The Role of Rhenium and Sulfur in Platinum-Based Hydrocarbon-Conversion Catalysts

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Chemisorption, ir, and XPS data indicate that rhenium atoms covered with chemisorbed sulfur atoms divide the metal surface of platinum-containing catalysts into ensembles consisting of a small number of contiguous platinum atoms. Data on the catalytic conversion of *n*-hexane show that it is the combined action of rhenium and sulfur that converts platinum into a catalyst of very high selectivity for mild dehydrogenation. It thus appears that the beneficial effects on catalyst selectivity and stability which are brought about by adding widely different catalyst modifiers (gold, tin, sulfur, carbon) to platinum catalysts are largely due to one common cause, namely, the division of the platinum surface into very small ensembles of platinum atoms.

1. INTRODUCTION

In the past few years an impressive number of novel catalysts have been developed for hydrocarbon-conversion processes. These catalysts contain, besides platinum and a supporting oxide, one or more modifiers, which are reported to improve the stability and/or the selectivity of the catalyst system. With respect to the selectivity, the main feature of interest is the reduced yield of hydrocarbons having a lower molecular weight than the molecules in the feed. In this group of catalysts the platinum–rhenium support system is of particular interest, since both metals are known to exhibit catalytic activity for hydrocarbon conversions under the conditions used. Published attempts to rationalize the catalytic performance of this system are based on the assumption that the particle size of platinum is reduced by the Re inhibiting sintering of Pt (*1*), or that a PtRe alloy is formed (*2*), or that Re is present in an oxidic form (*3, 4*), possibly interacting with the support. With one exception (*5*), however, it is being disregarded that in industrial practice the beneficial properties of this catalyst system are observed only in the presence of a nonnegligible fraction of

sulfur-containing compounds. In view of the known affinity of rhenium to sulfur, we therefore wondered whether it would not be more realistic to assume that under steady-state conditions of industrial hydrocarbon-conversion processes most rhenium atoms on the catalyst surface are covered with sulfur atoms and that, consequently, the catalyst system of interest is actually a PtReS/support system. The validity of this assumption was corroborated by observations reported in the literature (*2*) and by our own findings that PtRe alloys exhibit in fact a much poorer selectivity (very high rate of hydrogenolysis) than unmodified Pt. To explore the action of Re and S as modifiers of supported platinum, we have therefore combined catalytic tests with selective chemisorption and infrared and photoelectron spectroscopy studies.

2. EXPERIMENTAL

2.1. Catalyst Preparation

Catalysts were prepared using the method of incipient wetness by impregnating either low-surface-area SiO₂ (Davison 70; hydrothermally treated at 200°C; residual surface area 102 m²/g; pore volume 1.0 ml/g crushed pellets, mesh size 60–80) or

commercial Universal Oil Products γ-Al_2O_3 with aqueous solutions of $Pt(NH_3)_4(OH)_2$ and $HReO_4$. In the preparation of bimetallic catalysts the support was first impregnated with rhenium and then, after calcination and reduction, with platinum. This sequence was not very critical: in one case we performed a coimpregnation from a heated aqueous solution and obtained a catalyst virtually identical with the ones produced in the above way.

The bulk Pt_4Re alloy used in the n-hexane test (Fig. 3b) was obtained by argon-arc melting of the two metals, followed by mechanical fracturing of the alloy sample. In order to prevent the formation of bulk sulfides such as ReS_2 we used a very low p_{H_2S}/p_{H_2} ratio. A standard sulfidation treatment involved a 70-hr exposure to 5 ppmw (mol) H_2S in H_2 at 1 bar pressure and 500°C. The H_2S concentration was regulated by flowing pure hydrogen first over a high-temperature bed and then over a low-temperature bed of Cu_2S/CuS, while regulating the temperature of the second bed and monitoring P_{H_2S} by means of the very sensitive Dohrman microcoulometric method. The absence of sulfide phases was verified by X-ray photoelectron spectroscopy and X-ray diffraction.

