

## Platinum-Rhenium-Alumina Catalysts

### III. Catalytic Properties

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The activity of Pt-Re catalysts on  $\alpha$ - or  $\gamma$ -alumina has been determined for various reactions. In no case is the activity of bimetallic catalysts the sum of the activity of platinum and rhenium of which the catalyst is composed. Curves of activity as a function of the composition of the catalyst exhibit one or two maxima in benzene hydrogenation, benzene-deuterium exchange, cyclopentane, and butane hydrogenolysis, those maxima being more or less pronounced according to the reaction and the support. Conversely, the rate of 1,1,3-trimethyl cyclohexane dehydrogenation decreases when the percentage of rhenium is increased. A pronounced analogy has been established between, on the one hand, the changes of activity with bimetallic composition, and, on the other hand, with the position of the metal in the Periodic Table for the monometallic period Pt, Ir, Os, Re deposited on alumina.

#### INTRODUCTION

In previous papers of this series (1, 2), results were presented of studies of Pt-Re catalysts on alumina by means of various physical techniques showing that both metals are in strong interaction. It was therefore of interest to measure their activity in various reactions to see whether this is simply the sum of activities of platinum and of rhenium, or whether more complicated features are observed.

The literature shows that the activity of bimetallic catalysts can change in two ways according to their composition; either a simple change of activity can be observed (3-5), the activity becoming sometimes very low even when the percentage of

active metal is more than zero (6, 7), or the activity can be a maximum for an optimum composition of the catalyst (8-10). The same bimetallic catalyst can exhibit different behavior according to the reaction in question. For instance, the curve of activity as a function of the composition of Pt-Rh passes through a maximum in the hydrogenation of acrylic acid (11), methane-deuterium exchange (12), hydrogenation of benzene (13), but exhibits no extremum for electrocatalytic oxidation of methanol or of sodium formate (15). On the other hand, nickel-copper catalysts exhibit decreasing activity for a great number of reactions when the percentage of copper increases, e.g., oil hydrogenation (16), hydrogen-deuterium ex-

change (4), hydrogenolysis of ethane (17); however, in cyclohexane dehydrogenation, it was shown by Sinfelt *et al.* (17) that the activity of the alloy is slightly higher than those of nickel and copper for low percentages of copper, then remains constant up to 80% of copper, and finally rapidly decreases. In the same way, the rate of benzene hydrogenation is a maximum for 80 atom % of nickel. However, in this case of Ni-Cu, the analysis of these variations of activity vs catalyst composition is complicated by the fact that the surface composition is different from that of the bulk and is constant over a large range of bulk composition (34). Even so, the variations of catalyst activity are different for different reactions.

In this work, Pt-Re catalysts deposited on alumina have been tested in the following reactions, viz., dehydrogenation of 1,1,3-trimethyl cyclohexane, hydrogenation of benzene, hydrogenolysis of cyclopentane, and butane and benzene-deuterium exchange. These reactions can be classified into two categories for catalysts with platinum:

(i) Dehydrogenation of 1,1,3-trimethyl cyclohexane and benzene hydrogenation whose rates are proportional to the platinum surface area when this is modified by recrystallization (19, 20) or by poisoning with sulfur-containing products (22). This class of reaction has been called "structure-insensitive" by Boudart (23).

(ii) Hydrogenolysis of cyclopentane and butane and benzene-deuterium exchange, whose rates are not proportional to the amount of chemisorbed hydrogen (22, 24, 25, 27) when the catalyst is poisoned by a "selective" poison such as atomic sulfur.

## EXPERIMENTAL

### Materials

1,1,3-Trimethyl cyclohexane was prepared from isophorone which was hydro-

genated under hydrogen pressure on Raney nickel. The mixture of trimethyl cyclohexanols in solution with ethanol was dehydrated on alumina at 300°C. 1,1,3-Trimethyl cyclohexenes were purified by distillation and hydrogenated under pressure on Raney nickel at 100°C. The saturated hydrocarbon was finally distilled and percolated on silica.

"Pure crystallizable" benzene (Prolabo) was distilled, then maintained for 24 hr on a platinum-alumina catalyst to remove impurities, especially sulfur-containing impurities.

Cyclopentane "purum" (99% mole of cyclopentane) was obtained from Fluka and simply percolated on silica.

Butane, more than 99.95% pure (N-35 grade), was obtained from L'Air Liquide.

### Catalysts

Catalysts were prepared by impregnation of alumina with a solution of chloroplatinic acid (Caplain St. Andre) and perrhenic acid (Fluka). The support was covered with distilled water and then the required volume of solution was added. The solution was evaporated to dryness. During evaporation the catalyst was stirred continuously. Then it was placed overnight in an oven maintained at 100°C. It is very important that the temperature should never exceed 100°C in a nonreducing atmosphere in order to avoid volatilization of rhenium oxide. The metal was then reduced under a hydrogen flow for 7 hr at 500°C.

