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The Effect of Alloying Pt With Re on the Intermediates in Hydrocarbon Reactions: Reactions of 2,2-Dimethylbutane

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A series of Pt–Re catalysts has been prepared and studied for reactions of 2,2-dimethylbutane (neohexane). The results, obtained at temperatures of 500–580 K, have been compared with those obtained with two commercial catalysts. The results show that rhenium is (at least partially) reduced and forms bimetallic clusters with Pt. At Re bulk concentrations less than 50% Re, catalysts behave like slightly modified Pt catalysts. On Pt-rich catalysts, isomerization is (or can be caused to be) important, while the Re-rich catalysts resemble Re. On Re, hydrogenolysis prevails and the extent of multiple (consecutive) reactions increases substantially. Multiple reactions are also enhanced when the Pt particle size of Pt catalysts is diminished. The two commercial catalysts fit quite well into the pattern obtained, indicating that also in commercial catalysts bimetallic clusters are formed.

INTRODUCTION

In the years since the first patent on Pt–Re/Al_2O_3 catalyst appeared (*1*), bimetallic catalysts have replaced the monometallic platinum catalyst in naphtha reforming almost completely. Fundamental research on bimetallic catalysts also made considerable progress in the same period, although this does not mean that all problems have been solved and general agreement achieved. Two references with different conclusions can serve as an illustration of the situation (*2, 3*).

With regard to platinum–rhenium catalysts several specific problems are still unsolved. It is a matter of discussion in which form Re is present (Re^0 or Re^{n+}) and, if several forms are present, which form gives Re its beneficial effects on Pt? Last but not least, what is the detailed mechanism of the Re effects? A review (*4*) and a selection of leading references (*5–8*) will give the reader an impression of the state of the subject.

The beneficial effect of Re in industrial Pt–Re catalysts manifests itself mainly under reaction conditions where a substantial part of Re is blocked by sulfur, the support itself is active, and both the support and the bimetallic clusters (if formed at all) are covered by carbonaceous deposits. This is a very complicated situation, and its study requires a knowledge of surface processes identified under simplified conditions. The pure Pt catalysts have been studied in the last two decades with the same strategy and the results accumulated and progress made justify such an approach (*3, 9–11*).

The test reactions chosen for the present work are the skeletal reactions of neohexane (2,2′-dimethylbutane). The behavior of neohexane can supply information on several interesting aspects of hydrocarbon reactions. When the system and reaction conditions allow it, one can learn how neohexane is absorbed on the surface either (i) as complexes comprising two carbon atoms directly involved in the chemisorption bond, or (ii) as complexes with three carbon

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atoms involved in the formation of the reaction intermediates. Furthermore, one can see whether, with a given catalyst, the three-carbon intermediates show a preference for isomerization (as large-particle Pt catalysts usually do) or for hydrogenolysis (as do small particles of Pt, or Ni, Ir, and Re). A second important aspect of the reaction, which can be checked, is the propensity of a given catalyst to favor either the single-step reaction (single step during one sojourn of a molecule on the surface) or the multiple, consecutive reactions. The principles and details of such diagnostics have been outlined elsewhere (*12, 13*).

In the (rather low) temperature region in which this study has been performed, the catalytic properties of Pt can be influenced by the metal particle size (*14, 15*). Therefore, it was necessary to check the effect of (a) Pt particle size on the selectivity in neohexane reactions and (b) the effect of Re on the particle size of (bimetallic) clusters.

EXPERIMENTAL

The main body of new information concerning Pt–Re catalysts has been obtained with 2% wt Pt/γ-Al_2O_3 (CK300, Ketjen, Amsterdam) and a series of Pt–Re catalysts in which Pt has been replaced by the required amount of (at.%) Re. All catalysts were prepared by coimpregnation. Series I was prepared by using, as precursor, $H_2PtCl_6 \cdot 6H_2O$ and H_3ReO_5 dissolved in H_2O. Series II was prepared by using a precursor prepared by first dissolving Pt and Re in aqua regia, then crystallizing by careful drying at 383 K (to avoid sublimation of oxides) and finally by dissolving the precipitate again in H_2O. In addition, two commercial catalysts were used, CK433 and CK473, containing according to the specifications, 0.311% wt Re, 0.296% wt Pt (CK433) and 0.631% wt Re, 0.292% wt Pt (CK473). Commercial catalysts were used as such, without additional calcination; the homemade catalysts of both series were dried at 383 K and calcined in air at 723 K, for 2 h. Reduction was carried out *in situ* at 723 K for 4 h.

For the study of particle size effects, Pt catalysts were also prepared with various kinds of SiO_2 as support (see below). With these catalysts Pt loading was 1, 6, and 9 wt%. The precursor for impregnation was prepared by dissolving the required amount of Pt in aqua regia. These catalysts were not calcined before use. The particle size of Pt/SiO_2 catalysts was determined by H_2 and CO adsorption, using EUROPT I (*16, 17*) as a standard of which the metal dispersion (or particle size) is considered to be known exactly. These data were checked by electron microscopy and good agreement was found.