2.2. Catalytic Conversions of n-Hexane

The catalysts were characterized by testing them in the temperature-programmed conversion of n-hexane in hydrogen, at a pressure of 1 bar, a H_2/n-hexane molar ratio of 17, and a gas space velocity of 4 Nl $hr^{-1} g^{-1}$ cat. The tests were performed with samples 0.1–0.3 g in a quartz microreactor, and the products were analyzed with on-line glc. Usually the temperature in the reactor was increased with steps of 25°C at time intervals of 15 min between 300 and 550°C.

2.3. Auxiliary Equipment

Chemisorption measurements were performed in a metal–glass high-vacuum appa-ratus, equipped with a Baratron pressure transducer.

X-Ray photoelectron spectra were recorded with a Varian IEE-60 spectrometer. Prior to measurement the catalysts were ground and pressed into the grooves of a stainless-steel sample holder, which was subsequently mounted on a sample manipulator. The latter device allowed treatment with 1 bar hydrogen, as well as transfer of the sample into the spectrometer without its being exposed to the atmosphere.

The sample cell used in the ir study allowed *in situ* reduction and sulfidation. The spectra were recorded on a Digilab FTS-14 Fourier transform spectrometer.

3. RESULTS

3.1. X-Ray Photoelectron Spectroscopy (XPS)

The XPS data pertinent to the reduced samples before and after sulfiding are presented in Table 1. The Pt_{4f} signal appears at higher binding energy in $PtRe/SiO_2$ than in Pt/SiO_2. Sulfidation hardly affects the position of this platinum signal; however, some 20% of the intensity of the Re_{4d} signal shifts to higher binding energy.

3.2. X-Ray Diffraction (XRD)

In order to investigate what fraction of

TABLE 1

Binding Energies of Platinum and Rhenium Core Electrons, Obtained from X-Ray Photoelectron Spectroscopy

Sample[a]	BE[b] ($Pt_{4f_{7/2}}$) (eV)	BE[b] ($Re_{4d_{5/2}}$) (eV)
Pt/SiO$_2$	71.6 ± 0.1	—
Re/SiO$_2$	—	40.5 ± 0.1
PtRe/SiO$_2$	72.0	40.7
PtRe(S)/SiO$_2$	72.1	40.8/...[c]

[a] 4.0 wt% Pt/SiO$_2$; 2.0 wt% Re/SiO$_2$; and 1.8 wt% Pt, 2.0 wt% Re/SiO$_2$. Particle size, as measured from X-ray line broadening, between 6.0 and 8.0 nm.
[b] Reference: $Si_{2p_{3/2}}$ = 154.9 eV.
[c] Approximately 20% of the intensity is seen in a spectral feature displaced toward higher binding energy.

TABLE 2

Infrared Data on CO and CO_2 Chemisorption

Sample[a]	ν-CO (cm^{-1})	Intensity of CO band after exposure to CO ÷ intensity of CO band after exposure to CO_2
Pt/SiO$_2$	2050	4
Re/SiO$_2$	—	—
PtRe/SiO$_2$	2090	—
PtRe(S)/SiO$_2$	2070	20

[a] See Table 1.

the surface-exposed platinum could have been in an unalloyed state we subjected one preparation, viz., a 1.8 wt% Pt, 2.0 wt% Re/SiO$_2$ system, to a detailed XRD investigation. All of the platinum present (1.8 wt%, determined independently by wet analysis and neutron activation analysis) was observable by XRD, the accuracy of the calibrated XRD measurements being ±5% rel. The particles had an average size of 7.5 nm. The lattice was fcc and, judging from the observed lattice spacing in comparison with reference data (6), some 15 wt% rhenium was dissolved in the platinum particles. We did not observe any unalloyed platinum. In view of the inherently limited accuracy of the XRD measurements this implies that the upper limit for unalloyed platinum is of the order of 20% of all the surface-exposed platinum.