Two supports were used, namely, alumina SCS 9 (Rhône-Progil) and Degussa aluminumoxyd C. Alumina SCS 9,  $\alpha$ -alumina, available commercially in spheres of 2- or 3-mm diameter, was ground, sieved, washed with water to eliminate dust, and sieved again. Powder with granulometry of 0.08 to 0.125 mm was used for catalyst preparation. The support obtained in this way had a surface area of 24 m<sup>2</sup>/g and was non-microporous. The Degussa alumina was

$\gamma$ -alumina, with surface area of 180 m<sup>2</sup>/g; it was formed by microspheres and also was not microporous.

The catalysts contained  $6.2 \times 10^{19}$  metal atoms in 1 g of catalyst, which corresponds to a weight percentage of 2% of platinum for Pt-Al<sub>2</sub>O<sub>3</sub> and 1.9% of rhenium for Re-Al<sub>2</sub>O<sub>3</sub>.

### Apparatus and Procedure

(a) *Measurement of catalyst activities.* Hydrogenation of benzene, dehydrogenation of trimethyl cyclohexane, and hydrogenolysis of cyclopentane and butane were carried out in a continuous flow reactor at normal pressure. The apparatus and procedures have already been described in previous papers (24, 26, 27). Certain modifications have been made: these were the addition of a circuit for butane with a needle valve, a flowmeter, and a trap with molecular sieves 4A (Union Carbide) for drying the hydrocarbon. The charcoal previously used for purification of hydrogen and nitrogen was replaced by 13  $\times$  molecular sieves (Union Carbide).

Exchange of benzene with deuterium was carried out in a back mixed flow reactor which has already been described (24).

Experimental conditions are reported in Table 1.

(b) *Chemisorption measurements.* Metallic surface area has been measured by oxygen-hydrogen titration following the method of Benson and Boudart relative to platinum on the support (28, 29). The extension of that method to bimetallic Pt-Re alumina has been reported in the preceding paper of this series (2).

The apparatus consisted of a Setaram microbalance with a maximum range of 10 g and a vacuum system Sogev-Leybold including a primary pump and an oil-diffusion pump which made possible a vacuum of the order of 10<sup>-6</sup> Torr. A trap with liquid nitrogen protected the balance and catalyst from pollution by oil vapors.

TABLE 1  
Experimental Conditions<sup>a</sup>

Reaction	Weight of catalyst (g)	T (°C)	P <sub>H<sub>2</sub></sub> (atm)	P hydrocarbon (atm)
Benzene hydrogenation	0.02	100	0.95	0.05
1,1,3-Trimethyl cyclohexane dehydrogenation	1.25	310	0	1
Cyclopentane hydrogenolysis	0.50	180-300	0.9	0.1
Butane hydrogenolysis	1	160-300	0.9	0.1
Benzene-deuterium exchange	0.02	85	0.77	0.23

<sup>a</sup> For each experiment the initial activity of the catalyst was determined by extrapolating the deactivation curve to zero.

Hydrogen was purified by passing through a trap cooled by liquid nitrogen and oxygen was purified by passing through 13  $\times$  molecular sieves.

Before each chemisorption experiment, catalysts were reduced at 500°C under hydrogen atmosphere at a pressure of 100 Torr and evacuated at the same temperature.

## RESULTS AND DISCUSSION

### Selectivity in Hydrogenolysis Reactions

On platinum, hydrogenolysis reactions are simple since only one C-C bond is broken during a single contact of a molecule with the catalyst (26, 43). Cyclopentane gives only *n*-pentane and one molecule of butane initially gives either propane and methane or two molecules of ethane. As rhenium is added to platinum, the selectivity is strongly modified and secondary reactions appear. In cyclopentane hydrogenolysis, until the relative atomic percentage of rhenium attains 25%, the major product is *n*-pentane, but as the percentage of rhenium increases, the proportion of secondary products (methane, ethane, propane, and *n*-butane) increases continuously. On rhenium alone, only about 50% of hydrogenolyzed cyclopentane gives *n*-pentane. In hydrogenolysis of butane, changes in selectivity are different since when the

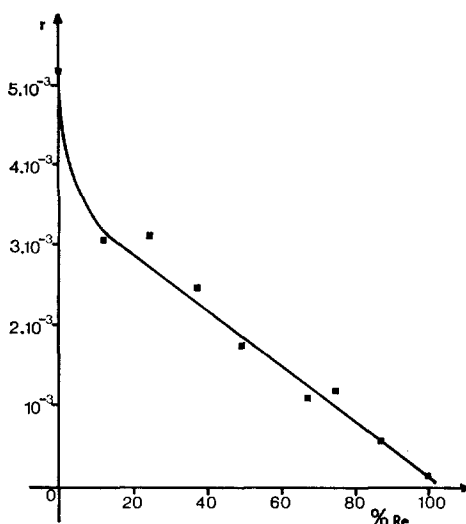


FIG. 1. Specific activity ( $\text{mole} \cdot \text{h}^{-1} \cdot \text{m}^{-2} \text{ Pt} + \text{Re}$ ) of Pt-Re on SCS 9  $\text{Al}_2\text{O}_3$  for 1,1,3-trimethyl cyclohexane dehydrogenation as a function of catalyst composition. Hydrocarbon pressure = 1 atm,  $T = 310^\circ\text{C}$ .

first atoms of rhenium are added the proportion of methane strongly increases, and thereafter the changes are less important.

