Catalytic Reactions of Hydrocarbons over Pt–Pd Alloys

I. Skeletal Reactions of C_5 and C_6 Alkanes over Pt–Pd Alloy Films

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The reactions of neopentane, n-pentane, and n-hexane in the presence of an excess of hydrogen have been studied on evaporated films of Pt–Pd alloys as catalysts. The selectivity in neopentane isomerization on a pure Pd film has been found to be nonnegligible, in contrast with previous work in the literature. A possible explanation of this involving the carbonization of the surface during the experiments and the effect of texture on the process is proposed. The neopentane isomerization vs alloy composition pattern is interpreted in terms of an "inferred" surface composition. The results may be easily explained assuming a one-Pt-site mechanism for isomerization and a two-Pd-site mechanism for hydrogenolysis. The 1,5-cyclization selectivity pattern in the n-pentane reaction is interpreted in terms of the change in active site number. In the n-hexane conversion the ratio of selectivity towards 1,6- versus 1,5-cyclization is higher for alloys than for pure metals.

INTRODUCTION

Platinum is unique among the catalytic metals for its activity in alkane rearrangements, and as a consequence most fundamental work on these reactions has been done with this metal (*1, 2*). The reasons for studying these reactions on Pt alloys is at least twofold. First, the technological superiority of many alloy catalysts in naphtha reforming, e.g., Pt–Sn (*3*) or Pt–Ru, Pt–Ir, Pt–Rh (*4*), calls for a rational explanation and, at the same time, for further search for other effective alloy catalysts. Second, besides that practical reason, it was suggested by Clarke and Rooney (*2*) that matrix isolation of the active metal, e.g., Pt, as discrete ensembles by alloying within an inactive metal (Sn, Au) offers a particular aspect of the stereochemical approach to the mechanism of hydrocarb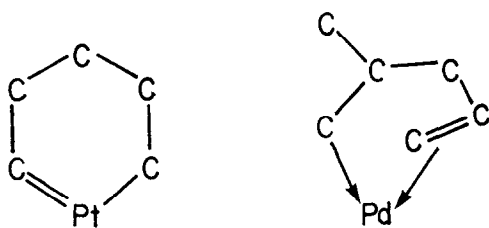on reactions on metal catalysts, although geometric and electronic factors are never separable variables (*5*). Van Schaik *et al.* (*6*) found that extremely diluted Pt in Au (1 and 2.5% Pt) catalyzed isomerization of *n*-pentane with a selectivity of 100%. This finding appears to support the one-metal site bond shift isomerization mechanism suggested by McKervey *et al.* (*7*). On 12.5% Pt alloy more cyclization than isomerization was found, whereas for pure platinum isomerization (in this case possibly via two-metal site mechanism (*1*)) prevailed over cyclization.

Obviously, from such studies, a more correct conclusion about the reaction mechanism could be drawn if the actual surface concentration of an alloy was known. The surface enrichment with one component may be in some cases quite serious, and the presence of a miscibility gap may introduce still more complications and make the interpretation very

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difficult. Hagen and Somorjai (8) were able to study the surface composition under reaction conditions on Pt–Au and Ir–Au alloys, but unfortunately, very frequently, as also in the present case, this is not possible, due to experimental limitations of one kind or another. Therefore, we have turned our attention to a platinum alloy of a kind which forms a continuous series of solid solutions, since we believe that use of *the whole* alloy composition range may still bring some interesting points for stereochemical considerations about the reaction mechanism, even if surface segregation exists.

Having these ideas in mind we have chosen the Pt–Pd alloy system, known as very good hydrogenation catalyst (9) but still not studied in an alkane isomerization. Platinum isomerizes neopentane but Pd does not (10, 11). For that reason a study of neopentane isomerization on Pt–Pd alloys, i.e., on Pt diluted in Pd matrix, could reveal, in our opinion, whether the bond shift isomerization is a surface-sensitive or a facile reaction (2).

It was also of interest to study the selectivity of Pt–Pd alloys in n-pentane and n-hexane conversion. Two different mechanisms for alkane cyclization were suggested for Pt and Pd by Muller and Gault (12), who postulated the existence of intermediate species such as:

and the considerations of Clarke and Rooney (2) are correct then a change of the ratio of 1,5- versus 1,6-cyclization with Pt–Pd alloy composition should show whether the catalytic character of the components in an alloy is conserved. Incidentally, a synergistic improvement in isomerization of n-pentane has been reported for different VIII–VIII group metal alloys (Pt–Ir, Pt–Os, and Pt–Ru (13)).