3.3. Infrared Spectroscopy

The chemisorption of CO was investigated by studying the intensity of the CO-stretching band (region 2000–2120 cm^{-1}) in the ir spectra.

Exposure of Re/SiO$_2$ to CO gave rise to a weak band which rapidly vanished and could not be restored on further exposure of the sample to CO. Apparently, the surface-exposed rhenium atoms were blocked irreversibly, presumably because of (surface) carbide formation. The CO frequencies measured for PtRe/SiO$_2$, listed in Ta-

ble 2, must therefore be attributed to CO chemisorbed onto *platinum* atoms. As can be seen from Table 2, the CO frequencies measured on different preparations differed widely.

When the samples were exposed to CO_2 the ir bands of CO were observed, pointing to dissociative chemisorption of CO_2:

$$CO_2 \rightarrow CO_{ads} + O_{ads}.$$

From the ratio of the intensities of the CO bands after exposure to CO and CO_2 (Table 2) it follows that modification of platinum with ReS suppresses the dissociative (CO_2) chemisorption relative to the nondissociative CO chemisorption.

3.4. H_2 and CO Chemisorption

We performed additional chemisorption experiments in a static apparatus with accurate pressure recording. Table 3 presents the results for H_2 and CO chemisorption. It shows that sulfiding suppresses the chemisorption of hydrogen and, to a lesser extent, of carbon monoxide as well. The term "total" in Table 3 refers to the total uptake in 10 min at a final pressure of 100 Torr. The term "strong" defines that part of the observed quantity which cannot be removed by evacuation for 10 min at room temperature.

TABLE 3

Amounts of H_2 and CO Chemisorbed on Various Catalysts

	PtRe/SiO$_2$	PtRe(S)/SiO$_2$
H$_2$ theory[a]	1245	1245
H$_2$ total	173	24.2
H$_2$ strong	67	5.1
CO theory[b]	2490	2490
CO total	393	147
CO strong	352	98.5
(CO/H$_2$) total	2.3	6.1
(CO/H$_2$) strong	5.2	19.3

[a] Torr-ml, 0°C, calculated for H/(Pt + Re + S) = 1.
[b] Torr-ml, 0°C, calculated for CO/(Pt + Re + S) = 1.

3.5. Catalytic conversions of n-hexane.
The *n*-hexane-conversion pattern, obtained over unmodified platinum catalysts by increasing the temperature from 200 to 500°C, shows two distinct regions of activity: a region of low-temperature activity (LTA) peaking around 350°C and characterized by the production of isomers, benzene, and crackates, and a high-temperature region (HTA), $\geq$450°C, in which the formation of benzene and crackates is predominant. These features are also found for bulk platinum (Fig. 1a) and for SiO$_2$-supported (Fig. 1b) and γ-Al$_2$O$_3$-supported platinum (Fig. 1c).

Unlike Pt and Re separately (Figs. 1 and 2), the binary system PtRe/SiO$_2$ exhibits a very pronounced cracking activity at low temperature (Fig. 3a). This low-temperature cracking is also observed with bulk PtRe alloys (Fig. 3b) and, to a lesser extent, with PtRe/γ-Al$_2$O$_3$.

Upon sulfidation Re/SiO$_2$ loses almost all its activity, whereas the conversion patterns measured over PtReS/SiO$_2$ and Pt(S)/SiO$_2$ become very similar to each other (cf. Figs. 4a and b) and to that of PtSn/γ-Al$_2$O$_3$ (see Fig. 5 of following paper). The patterns obtained over various combinations with γ-Al$_2$O$_3$ are very similar to the ones obtained over SiO$_2$.

As shown in Figs. 5a and b, the pattern obtained with PtNiS qualitatively resembles those observed with PtReS.

We finally wish to remark that in view of the deactivation during the tests, resulting in activity losses up to 50%, the conversion patterns are fingerprints rather than true representations of the initial activity and selectivity. Care has therefore been taken to record all the patterns using an identical time–temperature program.