### Activities

The influence of the atomic composition on the specific activity of Pt-Re catalysts for the five reactions studied is shown in Figs. 1 to 5.

It can be seen that catalyst activity never changes linearly as a function of the percentage of rhenium atoms, as would be expected if the catalysts were composed of platinum crystallites and rhenium crystallites without any interaction one with each other and if the composition of the surface was the same as that of bulk. Each reaction has its own characteristic curve.

For 1,1,3-trimethyl cyclohexane dehydrogenation, the curve is always decreasing (Fig. 1), the specific activity of bimetallic catalysts being always lower than the sum of the activities of platinum and of rhenium

in the catalyst. It should be noted that the decrease of activity takes place particularly when the percentage of rhenium is lower than 10%.

On the other hand, in benzene hydrogenation (Fig. 2) the specific activity first increases, then becomes a minimum at about 50% of rhenium, and reaches a maximum at about 67.5% Re. For each composition, the catalyst activity is higher than the sum of the activities of platinum and rhenium. It will be noted that the support influences the relative importance of the maxima but not their position.

In cyclopentane hydrogenolysis (Fig. 3), the activity seems to decrease slightly for low percentages of rhenium, but then rises markedly to be maximum at 67.5% in rhenium. The behavior of these catalysts is different again in butane hydrogenolysis since the activity increases considerably when the first rhenium atoms are added, as shown in Fig. 4. Here the maximum has shifted towards the higher rhenium percentages.

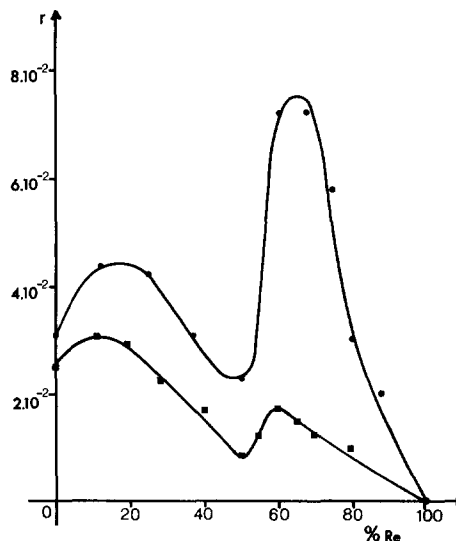


FIG. 2. Specific activity ( $\text{mole} \cdot \text{h}^{-1} \cdot \text{m}^{-2} \text{ Pt} + \text{Re}$ ) of Pt-Re for hydrogenation of benzene as a function of catalyst composition.  $\bullet$ : Pt- $\text{Al}_2\text{O}_3$ , SCS 9;  $\blacksquare$ : Pt- $\text{Al}_2\text{O}_3$ , Degussa;  $P_{\text{C}_6\text{H}_6} = 0.05$  atm;  $P_{\text{H}_2} = 0.95$  atm;  $T = 100^\circ\text{C}$ .

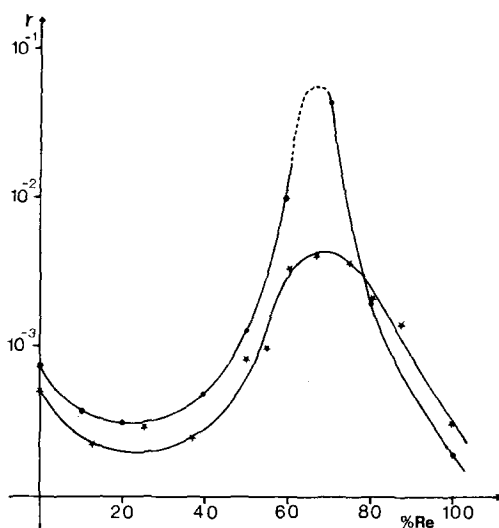


FIG. 3. Specific activity ( $\text{mole}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$  Pt + Re) of Pt-Re for cyclopentane hydrogenolysis as a function of catalyst composition.  $\star$ : Pt-Al<sub>2</sub>O<sub>3</sub> SCS 9;  $\bullet$ : Pt-Al<sub>2</sub>O<sub>3</sub> Degussa;  $P_{\text{C}_5\text{H}_{10}} = 0.1$  atm;  $P_{\text{H}_2} = 0.9$  atm;  $T = 240^\circ\text{C}$ .

