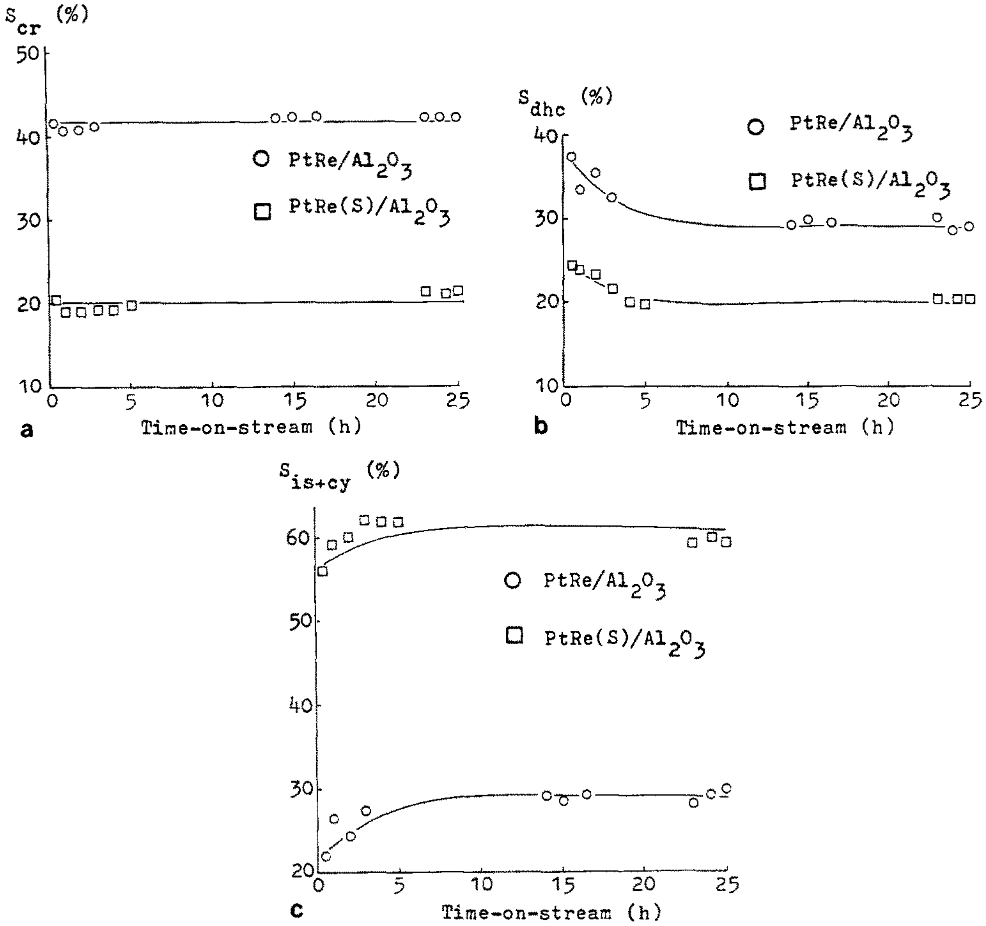

FIG. 2. Selectivity vs time-on-stream for unsulfided and presulfided $PtRe/Al_2O_3$. Reaction conditions: see Fig. 1.

TABLE 2

Hydrocarbon Conversion[a] on Unsulfided and Sulfided Catalysts

Catalyst	Reagent[b]	Conv. (%)	Selectivity[c] (%)			Yield[c] (%)		
			S_{cr}	S_{is+cy}	S_{dhc}	Y_{cr}	Y_{is+cy}	Y_{dhc}
Pt/Al_2O_3	nC_6	32	30	44	26	9.6	13.2	8.3
$Pt(S)/Al_2O_3$	nC_6	26	26	50	24	6.8	13.0	6.2
$PtRe/Al_2O_3$	nC_6	17	42	29	29	7.1	4.9	4.9
$PtRe(S)/Al_2O_3$	nC_6	24	20	60	20	4.8	14.4	4.8
$PtRe/Al_2O_3$	nC_7	28	30	40	30	8.4	11.2	8.4
$PtRe(S)/Al_2O_3$	nC_7	41	17	46	37	7.0	18.9	15.2

Note. Data reported are for 25 h-on-stream.

[a] Reaction conditions: $P = 1$ bar, $T = 500°C$, $H_2/nC_6 = 11$, $H_2/nC_7 = 8$, $SV = 6$ liters (NTP) h^{-1} g cat^{-1}.

[b] Abbreviations: nC_6, *n*-hexane; nC_7, *n*-heptane.

[c] Abbreviations: see Table 1.