4. DISCUSSION

Addition of rhenium to platinum without simultaneous sulfidation leads to severe hydrogenolysis, as shown in Figs. 3a and b. Under industrial conditions s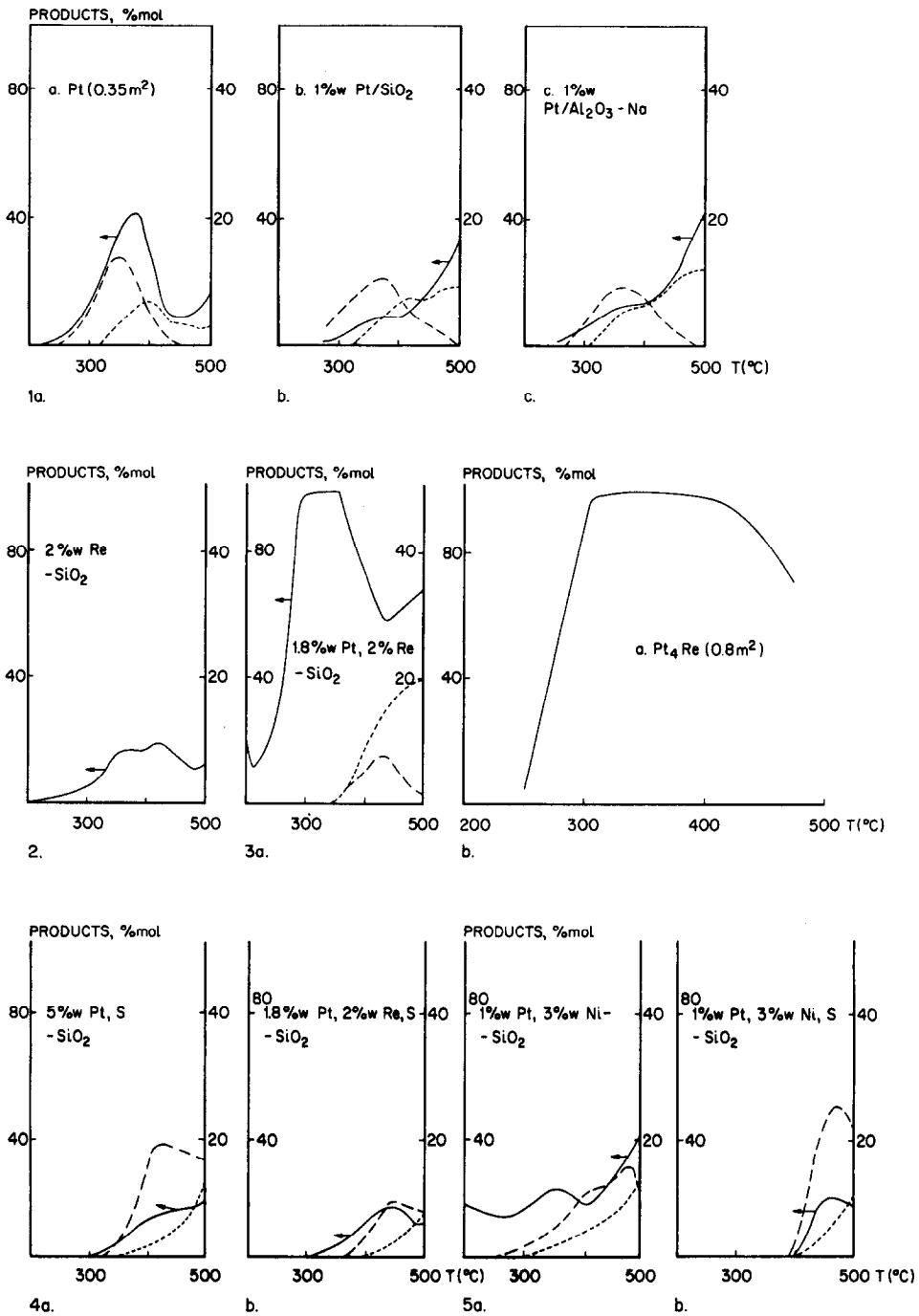uch a catalyst is likely to give rise to runaway hydrocracking. We therefore conclude that it is the *combined* action rather than the separate actions of rhenium and sulfur which must be considered.