For the present study evaporated Pt–Pd films were chosen as a convenient catalyst form.

EXPERIMENTAL METHODS

Reactions of hydrocarbons (neopentane and n-pentane, both Fluka puriss., n-hexane manufactured by Chemipan, Warsaw, Poland, purity of 99.9%) with excess of hydrogen were performed in a static system (volume of 600 cm³) as previously described (14). The method of Pt film preparation was the same as in Ref. (14), whereas the procedure for preparing Pd films was taken from Ref. (15). The component metals were simultaneously evaporated at a pressure of 10^{-5} Torr (1 Torr = 133.32 N m⁻²) onto the inner wall of a spherical Pyrex vessel maintained at 773 K, and the deposit was then annealed at the same temperature for 2 to 3 hr in the presence of 3 to 4 Torr of hydrogen in conjunction with a liquid nitrogen trap.

To test the adequacy of the geometry of the sources used for evaporation and in consequence to test the lateral homogeneity of an alloy several segments of 48 at.% Pd alloy film from a number of representative points of the reactor vessel were chemically analyzed. The mean deviation amounted to ±6 at.%. X-ray diffractometry of the films confirmed that they were single-phased, with lattice parameters in agreement with the literature data (16).

As Clarke and Rooney point out (2), consideration of the relative strain indicates that 1,5- is more likely than 1,6-cyclization by the carbene/alkyl insertion route (on Pt) but it is no ground for such a preference via the alkene/alkyl insertion route (on Pd). If the suggested mechanisms

In all runs the hydrocarbon partial pressure used represented 1.3 × 10¹⁹ molecules in the reactor. The reaction mixture

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TABLE 1

Reaction of Neopentane on Pt–Pd Films at 523 K: Rate of Conversion, Selectivities, and Initial Distribution of Hydrogenolysis Products

Film composition/ atom% Pd	Rate of overall conversion,[a] molec/cm² sec	Selectivity,[b] %		Hydrogenolysis product distribution,[c] %			
		Hydrogenolysis	Isomerization	CH_4	C_2H_6	C_3H_8	iC_4H_{10}
Thick films (~50 nm)							
0	4.21×10^{11}	21	79	16.0		7.4	76.5
5	1.47×10^{11}	54	46	10.7		28.0	61.3
20	3.60×10^{10}	55	45	27.9		27.9	44.3
30	3.24×10^{11}	59	41	19.3		19.3	61.3
54	1.59×10^{12}	85	15	24.2	12.9	19.3	43.5
65.5	1.26×10^{12}	84	16	21.7	17.8	17.8	42.7
75	1.10×10^{12}	90.5	9.5	35.9		13.4	50.8
76	1.10×10^{12}	95	5	28.3		16.8	54.8
80	2.56×10^{11}	89.5	10.5	30.0		16.5	53.5
95	9.21×10^{11}	85	15	23.8	14.2	15.3	46.6
98	3.41×10^{11}	87	13	23.7	6.2	9.4	60.6
100	1.93×10^{12}	96.5	3.5	21.7	8.8	11.9	57.5
Thin films (~9 nm)							
55	2.60×10^{10}	38	62	39.5		23.8	36.8
89.5	6.50×10^{10}	71	29	42.6		10.3	47.0

[a] Assuming that the roughness factor of all films is equal to 1. Geometrical surface area = 325 cm².
[b] Defined in the manner indicated in Fig. 1.
[c] As above but now assuming that Σ hydrogenolysis products = 100%.
Note: For pure Pt and Pd films the arithmetic mean values are reported (three runs for each metal), whereas only single runs for alloy films were performed.
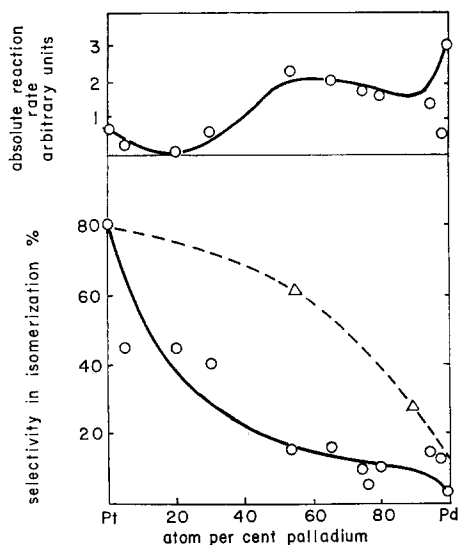

FIG. 1. Reaction parameters of neopentane conversion on thick (○) and thin (△) Pt–Pd films at 523 K. Selectivity expressed as percent neopentane consumed in isomerization divided by total consumption at the initial stage of the reaction. The absolute reaction rate is referred to the overall consumption of neopentane.