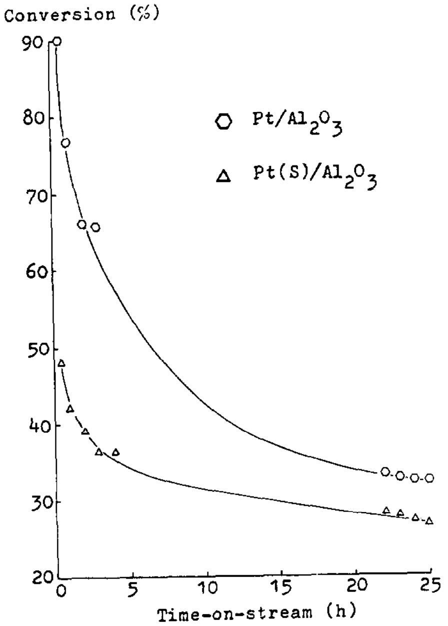

FIG. 3. Total conversion vs time-on-stream for unsulfided and presulfided Pt/Al_2O_3. Reaction conditions: see Fig. 1.

fided catalyst. Also, the effects of sulfidation on the selectivities for cracking, isomerization, and cyclization are qualitatively similar to those found with *n*-hexane. However, a striking difference between the two hydrocarbons is observed in the selectivity for dehydrocyclization. Whereas this selectivity is decreased upon sulfidation with *n*-hexane as the reagent, it is increased for *n*-heptane.

Experiments Investigating the Prevalence of Bifunctionality

According to the classical bifunctional reaction scheme (*33*), platinum-based alumina-supported hydrocarbon conversion catalysts are bifunctional in nature in that the metal function catalyzes dehydrogenations of paraffins to olefins, of naphthenes to aromatics, while the acid function catalyzes skeletal rearrangements of olefins. However, it is also known that the metal function alone can catalyze hydrogenolysis, dehydrocyclization, isomerization, and ring expansion, as well as opening and closure of five- and six-membered rings (*34*). Similarly, the acid function alone can catalyze hydrocracking, isomerization, ring expansion, ring-closure and ring-opening reactions (*35*). In order to investigate the prevalence of the bifunctional reaction routes at typical reforming temperatures, experiments with methylcyclopentane and *n*-hexane conversion on $PtRe/Al_2O_3$ and $PtRe/SiO_2$ were performed. The results are presented in Table 3.

The virtual absence of isomerization in the nonacidic $PtRe/SiO_2$ catalyst shows that acidity is of vital importance for this reaction type under the present conditions, and that nonchlorided Al_2O_3 displays sufficient acidity for catalyzing isomerization. On the other hand, hydrogenolysis, ring opening, ring expansion, and dehydrocyclization by direct 1,6-ring closure are also catalyzed by the monofunctional metal catalyst at 500°C and in full agreement with the findings of other authors, e.g., Ref. (*34*).

DISCUSSION

The experimental results show that a coimpregnated $PtRe/Al_2O_3$ catalyst and a physical mixture of Pt/Al_2O_3 and Re/Al_2O_3 have distinctly different catalytic properties. In particular, coimpregnated $PtRe/Al_2O_3$ exhibits severe cracking of *n*-hexane. Such catalytic results for $PtRe/Al_2O_3$ are in agreement with data obtained by Biloen *et al.* (*18*) for unsulfided PtRe alloys catalyzing the conversion of sulfur-free *n*-hexane. They have specifically determined that both

TABLE 3

Hydrocarbon Conversion[a] on $PtRe/SiO_2$ and $PtRe/Al_2O_3$

Catalyst	Reagent[b]	Conv. (%)	Yield[c] (%)		
			Y_{cr}	Y_{is+cy}	Y_{dhc}
$PtRe/SiO_2$	MCP	6	4.0	~0	2.0
$PtRe/SiO_2$	nC_6	6	3.7	~0	2.3
$PtRe/Al_2O_3$	MCP	15	3.0	2.0	10.0

Note. Data reported are for 1 h-on-stream.

[a] Reaction conditions: $P = 1$ bar, $T = 500°C$, $H_2/HC = 11$, $SV = 9$ liters (NTP) h^{-1} g cat^{-1}.

[b] Abbreviations: MCP, methylcyclopentane; nC_6, *n*-hexane.