The particle size of the Pt–Re catalysts has been determined by using high-resolution electron microscopy (HREM). For most of these experiments a 200-kV Joel 200CX microscope (operating at RUCA in Antwerpen) was used. Samples for EM were prepared by bringing a few droplets of the catalyst-in-methanol suspension onto a holey carbon-coated Formvar film. HREM established that, under the conditions used, the Re/γ-Al_2O_3 catalyst contained particles of Re metal.

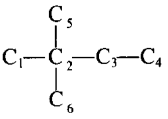
The reactions of neohexane (puriss grade, Fluka) were studied in a tubular fixed-bed, plug-flow reactor, working under differential conditions; details have already been described elsewhere (*18*). The neohexane partial pressure was 40 Torr, and the H_2/neohexane ratio was 18. Under standard conditions the total pressure was 1 bar and the flow rate 10 ml/min. The selectivity in neohexane reactions has been determined in the temperature range 500–580 K.

In several experiments deliberately "poisoned" catalysts were studied. These catalysts were prepared by allowing them to stand in a flow of hexane and hydrogen (1/16) for 6 h at 723 K and by re-reduction under standard reduction conditions.

Product analysis was performed by gas chromatography using a column (4 m, $\frac{1}{8}$ in.)

TABLE 1

Primary Products of Neohexane/Hydrogen Reactions



$$C_1{-}\overset{C_5}{\underset{C_6}{C_2}}{-}C_3{-}C_4$$

Group of reactions	Adsorption complex	Products used in diagnostics
Isomerization	$\alpha\gamma'(C_5{-}C_3)$	*2,3-Dimethylbutane* + 2-methylpentane
	$\alpha\gamma(C_1{-}C_6)$	*3 methylpentane*
Hydrogenolysis	$\alpha\gamma'$	C_1 + i-pentane C_2 + *i-butane*
	$\alpha\gamma$	C_1 + *i-pentane*
	$\alpha\beta(C_3{-}C_4)$	C_1 + *neopentane*

Statistical (random) reactions of neohexane

	Formation of complex (%)		
	$\alpha\beta$	$\alpha\gamma$	$\alpha\gamma'$
Number of C atoms determines the probability	14	43	43
Number of H atoms determines the probability	12	53	35

Note. C_1, C_5, and C_6 in the structural formula are actually identical.

with 15 wt% squalane on Chromosorb PAW with DMCS. The gas chromatograph was coupled to an integrator (Spectra Physics SP4270), which was also used to control the automatic analysis. The measuring cycle started at the lowest temperature, the total conversion and the selectivity at each temperature being determined after 30 min. The temperature was then increased by 8 K and the procedure repeated up to the upper temperature of the range studied. Activity and selectivity were almost the same when the changes in temperature were reversed.

Table 1 shows the primary products of neohexane reactions; from these products those that are italicized are used to calculate the respective selectivities. The 3C $\alpha\gamma$ complexes are those bound to the surface through the C_1 and C_5 (or C_6) of the 2,2-dimethylbutane; the 3C $\alpha\gamma'$ complexes involve C_5 and C_3 carbons. The 2C $\alpha\beta$ complex involves C_3 and C_4 carbons. The lower part of the table shows the selectivities calculated for a random reaction over all carbon atoms.

Besides the already mentioned primary products, "secondary" products also are formed, such as propane, butane, pentane, and hexane (or sometimes methylcyclopentane, cyclohexane, and benzene). None of these products can be formed by a single-step reaction. Either the molecules react several times before they desorb or they desorb after a one-step reaction, but are readsorbed and react again before they leave the reactor. By keeping the conversion very low, the contribution of these second-type multiple reactions is suppressed.

There are several possibilities (each having its advantage and disadvantage) as to how to characterize quantitatively the multiple reactions. One of them is the modified multifission parameter, as used previously (*13, 19*):

$$M_f^* = \frac{4(C_2 - iC_4) + 3C_3 + 2C_4 + neoC_5 + iC_5}{C_1}$$

where C_1 is the concentration of CH_4 formed in totality. This amount is compared with its potential sources in the numerator where iC_4 is 2-methylpropane, iC_5 is 2-methylbutane, and neoC_5 stands for neopentane. When no consecutive reactions occur and hydrogenolysis proceeds by a subsequent splitting off of C_1 groups (terminal splitting), $M_f^* = 1$. On the other hand, $M_f^* < 1$ indicates an extended multiple fission (e.g., an "explosion" of adsorbed molecules into C_1 fragments). When $M_f^* > 1$, some of the products in the numerator are formed without release of CH_4. Since several of these products are formed or can be formed by multiple-step reactions (e.g., propane, butane), a value higher than unity for M_f^* can mean a considerable contribution from the consecutive reactions, other than the already mentioned multiple fission. An example of such a reaction is

$$\text{2,2-dimethylbutane} \rightarrow \text{2-methylpentane} \rightarrow \text{propane (2 molecules)} \quad (1)$$

when taking place during a single sojourn of 2,2-DMB on the surface.