In benzene-deuterium exchange (Fig. 5), the curve exhibits two maxima, the first between 15 and 20% and the second at about 75% of rhenium. It is interesting to note that the minimum activity at 60% of rhenium is lower than the sum of activities of platinum and rhenium corresponding to this composition. The variation in the activity of catalysts for benzene deuteration which occurs simultaneously with the exchange reaction is exactly analogous to that represented in Fig. 2 for benzene hydrogenation.

Activation energies in cyclopentane and butane hydrogenolysis have been measured; their values are reported in Table 2. The margin of error is about 2 kcal/mole.

In Part II of this series (2), it was concluded that platinum and rhenium are chiefly alloyed after reduction of the catalysts under hydrogen at 500°C. A study of chemisorbed carbon monoxide by infrared spectroscopy (2) and of thermal desorption of hydrogen (33) showed that, although platinum and rhenium atoms largely retain their individuality, there is

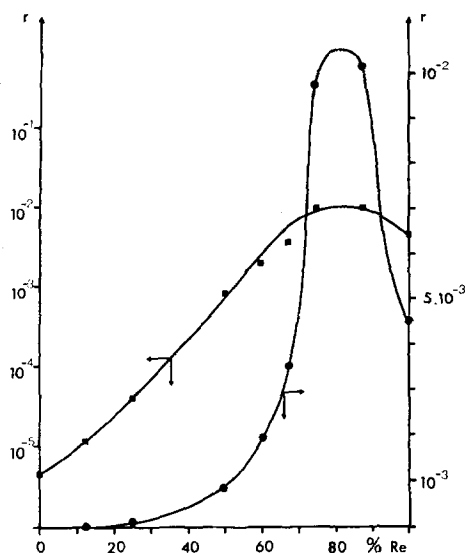


FIG. 4. Specific activity ( $\text{mole}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$  Pt + Re) of Pt-Re on SCS 9 Al<sub>2</sub>O<sub>3</sub> for butane hydrogenolysis as a function of catalyst composition.  $P_{\text{C}_4\text{H}_{10}} = 0.1$  atm;  $P_{\text{H}_2} = 0.9$  atm;  $T = 240^\circ\text{C}$ .

mutual electronic perturbation. However, these methods are not sensitive enough to rule out the hypothesis of very strong

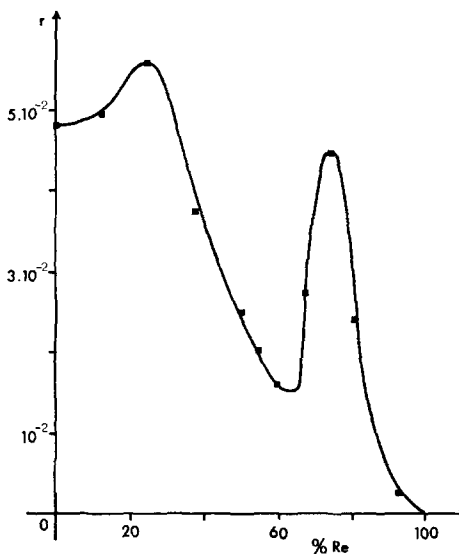


FIG. 5. Specific activity ( $\text{mole}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$  Pt + Re) of Pt-Re on SCS 9 Al<sub>2</sub>O<sub>3</sub> for exchange between benzene and deuterium as a function of catalyst composition.  $P_{\text{C}_6\text{H}_6} = 0.23$  atm;  $P_{\text{D}_2} = 0.77$  atm;  $T = 85^\circ\text{C}$ .

TABLE 2

Apparent Activation Energies  $E$  and Preexponential Factors for Cyclopentane and Butane Hydrogenolysis over Catalysts Deposited on SCS 9 Alumina

Catalyst	Cyclopentane hydrogenolysis		Butane hydrogenolysis	
	$E$ (kcal/ mole)	$A$ (mole/ h/m <sup>2</sup> )	$E$ (kcal/ mole)	$A$ (mole/ h/m <sup>2</sup> )
Pt-Re				
(% Re) 0	35	$3.3 \times 10^{11}$	34	$1.1 \times 10^9$
12.5	37	$1.0 \times 10^{12}$	38	$1.3 \times 10^{11}$
25	40	$2.5 \times 10^{12}$	36	$1.4 \times 10^{11}$
37.5	31	$3.1 \times 10^9$		
50	26	$8.5 \times 10^7$		
55			39.5	$6.8 \times 10^{12}$
60	22	$7.0 \times 10^6$	38	$2.3 \times 10^{12}$
67.5	23	$2.3 \times 10^7$	43	$5.6 \times 10^{12}$
75	26	$3.8 \times 10^8$	41	$2.2 \times 10^{12}$
87.5	23	$7.9 \times 10^6$	42	$6.1 \times 10^{12}$
100	12	$4.6 \times 10^1$	24	$6.5 \times 10^7$
Ir	28	$2.2 \times 10^{11}$	43	$4 \times 10^{17}$
Os	18	$6.0 \times 10^5$	34	$1.1 \times 10^{14}$

electronic modifications of a low part of metallic surface atoms.