(H_2/hydrocarbon = 10/1) was admitted to the reactor kept at the lowest reaction temperature, i.e., 523 K, 503 K, and 548 K for neopentane, n-pentane, and n-hexane conversion, respectively. After the first 30 min of the reaction (5–6 "injections" to the glc system), the temperature of the furnace was raised as quickly as possible to study the course of the reaction at higher temperature. The degree of conversion was never higher than 5% for the lowest temperature of each reaction.

RESULTS

The reaction of neopentane on Pt–Pd alloy films was examined in the temperature range 523–593 K. However, we wish to interpret the kinetic results for the lowest temperature only, i.e., 523 K. At higher temperatures a decline in isomerization, particularly for Pd, was very marked and we were able to detect even the decrease of isopentane content consumed in
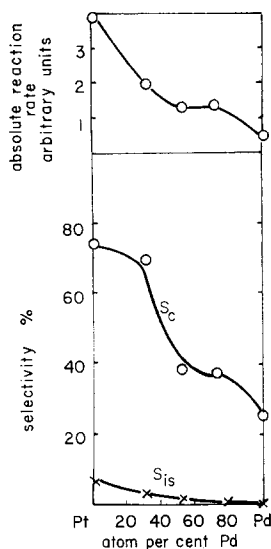
FIG. 2. Reaction parameters of n-pentane conversion on thick Pt–Pd films at 503 K. S_c and S_{is} are selectivities for cyclization (O) and isomerization (X) expressed as percent n-pentane consumed in the designated process divided in each case by total consumption.

low ($\sim 3.5\%$) but *not negligible*, in contrast to the work of Anderson and Avery (*10*). This value is rather comparable with the selectivity for isomerization in an isobutane reaction ($\sim 5\%$, Ref. (*10*)).

We noticed that the selectivity in isomerization dropped markedly during the course of the reaction probably due to the poisoning of metal catalysts by the deposition of carbonaceous residues. This poisoning was much stronger for Pd and Pt–Pd alloys than for Pt itself. It was striking that after raising the reactor temperature to 573 K the isomerization was stopped. However, when the reaction mixture was admitted onto a fresh Pd film kept at 573 K the isomerization proceeded for a few minutes and then stopped. Anderson and Avery (*10*) admitted the reaction mixture onto a film kept at 273 K and then slowly raised the reaction temperature. We suppose that they were not able to detect any isomerization due to the possible carbonization of the palladium surface that had taken place before the
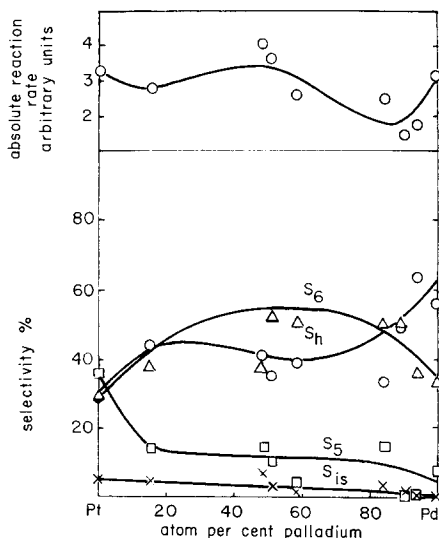
hydrogenolysis, although total conversion was still quite low (approx. 5%). The results of neopentane conversion at 523 K are presented in Table 1 and Fig. 1. It can be easily seen that there is a great difference between the behavior of thick (~ 50 nm) and thin (~ 9 nm) films. In a similar way we present the data for n-pentane and n-hexane conversion in Figs. 2 and 3.

DISCUSSION

The reaction rates on Pd and Pt films tended to be at the reproducibility level of about $\pm 50\%$, and depended somewhat on catalyst history, although selectivities for individual reaction routes were about $\pm 10\%$. Thus our discussion is largely concerned with the variation of selectivity. Figure 1 shows that the selectivity for isomerization on pure platinum is very high ($\sim 80\%$) which is in agreement with Anderson and Avery (*10*). However, on pure Pd the isomerization selectivity is

FIG. 3. Reaction parameters of n-hexane conversion on thick Pt–Pd films at 558 K. S_h, S_{is}, S_5, and S_6 are selectivities for hydrogenolysis (O), isohexane formation (X), methylcyclopentane production (□), and aromatization (△) defined in the manner indicated in Fig. 2.