Another possibility of evaluating the extent of multiple reactions is to use M_f^{**} defined as

$$M_f^{**} = \frac{\text{neo}C_5 + iC_5}{C_1}.$$

M_f^{**} is unity when no multiple splitting takes place and $M_f^{**} < 1$ when it does. In this case only those multiple reactions that produce CH_4 are considered; reactions such as Eq. (1) are then not included.

Unless specified otherwise, the results obtained with different catalysts are compared below at the standard temperature of 573 K. It should be noted that the conclusions drawn below hold equally well for other temperatures in the range studied.

RESULTS

Pt Catalysts of Different Particle Size

The catalysts studied are shown in Table 2. Figure 1 shows the selectivity data for these catalysts, obtained at 573 K. To facilitate the observation of the trend in the data, lines are drawn for hydrogenolysis (○) and isomerization (●). It can be concluded that the smaller particle size favors hydrogenolysis, but on large particles isomerization prevails. The trend seems to be quite clear in spite of the use of different supports and methods of preparation.

TABLE 2

Pt Catalysts Used in This Study

wt% Pt	Support used	Pt particle size, ϕ (nm)
1	SiO_2, Johnson Matthey (the same support as EUROPT 1)	4.0
1	Aerosil 200, Degussa	11.7
1	Aerosil Ox 50, Degussa	14.0
6	EUROPT 1	1.9
9	Kieselgel 60, Merck	5.0
2	γ-Al_2O_3 (CK300, Ketjen)	2
2	γ-Al_2O_3 (CK300, Ketjen)	1.6
1	γ-Al_2O_3 (CK300, Ketjen)	0.85

Figure 2 shows the selectivity to typical products as a function of the particle size. A percentage of the $\alpha\beta$ hydrogenolysis (splitting of the C_3–C_4 bond) is shown as is the relative concentrations (in %) of the two products (propane and butane) which are formed by multiple reactions. In both figures, the EUROPT I catalyst deviates most from the curves drawn.

Both selectivities shown in Fig. 2 increase with decreasing particle size (increasing metal dispersion). In particular, the increase of multiple reactions indicated by the increase in (P + B)% is worth mentioning.

Table 3 shows the selectivities for specified modes of hydrogenolysis and isomerization. These data are presented only for three typical catalysts with varying particle size. Information presented in Fig. 2 is further analyzed here: one can see that the increase in hydrogenolysis accompanying the decrease in particle size is caused by an increase in $\alpha\gamma$ and $\alpha\gamma'$ hydrogenolyses, by increasing multiple reactions, and by an in-

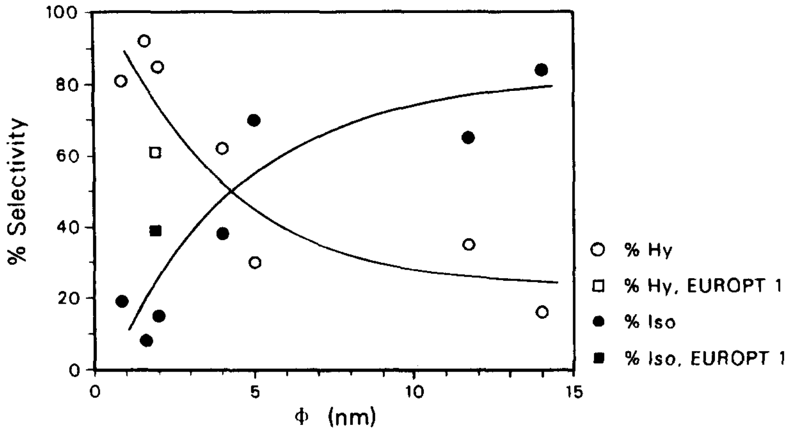


FIG. 1. Selectivity in isomerization and hydrogenolysis as a function of Pt particle size. Various Pt catalysts with Al_2O_3 and SiO_2 supports. Increasing function: isomerization; Decreasing function: hydrogenolysis

crease in $\alpha\beta$ hydrogenolysis. By comparing the data in Table 3 with the calculated random reaction products one observes another trend: large particles show a higher selectivity to one favored reaction: adsorbed complexes on small particles react more randomly.

Pt–Re Catalysts

Before a comparison between the various Pt–Re catalysts is presented, a remark should be made. All catalysts being compared have been calcined in a standard way. However, the Re catalyst (%Pt = 0) shown in this comparison has not been calcined. The reason is as follows. The activity of Re/Al_2O_3 decreased enormously when this catalyst was calcined. Such a phenomenon has already been noted in the literature (*20*) and ascribed to a possible sublimation (out of the reactor) of the volatile Re oxide(s). Knowing this, we performed Re elemental analysis of the catalysts before and after standard calcination.