With regard to the activities in all the reactions studied, the behavior of the bimetallic catalysts cannot be explained by a difference between surface and bulk composition. This interpretation could be correct for 1,1,3-trimethyl cyclohexane dehydrogenation if the surface is enriched by rhenium. This is consistent with the fact that the bond between hydrogen and rhenium is stronger than the bond between hydrogen and platinum (33). Thus, as the surface is usually supposed to be enriched by the alloy component which forms the strongest bond with the adsorbed reactant (3, 5), the surface could be richer in rhenium than the bulk. However, as both metals strongly chemisorb hydrogen, the difference between surface and bulk compositions must be small (if any) as shown by Bouwman and Sachtler (36) with Pt-Ru alloy in CO chemisorption. Moreover, although it is difficult to determine accurately the surface composition, we think that it is not very different from the bulk composition (2). In addition, this interpretation cannot, in any case, explain a specific

activity higher than the activity of the most active metal (Figs. 2-4).

The following hypotheses could be proposed to interpret our results: (i) Bimetallic catalysts can behave in a dual-functional manner, one step of the reaction being performed on platinum and another one on rhenium. (ii) The rhenium atoms could preferentially be located on certain positions, leaving platinum atoms on other places, for instance on edges, tops, or on certain faces where they would be more active. This phenomenon will be called "geometric effect of the first type." (iii) Some reactions can require the presence of groups of metallic atoms. This will be called the "geometric effect of the second type." (iv) The atoms of one metal could have their electronic configuration modified by the vicinity of the other metal and, by this effect, their activity in some reactions could be changed. Bond and Allison, in their recent review on palladium-silver and palladium-gold alloys (32), classified the electronic modifications of surface atoms into two categories: these were the rigid band theory model where atoms of the alloyed elements are indistinguishable, and the surface composition model where each surface atom preserves its individuality but can be more or less "disturbed" by the presence of a different neighboring atom. These two cases will not be distinguished and this phenomenon will be called the "electronic effect."

It must be pointed out that these appellations are only formal, and what has been called "geometric effects" are likely to imply some "electronic effect." Let us now consider the above hypothesis in turn:

(i) The possibility of a dual-functional process has been eliminated after experiments with mixtures of platinum-alumina and rhenium-alumina. When one measures the activity of a catalytic bed formed with three layers, namely, one of rhenium-alumina, another of pure alumina, and the third one of platinum-alumina, it can be

established that the activity after homogenization of the catalytic bed is exactly the same as before agitation. The role of the layer of pure alumina between the two catalysts was to prevent migration of rhenium towards platinum during reduction, as has already been pointed out (1).

(ii) The "geometric effect of the first type" assumption can also be ruled out. This assumption could account for our results in the case of "structure sensitive" reactions such as hydrogenolysis, but it cannot in any way account for the existence of maxima in the activity of benzene hydrogenation which is a "structure insensitive reaction" on Pt and for which the activity of rhenium is very low. In that reaction, which is supposed to take place indifferently on all platinum atoms and only on these, the activity should always be proportional to the platinum surface area and never greater than the specific activity of pure platinum.

(iii) Concerning the geometric effect of the second type, it may be imagined that there is an optimum composition of the group of metal atoms for which the rate of the considered reaction is greater. For instance, if one reaction requires three neighboring atoms, an ensemble of two platinum and one rhenium atoms could be more active than an ensemble of three atoms of platinum or of three atoms of rhenium. The most effective catalyst in a given reaction will be the catalyst for which the probability of finding those active sites is the greatest. Thus, it could be expected that the activity of the catalysts will pass through a maximum for a particular composition. This optimum composition would depend on the optimum composition of the catalytic site, on the crystal structure of the metal, and on the surface crystal faces (31). However, it has been shown (30) in poisoning experiments that the rate of benzene hydrogenation on platinum catalysts is always proportional to the metallic surface area. Now, unless we

suppose that the poison is in aggregates on the metal (and this does not seem to us to be consistent with the notion of selective poisons (24)), this can occur only if benzene hydrogenation takes place on a single platinum atom. These results do not seem to be in favor of a geometrical effect by groups of atoms, at least in the case of benzene hydrogenation.

(iv) There remains the last hypothesis, that of an electronic effect. If metallic atoms modify each other, certain bimetallic catalysts could be expected to exhibit some analogies with iridium or with osmium according to their composition. In the limit, if the rigid band theory model can be applied, the bimetallic crystal which contains one-third rhenium should have the same electronic structure as iridium and the crystal containing two-thirds rhenium should be electronically identical with osmium. However, this theory is more and more considered to be an oversimplification. On the contrary, if each surface atom preserves its individuality, the phenomenon should be attenuated but could be qualitatively analogous. For these reasons, the rates of the various reactions studied were measured on iridium-alumina and osmium-alumina catalysts with the same atomic percentage of metal as in platinum-rhenium catalysts. Results are reported in Table 3.

