

Catalytic Reactions of Hydrocarbons over Pt-Pd Alloys

II. Deuterium Exchange of Methane and Ethane over Pt-Pd Alloy Films. Surface Composition of Pt-Pd Alloy System.

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The exchange of deuterium with methane is proposed as a diagnostic tool to estimate the surface composition of Pt-Pd alloy films. Only stepwise exchange has been found on Pt, Pd, and Pt-Pd alloys. From the kinetic parameters (E_A and $\log A$) obtained on thick and thin films the surface composition of thick films is predicted. The occurrence of a well-defined compensation effect suggests that the total activity may be calculated from the contributions from platinum and palladium individual active centers, supporting the idea of using deuterium-methane exchange for solving the problem of surface composition. It seems that although the surface of Pt-Pd alloy is in fact enriched with Pd, this occurs to a lesser extent than is foreseen by the theory of alloy segregation. This conclusion finds support in the analysis of one Pt-Pd alloy by Auger electron spectroscopy. The results of a study of C_2H_6 - D_2 exchange are also reported.

INTRODUCTION

In Part I (1) the results of kinetic studies of C_5 and C_6 alkane conversions over Pt-Pd alloy films have been presented. Conclusions relevant to the current debate on the mechanism of catalytic alkane isomerization on metals have been drawn but their value depends considerably on the accuracy of the estimation of the alloy surface composition. We have concluded that it may be possible that the surface enrichment in palladium is not as large as is foreseen by the theory of Williams and Nason (2). It has therefore become ap-

parent that further work for more precise estimation of the surface composition of Pt-Pd alloys is urgently needed.

One way to solve this problem is to use Auger electron spectroscopy (AES), and we have attempted this. Unfortunately, we were not able to analyze the surface composition of alloy film deposited "in situ" in the AES chamber but only to examine samples prepared in another vacuum system and transferred through the atmosphere to the AES equipment. The usual surface cleaning by an argon ion beam could not be applied because of

the possibility of the selective removal of one of the alloy components from the surface. In the cleaning procedure we were, in fact, limited only to hydrogen treatment. It was clear that any conclusion drawn from the AES experiment might be of rather qualitative value.

Accordingly we looked for another method for the Pt-Pd alloy surface composition diagnosis. Methods involving the selective chemisorption of gases (3) were not very attractive because of the very similar chemisorptive properties of platinum and palladium. Instead, we decided to choose a catalytic reaction as a diagnostic tool for surface composition. In the selection of the appropriate reaction it was necessary to have in mind the following criteria:

- (1) different catalytic activities of both metals,
- (2) known (preferably simple) reaction mechanism over whole Pt-Pd alloy system,
- (3) similar reaction conditions as used in the study of alkane conversion (1).

The last criterion is clear if one considers the possible effect of adsorbate on the surface enrichment (2). We have chosen deuterium exchange of methane since there exists a good deal of mechanistic data on this reaction from previous works. An almost clean stepwise exchange has been reported on palladium unsintered films (4) as well as on Pd powders (5). The behavior of platinum is slightly more complex: Mainly stepwise exchange has been found on Pt and Pt-Pd powders (5), whereas some multiple exchange is detected, in addition, on Pt unsintered film (4). Furthermore, the proportion of multiple exchange grows with temperature increase.

Since deuterium exchange of methane has not been studied on heavily sintered Pt, Pd, and Pt-Pd alloy films (such as used in Part I (1)), we considered that besides the diagnostic aspect, the under-

taking of these studies was justified for their own sake. In addition we have briefly studied deuterium exchange with ethane, where due to the higher complexity of the ethane molecule the presence of several adsorbed hydrocarbon intermediates is possible.

EXPERIMENTAL METHOD

All exchange experiments were performed in a circulation apparatus (volume of 700 cm³). Methods of film preparation, annealing (773 K) and characterization were given in Part I (1). The reaction was followed with an AEI MS10c2 mass spectrometer attached via a capillary leak to the reaction system. Usual corrections were applied for natural isotopic abundance and fragmentation (electron energy of 25 eV). Methane and ethane were purified before use by removal of trace amounts of oxygen and triple distillation at liquid nitrogen temperature. Deuterium was purified by passing it through a heated palladium-silver thimble. The standard reaction mixture consisted of 2.41×10^{20} molecules of CH₄ and 1.69×10^{21} molecules of D₂ (D₂/CH₄ = 7/1). For C₂H₆-D₂ exchange we used 1.93×10^{20} molecules of C₂H₆ and 1.71×10^{21} molecules of D₂ (D₂/C₂H₆ = 9/1).