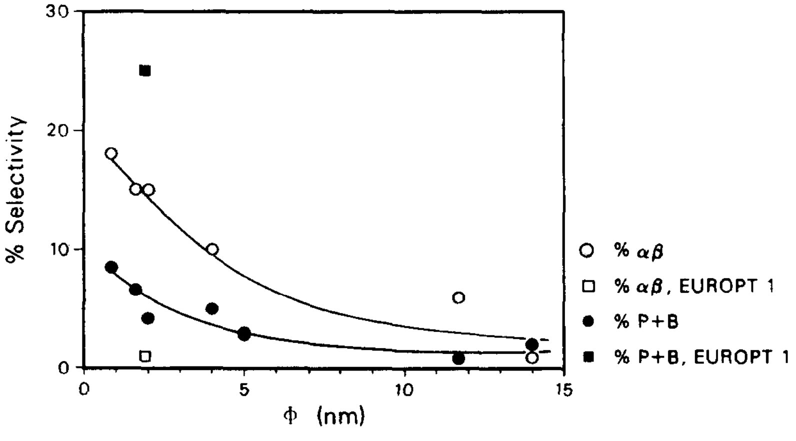


FIG. 2. Selectivity in 2C $\alpha\beta$ chemisorption complex formation and in consecutive products (i.e., propane and butane) as a function of Pt particle size.

TABLE 3

The Selectivities of Pt Catalysts

Pt particle size, ϕ (nm)	% Hydrogenolysis			% Isomerization		% Products of consecutive reactions, P + B
	$\alpha\beta$	$\alpha\gamma$	$\alpha\gamma'$	$\alpha\gamma$	$\alpha\gamma'$	
0.85	18	24	29	4	15	8.5
4.0	10	21	28	7	29	5
14.0	1	5	8	17	67	2

TABLE 4

Metal Particle Size of Pt–Re Catalysts as Measured by HREM

% Re	Series in preparation[a]	Calcined	Particle size, ϕ (nm)
0	1	–	2.0
0	1	+	2.0
20	1	+	1.3
40	1	+	1.0
40	2	+	1.0[b]
50	2	+	1.1
70	1	+	1.0[b]
80	1	–	1.7
80	1	+	1.0
100	1	–	2.0

[a] See Experimental.

[b] In this sample also a smaller fraction of particles is present with ϕ = 2.5 nm.

However, we did not detect any appreciable loss of Re by calcination. Therefore, we consider it to be more likely that Re oxide has merged with Al_2O_3 upon calcination and has become unreducible, or else Re has otherwise moved out of reach of the neohexane molecules.

Table 4 shows the particle size of various Pt–Re catalysts used in this study. For the discussion below it is essential to note that all catalysts studied belong to the "small-particle catalysts" and that the single-metal catalysts show the largest average particle size.

Figure 3 shows the activity of various Pt–Re catalysts in neohexane reactions. Activity is expressed as conversion (always low) per milligram of catalyst at a standard temperature. Values for the two commercial catalysts are plotted in the same graph. It can be seen that under standard conditions Re is more active than Pt (the particle size is equal). The catalysts with about 70% Re are the most active ones (per gram of catalyst), while the metal surface area of these catalysts is comparable with that of the other Pt–Re catalysts.

The most pronounced changes in selec-

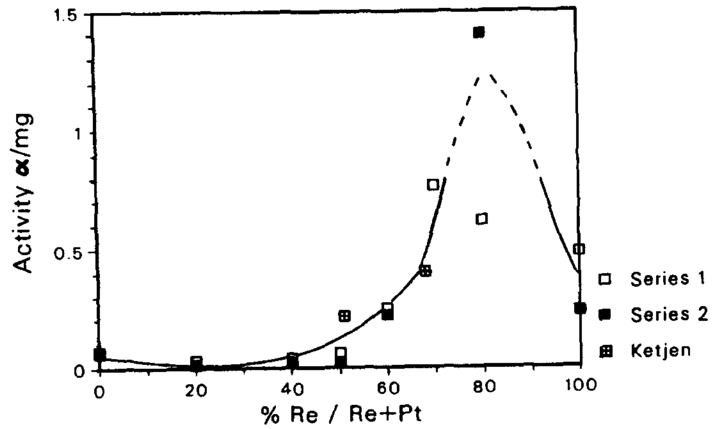


FIG. 3. Activity (expressed as conversion per milligram) as a function of metal composition. Catalysts compared at 548 K: series I (dissolved salts), series II (aqua regia), commercial (CK) catalysts.

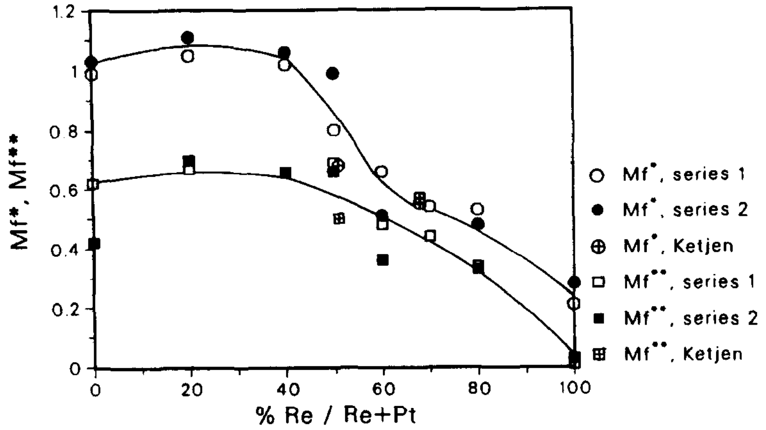


FIG. 4. M_f^* and M_f^{**} as functions of metal composition. Comparison at 573 K.

tivities set in at about 50% Re. This can be seen, for example, in Fig. 4, where M_f^* and M_f^{**} are plotted as functions of the composition of catalysts. The increase in activity in Fig. 3 coincides with the decrease in M_f values in Fig. 4.