film reached the temperature appropriate for the isomerization. Our opinion may be supported by the results of Ross et al. (17) who found that heating a Pd film to 453 K in neopentane + D_2 mixture reduced the amount of the exchange with deuterium. The authors attributed the effect to an increase in the number of adspecies (including single carbon species) multibonded to the palladium surface and consequently less suitable for exchange on this metal. The absence of neopentane isomerization on silica-supported palladium noticed by Boudart and Ptak (11) in a batch reactor study also calls for a rational explanation. Although the authors did not specify precisely either the reaction conditions (temperature, purity of the catalyst, etc.) or the results obtained on their Pd/SiO_2 (see Ref. (11), Table 1), we consider that a fast surface carbonization in the initial stage of the kinetic run cannot be excluded. Hence everything goes to show that the selectivity in isomerization on pure Pd depends strongly on the manner in which the experiment is performed. Because of the carbonization the isomerization proceeds only at the beginning of the process if, of course, the temperature is sufficiently high. Possibly, an increase of the H_2/hydrocarbon ratio would keep the isomerization selectivity for a longer period.

The discrepancies between our results and those obtained by others (10, 11) may also be explained by an effect of the surface texture of palladium on the extent of poisoning. Available data suggest that more carbonization is caused by adsorption of hydrocarbons on other than (111) crystallographic planes of Ni and Pd (18, 19). In fact, our palladium films were very strongly textured (15), exposing a higher proportion of (111) faces than the less tempered films of Anderson and Avery (10) and the supported catalysts of Boudart and Ptak (11).

It is shown in Fig. 1 that the selectivity in isomerization decreases markedly with increase of Pd content. This fact would strongly suggest a surface structure sensitivity for the isomerization. One should, however, consider this fact in terms of the alloy surface composition induced by the actual reaction conditions. Unfortunately such important data are not available. Therefore we have taken, as a first approximation, the necessary data as predicted by the theory of the ideal alloy solution developed by Williams and Nason (20). Platinum has a much higher heat of sublimation than palladium; the characteristic parameter determining segregation for the Pt–Pd alloy system, ΔH sub/kT, is greater than 22.5 for temperatures less than 1000°K. The conclusion (from Ref. 20, Fig. 8) is that the platinum surface concentration should be negligible when the bulk composition of the Pt–Pd alloy is in the region of 20 to 100% Pd. Further, due to the similar chemisorptive properties of Pd and Pt with respect to the reactants, one can hardly expect any surface composition changes caused by the actual reaction mixture (21).

Therefore one should expect a drop in isomerization selectivity rather more dramatic than actually observed (Fig. 1) on adding very little palladium to platinum and, later, an almost constant low selectivity characteristic for pure palladium. Two factors could, in our opinion, cause this "deviation": First, the texture of the alloy film could change with the Pt–Pd alloy composition and, second, the actual surface composition is not as predicted by Williams and Nason. It is known (10) that the selectivity for isomerization versus hydrogenolysis of isobutane on evaporated Pt films, claimed to expose (111) faces predominantly, was found to be enhanced by a factor of five relative to unoriented films. Therefore, if the degree of orientation is a function of Pd content it would affect the selectivity pattern. It is known (10) that palladium film prepared in the

same way as ours shows a very distinct (111) texture. Platinum-on-Pyrex films deposited at 723 K also showed some (111) orientation with respect to the support but with the degree of orientation depending in an uncontrolled way on the history of the glass (10). In any case, our platinum film sintered at 773 K was unoriented, whereas Pd and alloys of 12 and 90 at.% Pd showed very strong (111) orientation as checked by the X-ray method. There-fore, because the texture changes with alloy composition were not very pro-nounced we cannot regard them as having a great influence on the selectivity pat-tern. Another factor that probably plays a most important role is the apparent surface composition, which in practice could differ from that predicted by the theory (20). From the comparison of the selectivity for thick ($\sim$50 nm) and thin ($\sim$9 nm) Pt–Pd alloy films (Fig. 1) it can be concluded that a surface enrichment with Pd takes place. The selectivity of thin alloys is much higher than that of thick films of the same composition sug-gesting that the surface of the former is less enriched with Pd than the latter. The conclusion is in agreement with the theory of Williams and Nason (20) which considers the effect of alloy particle size on the effective surface segregation (less segregation for small particles). If the isomerization selectivities of pure Pt and Pd films of thickness >5 nm are not much different from those of thick films (22), we can roughly describe the selectivity as a gentle monotonic function of alloy sur-face composition.