Both the shift in stretch frequency of CO$_{ads}$ and the shift in Pt$_{4f}$ binding energy observed on going from Pt/SiO$_2$ to PtRe/SiO$_2$ point to a change in the electronic properties of the surface-exposed platinum atoms, which may be expected when PtRe bands are formed. Thus, ir and X-ray photoelectron spectroscopy strongly indicate that, prior to sulfidation, the surface-exposed platinum is present as an *alloy,* corresponding to:
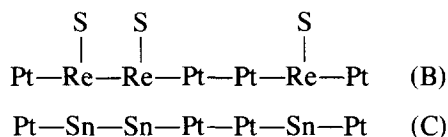
$$Pt-Re-Re-Pt-Pt-Re-Pt. \qquad (A)$$
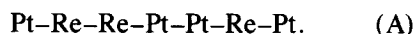
The presence of the surface alloy (A) is confirmed by the pronounced low-temperature hydrogenolysis observed over unsulfided (supported) PtRe preparations (Fig. 3a). This LTA is identified as being typical of a true PtRe alloy on the strength of our measurements on an unsupported PtRe alloy (Fig. 3b), and it is in line with the synergistic effects observed by Betizeau *et al.* (2).

The changes in surface structure occurring upon sulfidation are quite evident from the XPS data (Table 1). Whereas the conversion from metal into sulfide usually shows up as an increase in the core-electron binding energies of the metal (7), such an increase has *not* been observed by us for platinum. Accounting for the limits of the sensitivity in the prevailing measurements, we therefore conclude that of all the platinum present less than 5%, and of the surface-exposed platinum less than 25%, could have been converted into sulfide. For rhenium, however, we find that $\approx$20% of the 4d signal has shifted to higher binding energy. In principle, this could be due to the formation of a bulk sulfide ReS$_2$ to such an extent that 20% of *all* the rhenium atoms are engaged in a metal–sulfur bond. However, our XRD results did not indicate that appreciable amounts of low-disperse *bulk* sulfides are formed, and we are inclined to

PRODUCTS, %mol

80 | a. Pt (0.35 m²) | 40

80 | b. 1%w Pt/SiO₂ | 40

80 | c. 1%w Pt/Al₂O₃ - Na | 40

40 | 20

40 | 20

40 | 20

300　500

300　500

300　500　T(°C)

1a.

b.

c.

PRODUCTS, %mol

PRODUCTS, %mol

PRODUCTS, %mol

80 | 2%w Re - SiO₂ | 40

80 | 1.8%w Pt, 2% Re - SiO₂ | 40

80

40 | 20

40 | 20

40 | a. Pt₄Re (0.8 m²)

300　500

300　500

200　300　400　500　T(°C)

2.

3a.

b.

PRODUCTS, %mol

PRODUCTS, %mol

80 | 5%w Pt, S - SiO₂ | 40

80 | 1.8%w Pt, 2%w Re, S - SiO₂ | 40

80 | 1%w Pt, 3%w Ni - SiO₂ | 40

80 | 1%w Pt, 3%w Ni, S - SiO₂ | 40

40 | 20

40 | 20

40 | 20

40 | 20

300　500

300　500　T(°C)

300　500

300　500　T(°C)

4a.

b.

5a.

b.