In Fig. 5, the selectivities for isomerization and hydrogenolysis at 573 K are plotted as a function of the alloy bulk composition. In the Re-rich area only hydrogenolysis products are formed. In the Pt-rich area isomerization products are also formed. The main contribution of isomerization comes from $S(\alpha\gamma')$; $S(\alpha\gamma)$ is mostly less than 4% of all products. The catalysts containing 20% Re in the bulk show a higher S_{iso} than pure Pt catalysts. The selectivities in the particular 3C mechanisms, i.e., $\alpha\gamma$ and $\alpha\gamma'$, plotted as a function of bulk composition are presented in Fig. 6. It is demonstrated that $\alpha\gamma'$ plays a more important role than the $\alpha\gamma$ mechanism in the whole region. In Figs. 7 and 8 the selectivities in the 2C $\alpha\beta$ mechanism and in the consecutive products (propane and butane) are shown again as functions of Re/(Re + Pt).

$S_{consecutive}$ (S_{cons}) and $S(\alpha\beta)$ increase with increasing Re content. This effect is notice-

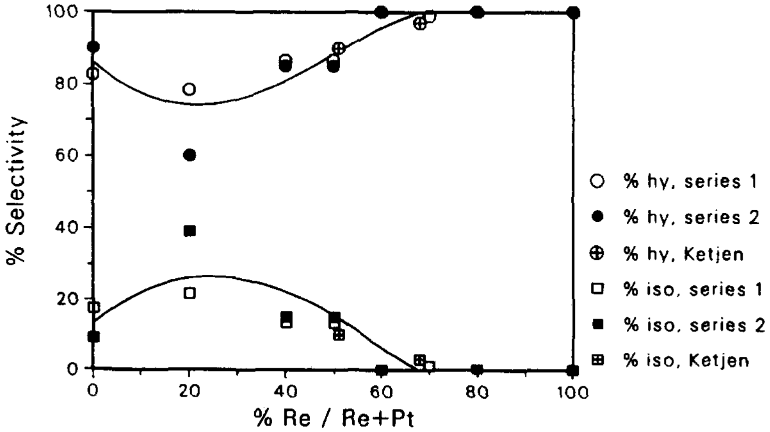


FIG. 5. Selectivity in isomerization and hydrogenolysis as a function of catalyst composition.

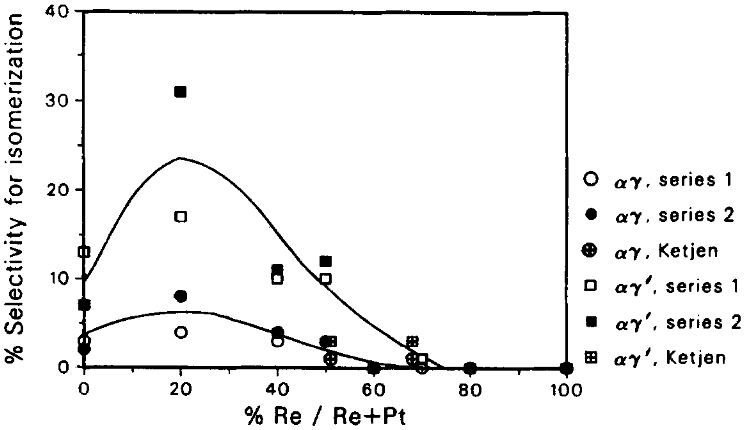


FIG. 6. Selectivity in the 3C $\alpha\gamma$ and $\alpha\gamma'$ mechanisms (isomerization and hydrogenolysis together) as a function of catalyst composition.

able above 40% Re/(Re + Pt). The apparently lower selectivity $S(\alpha\beta)$ at 100% Re than at 80% Re/(Re + Pt) is actually an artifact, explained by the fact that on 100% Re much more consecutive reactions take place (as is demonstrated by S_{cons} in Fig. 8 and also by the decrease in the M_f^* factor in Fig. 2) and these consecutive reactions destroy the molecules, which are taken as a measure of $\alpha\beta$ splitting (neopentane):

$$\text{neohexane} \xrightarrow{-\text{methane}} \text{neopentane} \xrightarrow{-\text{methane}} \text{isobutane, etc.} \quad (2)$$

The effect shown in Fig. 6, i.e., the increase in $\alpha\gamma'$ selectivity, can also be explained in the same way. The only contribution to the $\alpha\gamma'$ selectivity with the Re-rich catalysts consists of the hydrogenolysis product isobutane (see Fig. 5 and Table 1). Since isobutane can also occur due to consecutive reactions, according to reaction (2), the presence of consecutive reactions would explain the apparent increase (or a part of it) observed in $S(\alpha\gamma')$.