[c] Abbreviations: see Table 1.

supported and bulk PtRe alloys show a remarkably high selectivity for cracking prior to sulfidation. It is obvious from our results that some interaction between platinum and rhenium is present in our cosupported PtRe catalyst, resulting in active sites of a different nature. These sites are absent (at any rate, much less numerous) in the physically mixed Pt + Re catalyst. This suggests that under the conditions of our experiments interparticle migration of metal atoms is of little significance. To the extent that catalytic performance may be used as a diagnostic criterion, the present results suggest that the formation of a PtRe *alloy* or of bimetallic clusters is dominantly responsible for the *catalytic* performance of $PtRe/Al_2O_3$. This high selectivity of unsulfided PtRe particles for hydrogenolysis can be tentatively rationalized by accepting that Re–C bonds are stronger than Pt–C bonds. Therefore, the chance for obtaining multiadsorbed molecules, i.e., forming chemisorption bonds with more than one carbon atom of the same molecule, increases for a given size of the adsorbing ensemble in the order: Pt ensemble < mixed ensemble < Re ensemble. As such multiple adsorption is likely to be the precursor of hydrogenolysis (see Refs. (*38, 39*)), it is easy to see that mixed ensembles will have a higher hydrogenolysis activity than Pt ensembles. On ensembles containing many Re atoms and on pure Re ensembles the chemisorption bonds may be so strong that desorption of the fragments may become rate limiting; in other words, these adsorption complexes are located on the descending branch of the "volcano"-shaped curve relating catalytic reaction rates with adsorption bond strengths (*48*). A very similar interpretation of the hydrogenolysis activity of PtRe catalysts has been proposed in Ref. (*49*).

We do not, however, exclude the possibility that oxidic rhenium may also be present on the surface of a working catalyst. Whereas, under the operating conditions used in our study, interparticle migration of metal is incomplete or absent in a physical mixture of Pt/Al_2O_3 and Re/Al_2O_3, it remains quite conceivable that under the more severe operating conditions with halides and moisture in the feed as in industrial reforming and used by Bertolacini and Pellet (*23*), interparticle migration of metal is nonnegligible. Significant interparticle migration of rhenium has indeed been detected by Bolivar *et al.* (*8*) who used mild conditions but a low-surface-area α-alumina support.

Sulfidation of Pt/Al_2O_3 and $PtRe/Al_2O_3$ under our conditions should have negligible effect on the alumina support. It follows from basic inorganic chemistry and is confirmed by ample evidence in the literature (*17–20*) that sulfur introduced under conditions similar to ours is mainly associated with the metal component. Biloen *et al.* (*18*) have also shown, using XRD and XPS measurements, that after a 70-h exposure to a flowing stream of 5 ppm H_2S in H_2 at 500°C, there is no bulk sulfide formed in $PtRe(S)/SiO_2$ and virtually all of the surface rhenium of PtRe alloy particles is covered with sulfur. These results also show that no disintegration of alloy particles other than the usual "chemisorption-induced surface segregation" of one element is caused by sulfidation under these conditions. On the basis of thermodynamic data (*36*), it is expected that sulfur adsorbed on the PtRe surface should be preferentially bound to rhenium. In a previous paper (*18*) we depicted this situation for the surface topography of PtRe(S)/support by a model assuming that all surface Re atoms are capped by S_{ads}, as shown schematically in Fig. 4. The "catalytically inert" ReS_{ads} species, like Au

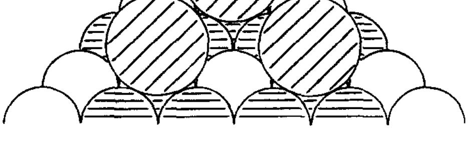

FIG. 4. Schematic model of sulfided PtRe alloy surface with S_{ads} on Re. $r_{Pt^0} = r_{Re^0} = 1.37$ Å, $r_{S^{2-}} = 1.84$ Å. ○, Pt; ⊜, Re; ⊘, S.

in PtAu catalyst, divides the large metal ensembles into smaller ones. It appears tempting to ascribe the changes in selectivities caused by sulfidation of $PtRe/Al_2O_3$ to the ensemble size effect (*37–39*) of alloy catalysis.

There is general agreement (*38–40*) that larger ensembles are required for hydrogenolysis than for other metal-catalyzed skeletal reactions, and (de)hydrogenation requires the smallest ensembles. Moreover, it has been observed (*29, 41*) that adding "catalytically inert" tin to platinum in Pt/Al_2O_3 causes significant changes of the selectivities in *n*-hexane conversion at 500°C and 1 bar: the selectivity decreases markedly for hydrogenolysis, slightly for dehydrocyclization, but it increases for isomerization. The presence of "catalytically inert" Au in PtAu single crystals causes the same changes in selectivities for *n*-hexane conversion at 300°C (*42*). Quite remarkably, for *n*-heptane conversion at 500°C and atmospheric pressure, the presence of tin in Pt/Al_2O_3 has been observed (*43*) to cause both the initial selectivities for isomerization and dehydrocyclization to increase. This observation is reminiscent of our present results on the selectivity changes due to sulfidation with *n*-heptane as the reagent. The available data suggest that *n*-hexane and *n*-heptane are dehydrocyclized to aromatics on Pt via different reaction pathways as a result of the fact that the dehydrocyclization of *n*-hexane involves only primary carbon atoms. It appears that the dehydrocyclization of *n*-hexane requires larger Pt ensembles than that of *n*-heptane. Further clarification by more experiments is necessary.