The activities reported in Table 3 for platinum catalysts are much smaller than those that can be extrapolated from the results of Anderson and Kemball (37) for reactions between benzene and deuterium, but are higher than those reported by Kubicka (38) in benzene hydrogenation ( $5.1 \times 10^{-3}$  moles/h/m<sup>2</sup> Pt at 127°C). However, it appears that the turnover number obtained here (1330 to 1600 h<sup>-1</sup> at 100°C) is in the same range as the turnover numbers calculated from many other authors. Basset *et al.* (39) found  $800 \pm 50$  hr<sup>-1</sup> at 50° which gives at 100°C, 6300 h<sup>-1</sup> with  $E = 10$  kcal/mole or 4200 h<sup>-1</sup> with

TABLE 3  
Comparison of Activities of Platinum, Iridium, Osmium, and Rhenium Deposited on Alumina

Reaction	Specific activity (c)			
	Pt	Ir	Os	Re
1,1,3-Trimethylcyclohexane dehydrogenation; $T=312^{\circ}\text{C}$	(a) $52 \times 10^{-4}$	$1.31 \times 10^{-4}$	$1.2 \times 10^{-4}$	$1.17 \times 10^{-4}$
Benzene hydrogenation	(a) $3.0 \times 10^{-2}$	$5.1 \times 10^{-2}$	$0.9 \times 10^{-2}$	low
$T=100^{\circ}\text{C}$	(b) $2.5 \times 10^{-2}$	$1.8 \times 10^{-2}$	$0.2 \times 10^{-2}$	low
Cyclopentane hydrogenolysis	(a) $5.1 \times 10^{-4}$	$3200 \times 10^{-4}$	$145 \times 10^{-4}$	$3.2 \times 10^{-4}$
$T=240^{\circ}\text{C}$	(b) $6.25 \times 10^{-4}$	$8900 \times 10^{-4}$	$151 \times 10^{-4}$	$1.9 \times 10^{-4}$
Butane hydrogenolysis				
$T=240^{\circ}\text{C}$	(a) $0.046 \times 10^{-4}$	$2500 \times 10^{-4}$	$4450 \times 10^{-4}$	$45.5 \times 10^{-4}$
Benzene-deuterium exchange				
$T=85^{\circ}\text{C}$	(a) $47 \times 10^{-3}$	$0.89 \times 10^{-3}$	$3.65 \times 10^{-3}$	low
Benzene deuteration				
$T=85^{\circ}\text{C}$	(a) $1.45 \times 10^{-2}$	$1.77 \times 10^{-2}$	$0.19 \times 10^{-2}$	low

(a) Catalysts on SCS 9 alumina.

(b) Catalysts on Degussa alumina.

(c) Moles converted per hour per square meter of metal. For experimental conditions, see Table 1.

$E = 8$  kcal/mole. From the results of Dorling and Moss (40) one obtains 3300 or 1600  $\text{h}^{-1}$  at  $100^{\circ}\text{C}$  if 10 or 8 kcal/mole are taken, respectively, as values of the activation energy. In the same fashion we have obtained the value of 420  $\text{h}^{-1}$  from the paper of Aben, Platteuw, and Stout-hamer (20). The great discrepancy between the results in the literature on reaction rates of benzene with hydrogen and deuterium is puzzling and has never been explained.

On rhenium, our measurements are in agreement with those of Kubicka (38) who has shown that rhenium has a very poor activity for benzene hydrogenation.

In butane hydrogenolysis, our results are consistent with those of Sinfelt (41) and Boudart and Ptak (42) for ethane and neopentane hydrogenolysis. Both authors found the same sequence of activities as we did, namely,  $\text{Os} > \text{Ir} > \text{Re} > \text{Pt}$ . Thus, it seems that the mechanism might be the same for hydrogenolysis of all aliphatic hydrocarbons. On the contrary, there are somewhat surprising differences between the hydrogenolysis of butane and of cyclopentane. First, on platinum, hydrogenolysis

of the cyclic hydrocarbon is about 100 times faster than that of aliphatic hydrocarbons; it is the opposite on osmium and the sequence of activities is different; for cyclopentane hydrogenolysis the sequence is  $\text{Ir} > \text{Os} > \text{Pt} > \text{Re}$ . The reasons for these differences are not evident. They might be due to different rate determining steps for the two reactions.