One should also note from Figs. 7 and 8 that the pure Pt catalysts show a higher S_{cons} and $S(\alpha\beta)$ than the Pt-rich alloy cata-

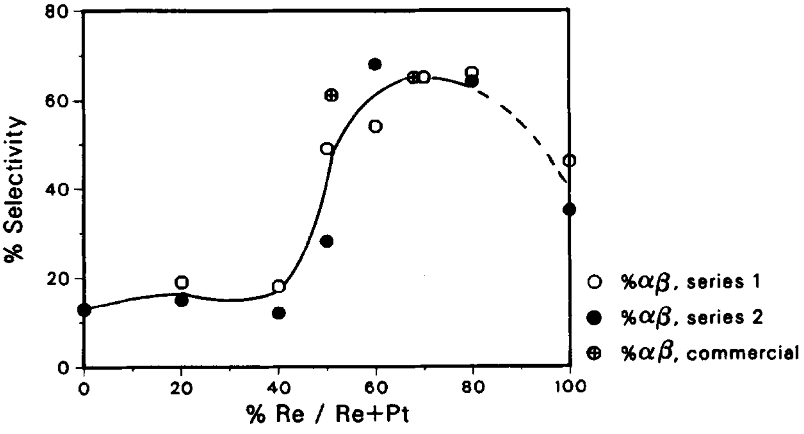


FIG. 7. Selectivity to 2C $\alpha\beta$ splitting vs catalyst composition.

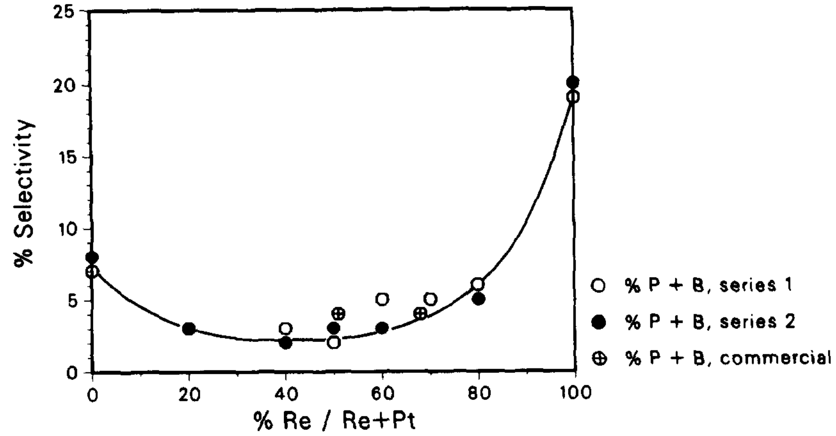


FIG. 8. Selectivity of S(P + B) (propane and butane formation) vs catalyst composition.

lysts. We shall return to this point in the discussion.

Pt–Re Catalysts Covered by a Carbonaceous Layer

Since the beneficial effect of Re in the commercial catalysts manifests itself under conditions of a rather heavy poisoning (sulfur) and self-poisoning (carbon), the following experiments have been performed.

With some catalysts of series 1 the activity and the selectivity were studied after deliberate deposition of a carbonaceous layer. From the activities of the catalysts before and after poisoning (data are presented in Table 5) one can observe the poisoning treatment with hydrocarbons severely reduced the activity. Since almost no hydrogenolysis products were formed on poisoned catalysts the error in M_f factors was too high, making the values of M_f unreliable, but the general trend observed was clear, namely, an increase in M_f^* and in M_f^{**} with poisoning.

In Fig. 9 the selectivities for isomerization and hydrogenolysis are shown as functions of metal compositions. It is obvious that after poisoning by carbonaceous deposition the S_{iso} is of more importance than $S_{hydrogenolysis}$ (S_{hy}). The 100% Pt and 60% Pt catalysts show less than 10% hydrogenolysis, while the original (not poisoned) catalysts show more than 80% hydrogenolysis. Above 40% Re the selectivity S_{hy} increases with increasing Re content.

In Fig. 10 the selectivities in the formation of different hydrogenolytic complexes are shown as well as the selectivity for consecutive reactions. For the catalysts studied, 3C $\alpha\gamma'$ is the most frequent chemisorption complex. However, above 40% Re the influence of the other intermediates, as well as of those involved in the reactions leading to propane and butane, increases.

An attempt to poison the 100% Re cata-

TABLE 5

Activity of Some Fresh and Deliberately Poisoned Catalysts (Carbonaceous Layer Deposited)

% Re	Activity (arbitrary units/g catalyst)	
	Fresh	Poisoned
0	60	3.6
20	30	n.m.[a]
40	38	1.2
50	60	7.5
60	246	4.6
100	483	n.m.

[a] Not measured.