The participation of acid-catalyzed reactions can be derived by comparing $PtRe/Al_2O_3$ with $PtRe/SiO_2$. On $PtRe/Al_2O_3$, saturated C_6 products are formed from methylcyclopentane and *n*-hexane, and their formation is not suppressed by sulfidation. On $PtRe/SiO_2$, these products are not formed. These observations show that acid sites participate in isomerization and cyclization even on the chlorine-free catalysts used in the present work.

The changes in selectivities observed for sulfiding Pt/Al_2O_3 can also be rationalized using the argument that S_{ads} divides the bare metal surface into small ensembles. The major differences between the Pt(S) and PtRe(S) surfaces are: (a) more sulfur is retained by the PtRe(S) surface than the Pt(S) surface after identical sulfidation treatment (*20*), and (b) sulfur on the PtRe(S) surface is essentially fixed on the Re atoms, whereas sulfur on the Pt(S) surface might be more mobile. These differences thus explain why the changes in selectivities observed on sulfiding Pt/Al_2O_3 are more moderate than those observed on sulfiding $PtRe/Al_2O_3$.

It has been quite clearly established that the cause of deactivation of bifunctional hydrocarbon conversion catalysts is mainly due to the deposition of carbonaceous deposits. Our recent data show (*44*) that the metal function is the critical function of a bifunctional hydrocarbon conversion catalyst in the sense that the dehydrocyclization activity and consequently the octane rating of the reaction products decreases with decreasing activity of the metal function. The implication is that the observed decay of the relevant activity of the bifunctional catalyst is mainly due to deactivation of its *metal* function by carbonaceous deposits. Carter *et al.* (*24*) report that the *quantity* of coke on platinum-based hydrocarbon conversion catalysts is not reduced by the presence of rhenium under steady-state conditions of industrial reforming, but the *quality* of coke is different. Therefore, we should explain why rhenium in the presence of adsorbed sulfur changes the quality of the coke on the metal function to render it less harmful. A tentative model has been proposed (*45*) by one of the present authors—it assumes that S_{ads} fixed on Re impedes the reorganization of hydrocarbonaceous fragments into pseudographitic entities which have been demonstrated (*46*) to be the kind of coke that eliminates all catalytic activity of Pt. Nucleated growth of these graphitic entities has also been shown (*47*) to be sensitive to surface structure on Ni. On presulfided catalysts as used in this study, less S_{ads} is retained by Pt than PtRe; therefore, the formation of pseudographitic entities will be more impeded on the latter. Under reaction conditions where nonnegligible amounts of sulfur-containing molecules are present in the feed, the differences in activity maintenance between Pt/Al_2O_3 and $PtRe/Al_2O_3$ will be even more pronounced. On a Pt(S) surface in the steady state under such conditions, a given individual S atom leaves the surface by reacting with hydrogen, while elsewhere another S atom is adsorbed. The S atoms in this dynamic equilibrium form much less of an obstacle to the reorganization of the incomplete carbonaceous overlayer into graphitic entities than the S atoms which are permanently anchored onto surface Re atoms. This model seems to be consistent with the results reported in the present paper. Therefore, it might form a suitable basis to rationalize why $PtRe(S)/Al_2O_3$ has a much higher steady-state activity than $PtRe/Al_2O_3$, whereas $Pt(S)/Al_2O_3$ has a much lower steady-state activity than Pt/Al_2O_3.

CONCLUSIONS

Within the limitations in the use of halide-free catalysts at atmospheric pressure, the following conclusions emerge.

(a) PtRe *alloy* particles are dominantly responsible for the *catalytic* performance of $PtRe/Al_2O_3$.

(b) The *combined* action of rhenium and sulfur is responsible for the differences in performance between sulfided Pt/Al_2O_3 and $PtRe/Al_2O_3$.

(c) Adsorbed sulfur on Pt/Al_2O_3 and $PtRe/Al_2O_3$ causes changes in the selectivity patterns which can be rationalized in terms of reduced ensemble sizes of surface metal atoms.

(d) The present results are consistent with a model which assumes that sulfur atoms strongly adsorbed on the surface Re atoms of PtRe alloy particles impede the reorganization of hydrocarbonaceous fragments into pseudographitic entities, and thus enhance the activity maintenance of $PtRe/Al_2O_3$.

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