From Table 3 it can be seen that when iridium or osmium are more active than platinum and rhenium, the curves of the activities of Pt-Re catalysts as a function of their composition pass through a maximum higher than the rate of pure platinum, beyond 50% Re. Temporarily the first maximum in benzene hydrogenation will not be taken into account. On the contrary, in the case of 1,1,3-trimethyl cyclohexane dehydrogenation where iridium and osmium are less effective than platinum, the Pt-Re activity is lower than the sum of the activities of platinum and rhenium. However, let us note that the position of the maximum in activity does not correspond with the bimetallic catalyst whose mean electronic composition would be the same as that of iridium but is shifted towards



higher rhenium percentages. Moreover, the increase of bimetallic catalyst activities is often less important than that obtained with iridium or osmium. Nevertheless, the higher the ratio of activities of iridium (or of osmium) and platinum, the greater the maximum activity (Table 4). In increasing order are placed benzene hydrogenation, cyclopentane hydrogenolysis, and butane hydrogenolysis. Furthermore, in the case of butane hydrogenolysis, where osmium is the most active metal, the position of the maximum in activity is shifted towards higher rhenium percentages than when iridium is the most efficient.

On the other hand, concerning energies of activation, an analogy between bimetallic catalysts and iridium and osmium on alumina can be noted. In cyclopentane hydrogenolysis, the energy of activation decreases when the relative percentage of rhenium is increased (Table 2). The same arises in the series Pt, Ir, Os, and Re where the energies of activation are, respectively, 35, 28, 18, and 12 kcal/mole. On the contrary, in butane hydrogenolysis the energy of activation slightly increases and then decreases to a lower value for rhenium (Table 2). This has to be compared to the changes of this parameter in the sequence of pure metals for which the energy of activation is, respectively, 34, 43, 34, and 24 kcal/mole for Pt, Ir, Os, and Re on SCS 9 alumina.

TABLE 4  
Relative Specific Activities

Reaction	Ratio of activities		
	Ir/Pt	Os/Pt	Max/Pt
1,1,3-Trimethyl cyclohexane dehydrogenation (a)	0.025	0.028	
Benzene hydrogenation (a)	1.72	0.31	2.63
	(b)	0.71	0.77
Cyclopentane hydrogenolysis (a)	630	28	9.5
	(b)	1,425	24
			74
Butane hydrogenolysis (a)	58,000	101,000	2,200
Benzene-deuterium exchange (a)	0.019	0.078	

(a) Catalysts on SCS 9 alumina.  
(b) Catalysts on Degussa alumina.

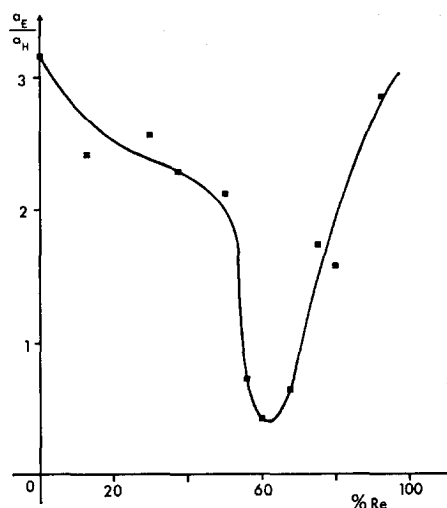


Fig. 6. Selectivity of Pt-Re on SCS 9 Al<sub>2</sub>O<sub>3</sub> in reactions between benzene and deuterium.

The analogy between the bimetallic catalysts and catalysts with iridium and osmium is not as close in the exchange between benzene and deuterium. However, the minimum of activity at about 60% rhenium should be compared to the fact that iridium is less active than platinum, and the second maximum to the fact that osmium is more active than iridium. Furthermore, it is noteworthy to compare the ratio of the activities of various catalysts in the exchange between benzene and deuterium and the deuteration of benzene. In the series of bimetallic catalysts (Fig. 6) that ratio is a minimum at 60% rhenium, and then increases for higher relative percentages of rhenium. With regard to the sequence Pt, Ir, Os, Table 4 enables us to calculate ratios  $aE/aH$  equal to 3.26, 0.05, and 1.9, respectively.

Nevertheless, it is not possible to explain the presence of the first maximum at 20% rhenium in exchange and hydrogenation of benzene. Possibly there is an electronic structure intermediate between platinum and iridium which is more favorable to both reactions.

Thus, it is possible to explain our results by assuming that in a Pt-Re bimetallic

catalyst there are "pure" atoms of platinum and rhenium, i.e., independent of each other or in a weak interaction, but also platinum and rhenium atoms electronically modified by the presence of the other metal, the activity of which should be related to that of iridium or osmium atoms. The number of these "activated" atoms is greater at higher relative percentages of rhenium, but the difference between the maximum activities of bimetallic catalysts and that of iridium or osmium suggests that the number of these atoms is probably low compared to the total number of atoms.