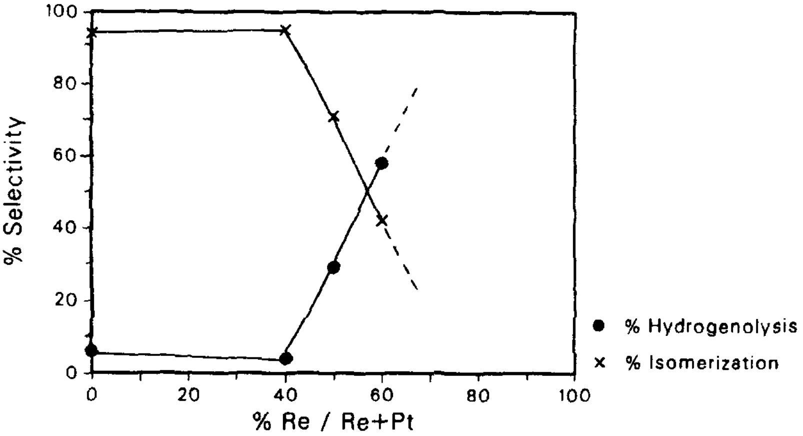


FIG. 9. Selectivity in isomerization and hydrogenolysis for some poisoned catalysts of series I vs catalyst composition.

lyst in the standard way failed, indicating that with increasing Re/Pt ratio the contribution of $S_{(hy)}$ would continue to increase.

DISCUSSION

Effect of Varying Pt Particle Size

Let us consider in brief what is known about hydrogenolysis of hydrocarbons on platinum and compare it with the data presented. As Table 3 demonstrates, Pt can catalyze fission of both 2C $\alpha\beta$ and 3C $\alpha\gamma$ complexes. While the first type of fission is assumed to require a multisite ensemble of active sites (*3*), the 3C $\alpha\gamma$ complex can probably be formed both on large ensembles and on single atom sites (*3*). In the latter case the structure of the intermediates is that of (substituted) metallocyclobutane.

When several metal atoms are involved, structures likes those shown in Scheme 1 can be expected. Tripod-like structures, if formed at all (there is no definitive evidence for them at the moment), would require more than one metal site per neohexane molecule for their formation. Although not

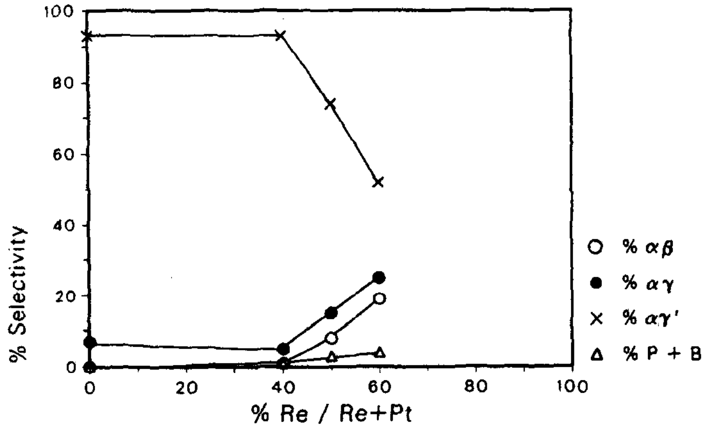
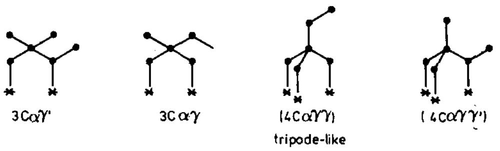


FIG. 10. Selectivities in the different chemisorption mechanisms and consecutive reactions on poisoned catalysts vs catalyst composition.



SCHEME 1

proven, the tripods are good candidates to help explain how the multiple formation of CH_4 (more than one CH_4 per neohexane molecule formed during one sojourn of neohexane on the surface) is induced, or how the formation of butane, propane, etc. proceeds. When C–C bonds are broken in whatever complex (2C, 3C, or 4C), then, at a certain stage of the reaction, a multiple metal–C bond is most probably formed. With this background information, an attempt can be made to explain the particle size effect.

Making the particles small should promote hydrogenolysis and multiple reactions by one of the following effects considered here: (i) by easier formation of metal–C multiple bonds; (ii) by turning the complexes shown in Scheme 1 into more dehydrogenated species, since it is known (*3*) that the higher the degree of dehydrogenation of the chemisorption complexes, the higher the probability of breaking the C–C bonds (as compared to nondestructive reactions); and (iii) by offering larger ensembles of contiguous sites (poison free) than can the large particles.

With the knowledge available (*14, 15*), the effect under (i) can be discarded: the smaller particles appear to be worse in this respect and not better. Effect (iii) looks at first glance not very probable either, since for a clean surface one would expect just the opposite situation. However, it is well known that small particles are less covered by carbonaceous layers than large particles, and that is the main reason to consider effect (iii) as possible. For the same reason, i.e., lower coverage by carbonaceous layers, the small particles might possess a greater power to dehydrogenate the 3C and 4C complexes [effect (ii)] than the large particles, and this would lead to the selectivity shifts observed. Less coverage of small particles by carbonaceous species would also explain why the small particles induce more "random" reactivity (see Table 3). A similar situation is also encountered with iridium catalysts (*19*).