Furthermore, it seems that the theory may overemphasize the surface enrichment with a metal of a lower heat of sublima-tion (23), i.e., here, with palladium. Pos-sibly the surface composition changes with bulk content in a similar way to the selectivity in isomerization (Fig. 1).[1] Thus,

[1] The problem of the surface composition of Pt-Pd alloys is treated in a more exhaustive way

the selectivity of thick films vs "inferred" surface content may be almost a linear function.

Now the question arises as to how to refer the results to a possible reaction mechanism. The question is not simple because both hydrogenolysis and isomeri-zation compete in the reaction system. However, we shall try to show that the one-site isomerization can operate in this case.

Let us suppose that hydrogenolysis of neopentane involves $\alpha\alpha\gamma$ or (and) $\alpha\alpha\gamma\gamma$ multiadsorbed species and takes place only on Pd–Pd atomic doublets as a demanding reaction (10, 24, 25). The neglecting of the hydrogenolysis on Pt is justified by its high selectivity towards isomerization ($\sim$80%). In order to make our considera-tion simpler we ignore also hydrogenolysis on Pt–Pd "mixed" ensembles. At the same time the isomerization may go via only one-Pt-site adsorbed species (7). Taking into account only simple geometric con-siderations and neglecting the so-called "ligand effect," it is possible to write simple expressions for r_h, r_{is}, r_t, and S_{is}, where the symbols denote rate of hydro-genolysis, rate of isomerization, total re-action rate, and isomerization selectivity (in percent), respectively, as a function of the palladium surface atomic ratio, x:

$$r_t = r_h + r_{is} = ax^2 + b(1-x),$$
$$S_{is} = 100b(1-x)/ax^2 + b(1-x).$$

Substitution of $a = 3$ and $b = 1$ as rea-sonable values (see Fig. 1) allows us to predict the selectivity for isomerization and the total reaction rate (Fig. 4). A shallow minimum in total reaction rate for $\sim$20 at.% Pd is reasonable agreement with that found experimentally (Fig. 1), if of course, one neglects the severe surface enrichment with Pd. The isomerization

in Part II of this work (21) and a final conclusion from a discussion presented there is in agreement with the suggestion given above.
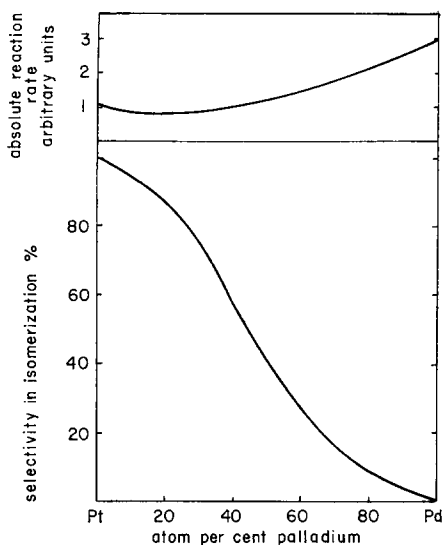
selectivity against the surface composition is almost a linear function as is the predicted selectivity of thick films against the "inferred" surface concentration pattern. This simple description of the relatively complex process does not prove the reaction mechanism unequivocally; however, it shows, in our opinion, that isomerization may go via the one-site mechanism suggested by McKervey et al. (7) as has been supported recently by the appreciable amount of isopentane-d_1 found in deuteroisomerization of neopentane on a heavily sintered Pt film (26).

The selectivity for n-pentane conversion on Pt–Pd films at 503 K is shown in Fig. 2. The selectivity towards 1,5-cyclization decreases less markedly with Pd content than for neopentane isomerization. According to Gault (27), low coordination single metal sites on supported Pt catalysts are most suitable for cyclization. It may happen that in our case the "excess" cyclization selectivity simply follows from a somewhat higher proposition of isolated single Pt sites with only Pd atoms as nearest neighbors (a variation of isolated

single B atoms in AB alloy goes through a maximum for 20 at.% of B (28)).

The isopentane formation is generally quite low. It is due to the fact that for thermodynamic reasons the cyclization is favored over the isomerization at very low pressures of hydrocarbon.

Figure 3 shows the n-hexane conversion at 553 K. The selectivity pattern is rather complex. It is worth noting that the selectivity in 1,6-cyclization goes through a gentle maximum. At the same time the selectivity in methylcyclopentane formation is rather low, $\sim 10\%$, and almost the same for alloys and for pure palladium. In this respect the ratio $S_{1,6\text{-cyclization}}/S_{1,5\text{-cyclization}}$ may also be somewhat higher on alloys than on pure metals. Reasons for the occurrence of this mild synergistic effect are not known.

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