## REFERENCES

- Bolivar, C., Charcosset, H., Frety, R., Primet, M., Tournayan, L., Betizeau, C., Leclercq, G., and Maurel, R., *J. Catal.* **39**, 249 (1975).
- Bolivar, C., Charcosset, H., Frety, R., Primet, M., Tournayan, L., Betizeau, C., Leclercq, G., and Maurel, R., *J. Catal.* **45**, 163 (1976).
- Masahide, O., Yukio, A., and Kuniharu, S., *Nippon Kagaku Kaishi* **10**, 1824 (1972).
- Byrne, J. J., Carr, P. F., and Clarke, J. K. A., *J. Catal.* **20**, 412 (1971).
- Sinfelt, J. H., *J. Catal.* **29**, 308 (1973).
- Cinneide, A. O., and Clarke, J. K. A., *J. Catal.* **26**, 233 (1972).
- Plunkett, T. J., and Clarke, J. K. A., *J. Chem. Soc. Faraday Trans. I* **68**, 600 (1972).
- McKee, D. W., *Trans. Faraday Soc.* **61**, 2273 (1965).
- Inami, S. H., and Wise, H., *J. Catal.* **26**, 92 (1972).
- Bizhanova, N. B., Erzhanova, M. S., and Sokolskii, D. V., *Tr. Inst. Khim. Nauk, Akad. Nauk Kaz. S.S.R.* **26**, 85 (1969).
- Manankova, G. S., Grishnia, T. M., Khomchenko, G. P., and Vovchenko, G. D., *Vestn. Mosk. Univ. Khim.* **11**, 427 (1970).
- McKee, D. W., and Norton, F. J., *J. Catal.* **4**, 510 (1965).
- Alchudkhan, A. A., Edogaryan, N. Z., and Mautikyan, M. A., *Arm. Khim. Zh.* **23**, 3 (1970).
- Yoshida, K., *Nippon Kagaku Zasshi* **88**, 125 (1967).
- Masahiro, W., Takashi, S., and Satoshi, M., *Deukii Kagaku* **40**, 210 (1972).
- Pezinsli, W., *Thuszpe Kadamne* **15**, 123 (1971).
- Sinfelt, J. H., Carter, J. L., and Yates, D. J. C., *J. Catal.* **24**, 283 (1972).
- Cadenhead, D. A., and Masse, N. G., *J. Phys. Chem.* **70**, 3558 (1966).
- Barboux, Y., Roger, B., Beaufils, J. P., and Germain, J. E., *J. Chim. Phys.* **67**, 1041 (1970).
- Aben, P. C., Platteeuw, J. C., and Stouthamer, B., *Rec. Trav. Chim. Pays Bas* **89**, 449 (1970).
- Ratnasamy, P., *J. Catal.* **31**, 466 (1973).
- Maurel, R., Leclercq, G., and Barbier, J., *C.R. Acad. Sci. Paris* **277**, 1075 (1973).
- Boudart, M., *Advan. Catal.* **20**, 158 (1969).
- Maurel, R., Leclercq, G., and Barbier, J., *J. Catal.* **37**, 324 (1975).
- Leclercq, G., Trochet, J., and Maurel, R., *C.R. Acad. Sci. Paris* **276**, 1353 (1973).
- Maurel, R., and Leclercq, G., *Bull. Soc. Chim. France*, 1234 (1971).
- Maurel, R., Leclercq, G., and Leclercq, L., *Bull. Soc. Chim. France*, 491 (1972).
- Benson, J. E., and Boudart, M., *J. Catal.* **4**, 705 (1965).
- Barboux, Y., Roger, B., Beaufils, J. P., and Germain, J. E., *J. Chim. Phys.* **67**, 1035 (1971).
- Barbier, J., Thèse, Poitiers, 1975.
- Rushford, H. G., and Whan, D. A., *Trans. Faraday Soc.* **67**, 3577 (1971).
- Bond, G. C., and Allison, E. G., *Catal. Rev.* **7**, 233 (1973).
- Bolivar, C., Charcosset, H., Frety, R., Leclercq, G., and Neff, B., *First European Symposium on Thermal Analysis*, Salford, Sept. 1976.
- Van der Plank, P., and Sachtler, W. M. H., *J. Catal.* **12**, 35 (1968).
- Bouwman, R., and Sachtler, W. M. H., *J. Catal.* **19**, 127 (1970).
- Bouwman, R., and Sachtler, W. M. H., *J. Catal.* **26**, 63 (1973).
- Anderson, J. R., and Kembal, C., *Advan. Catal.* **9**, 51 (1957).
- Kubicka, H., *J. Catal.* **12**, 223 (1968).
- Basset, J. M., Dalmai-Imelik, G., Primet, M., and Mutin, R., *J. Catal.* **37**, 22 (1975).
- Dorling, T. A., and Moss, R. L., *J. Catal.* **5**, 111 (1966).
- Sinfelt, J. H., *Catal. Rev.* **3**, 173 (1970).
- Boudart, M., and Ptak, L. D., *J. Catal.* **16**, 90 (1970).