In conclusion, it has been discovered recently (*22*) that, with the EUROPT I catalyst, the small particles still show hydrogenolysis at higher temperatures than the large particles; at a given temperature the small particles are better in hydrogenolysis of *n*-hexane than are the large particles and the explanation is the same as suggested above. Also, another aspect of the findings presented above has its analog in other reactions. Several authors report (*23, 24*) that with methylcyclopentane smaller particles induce a more random reactivity in adsorbed complexes in ring opening than large particles.

The reason why the results for EUROPT I deviate most from the other results obtained can be explained by the very probable inhomogeneity of our part of the EUROPT I sample.

Pt–Re Catalysts

Let us discuss, for the sake of simplicity, two regions separately, namely, Pt-rich and Pt-lean bimetallics (alloys).

Addition of a small percentage of Re to Pt leads to several remarkable effects: (a) a decrease in the activity per gram of catalyst, although the particle size is smaller than that of Pt and Re itself is more active than Pt; (b) an increase in the selectivity of isomerization, although Re itself is a hydrogenolytic rather than an isomerization catalyst (see Fig. 5) and diminishing particle size should promote hydrogenolysis as well (see the first section of this discussion); (c) a decrease in propane formation, although this is higher on pure Re than on Pt. These observations are also important for one more reason: they show that Pt and Re together form bimetallic clusters or alloys; one would not observe effects (a) to (c) if the components Pt and Re were separated.

A possible explanation of the results just mentioned can be offered on the basis of the ideas expressed by Haining *et al.* These authors (*25*) showed convincingly that hydrocarbon fragments tend to reside longer on Re than on Pt sites. If a fragment on Re has again Re atoms as neighbors, which are all difficult to invalidate by carbonaceous deposits, the fragment will tend to react further to undergo multiple reactions and to leave the surface in the form of small(est) fragments (C_1). However, when a strongly bound fragment on a Re atom is surrounded by Pt, it will do this less and, moreover, it will be in its turn an obstacle for multiple (large ensemble) reactions on Pt. In this way, we can rationalize why multiple reactions (indicated by P + B) and hydrogenolysis are blocked to a certain extent when some Re is added to Pt and why isomerization is slightly promoted by this addition (see Fig. 5).

Let us mention that very similar behavior has also been observed with Pt–Cu catalysts, in the Pt-rich region (*12*). Possibly the same explanation could apply, although Cu is not a metal that binds hydrocarbon fragments strongly. In any case, we do not suggest that any effect originating from the electronic structure changes due to cluster (alloy) formation should be responsible for the observed fact (Fig. 5), since CO adsorption studied by IR did not detect a pronounced effect of alloying either with Pt–Cu or with Pt–Re (*26, 27*).

Let us now turn our attention to the Re-rich region. When some Pt is added to Re, the activity per gram and the metal dispersion both increase (Table 4), the latter from about 60–70% up to 100%. Parallel to it, also the total amount of metallic Re might be increasing, since Pt promotes the reduction of Re (*5*) and this might prevent intrusion (escape) of Re^{n+} into the Al_2O_3 lattice. Because of all this, very little can be said about the increase in activity when going from 100 to 70% Re catalysts; except again that this behavior (Pt itself is less active than Re) indicates that also in this range of composition, Pt and Re obviously form common clusters (alloy). Further, it should be noted that an increase in activity in the mentioned range of catalyst compositions has also been found by other authors (*20*) for various reactions.

It is interesting that in the region from about 60 to 100% Re, the catalysts do not resemble Pt in almost any respect: they show very extended multiple reactions (highest on pure Re) and virtually no isomerization.

The commercial catalysts fit the overall picture obtained with the model catalysts and this indicates that also the commercial catalysts consist of bimetallic (and not single metal) clusters.

Deposition of an appreciable amount of carbonaceous species on Re is impossible under our standard conditions of carbonaceous layer deposition. However, the Pt-rich Pt–Re catalysts can be poisoned and modified, and the main effect of this modification is considerable enhancement of isomerization. This observation supports, among others, the explanation (as suggested above) of the effects of diminishing Pt particle size (Table 3) and of the effect of addition of some Re to Pt (Fig. 5).

CONCLUSIONS

New evidence is gained that Pt shows a pronounced particle size-sensitive selectivity in hydrocarbon reactions. The tentative explanation of this is related to the formation of carbonaceous layers on Pt, the latter being less extended on small particles.

A strong indication is found that Pt and Re form common clusters (or an alloy). The effects caused by this can be explained by considering the difference between Pt and Re (electronic structure effect) and the formation of ensembles of sites varying in size and/or composition. Ensembles of a certain size are essential for some reactions to occur (hydrogenolysis, carbonaceous layer formation). The fact that commercial catalysts fit the picture obtained with model catalysts indicates that also in commercial catalysts, a substantial part of Re is reduced and forms common clusters with Pt.

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