FIGS. 1–5. Conversion patterns observed in the temperature-programmed n-hexane test. (——) ΣC_1–C_5 compounds; (— — —) 2-methylpentane + 3-methylpentane + methylcyclopentane; (- - - -) benzene.

relate the changes in XPS to the formation of a *surface* sulfide. As to the extent of surface sulfide formation, we infer, assuming a mean free path for inelastic electron scattering of 1.5 nm, that virtually all the surface rhenium is engaged in bonding to sulfur. Models (B) and (C) probably give the very essentials of the topography of PtRe(S) and PtSn surfaces.

$$
\begin{array}{ccccc}
S & S & & S & \\
| & | & & | & \\
Pt{-}Re{-}Re{-}Pt{-}Pt{-}Re{-}Pt & & & & (B)
\end{array}
$$

$$
Pt{-}Sn{-}Sn{-}Pt{-}Pt{-}Sn{-}Pt \quad (C)
$$

ReS replaces Sn and divides the Pt surface into ensembles of a small number of contiguous platinum atoms.

Sn and ReS show a close similarity not only in a topographical sense, but also in the influence they have on the chemisorptive and catalytic properties of platinum. The suppression of the dissociative chemisorption, for instance, which is observed here as the effect of ReS, was earlier observed by Verbeek and Sachtler as the effect of Sn (8). The catalytic effect of Re(S), shown in Fig. 5b, which can be summarized as "suppression of the LTA in the *n*-hexane conversion," is essentially the same as the effect observed with tin (see the following paper). We thus conclude that not only the topographical but also the catalytic actions of Sn and ReS are very similar in that both systems enhance the selectivity of the platinum catalyst for mild dehydrogenation, i.e., dehydrogenation of paraffins to the corresponding (poly-) olefins.

As mentioned in the following paper we assume that there is a causal relation between the dividing of the platinum surface into small ensembles of contiguous platinum atoms and the enhancement of the selectivity for mild dehydrogenation. The idea underlying this assumption is the notion that different reactions are likely to involve a different number of adsorbate–metal bonds in the rate-determining step(s)

(10, 11). With regard to the actual size of the ensembles involved in the rate-determining steps we would like to mention some (semi-)quantitative experiments in which an active metal is diluted with inactive spacer atoms and concurrently the reaction rates are determined per unit alloy surface at various extents of dilution. From this type of experiment Burton and Hyman (10) concluded that *two* Ni atoms are involved in ethane hydrogenolysis, and we (11) concluded that *one* Pt atom is involved in the dehydrogenation of propane to propene. Thus, in the present context "small" platinum ensembles are ensembles consisting of one, two, or possibly three atoms.

Finally we will consider whether the phenomenon discussed at the moment, i.e., the enhanced selectivity for dehydrogenation of paraffins to olefins, is confined to Sn and ReS as the modifiers. On the strength of the ensemble picture developed above, with emphasis on the geometric partitioning of the platinum surface rather than on the electronic interaction (ligand effect) between platinum and the modifier, one would expect the dehydrogenation enhancement to be a rather general phenomenon. That this is actually the case is demonstrated, for instance, by the action of gold being very similar to that of tin (11) (see also the following paper), and that of NiS being very similar to that of ReS (compare Figs. 5a and b with Figs. 3a and 4b). In our opinion this case clearly demonstrates the usefulness of separating the overall effect into ensemble and ligand effects (9), because one effect (in the prevailing case the ensemble effect) may dominiate over the other.

Finally, we would like to mention that metal oxides, surface sulfur, and surface carbon are likely to exert the same moderator action as the moderators discussed so far.

5. CONCLUSIONS

(1) In the modification of platinum-based hydrocarbon-conversion catalysts with rhe-

nium and sulfur it is the *combined* action of the two elements that is essential.

(2) The modifiers act by dividing the platinum surface into small ensembles, separated by ReS_{ads}. In this context "small" refers to ensembles of the order of 1–3 platinum atoms.

(3) S_{ads}, C_{ads}, Sn, Au, and many other "catalytically inert" modifiers act in essentially the same way as ReS.

(4) As a result of the modification mentioned under (2) the selectivity of the catalyst for the dehydration of paraffins to the corresponding olefins is enhanced considerably.

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