RESULTS

I. METHANE-DEUTERIUM EXCHANGE

1. Thick Films (effective thickness of ~50 nm)

Only stepwise exchange of D₂ with CH₄ was found over all Pt-Pd alloys (0, 14, 41, 60, 66, and 100 at.% Pd) in the temperature range from 573 to 673 K. At lower temperatures the activities of the heavily sintered films were extremely low. Pure platinum was the least efficient catalyst whereas palladium and Pd-rich alloys were the most active ones. Arrhenius plots of the exchange are presented in Fig. 1,

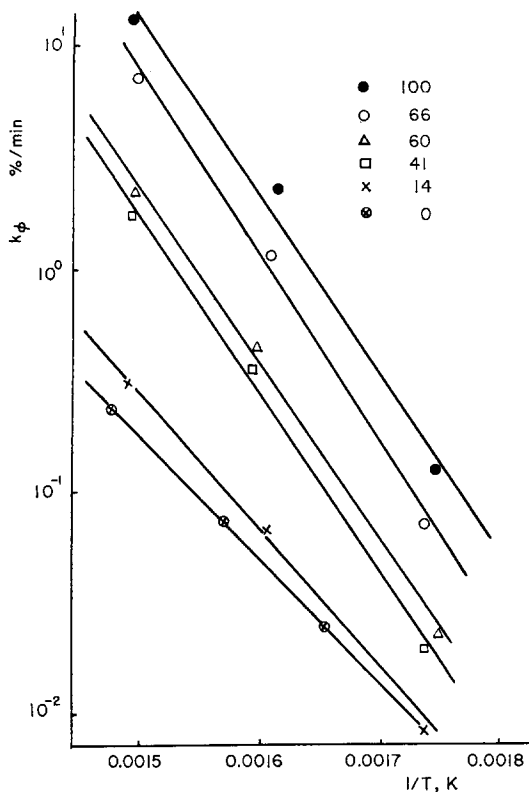


FIG. 1. Arrhenius plots for $\text{CH}_4\text{-D}_2$ exchange on Pt-Pd thick films. Identifying symbols indicate composition of film in atom per cent Pd.

where the rate constant k_ϕ is defined as by Kemball (6). In Fig. 2a and b there are presented the dependences of the apparent activation energy (1 kcal = 4.1868

kJ) and frequency factor on the bulk composition of the Pt-Pd alloy system: The circles are characteristic of thick films (~ 50 nm) and the triangles of thin ones (< 10 nm, see below). In Fig. 2c the compensation effect is presented, and a comparison made with the data of McKee and Norton (5) for Pt-Pd powders.

2. Thin Films (less than 10 nm)

Again only the stepwise exchange of deuterium with methane was found on these thin Pt-Pd films. Table 1 shows activation energies and frequency factors for $\text{CH}_4\text{-D}_2$ exchange on thin films of Pt, Pd, and two alloys, 60 and 87 at. % Pd.

II. ETHANE-DEUTERIUM EXCHANGE

The above reaction was performed only on thick (~ 50 nm) Pt-Pd alloy films (0, 4, 13, 80, and 100 at. % Pd). Table 2 shows kinetic parameters (E_A and $\log A$) and initial product distributions of deuterioethanes. Despite high reaction temperatures hydrogenolysis was negligible. Again platinum was the least active catalyst and palladium the most active one.

III. AES ANALYSIS

One of the thick alloy films (43 at. % Pd) not used previously in any catalytic run

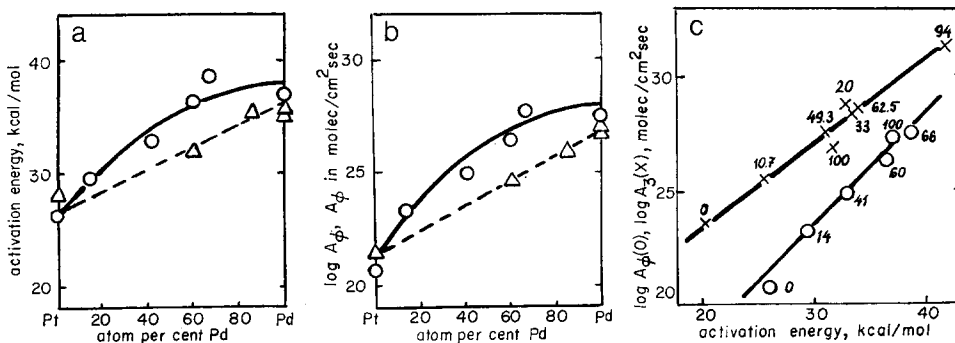


FIG. 2. Reaction parameters of $\text{CH}_4\text{-D}_2$ exchange on thick (O) and thin (Δ) Pt-Pd alloy films: (a) activation energy, (b) frequency factor, definition in the text, and (c) compensation effect; comparison is made of our data (O) with McKee and Norton data for Pt-Pd powders (X) (5). Identifying numbers indicate composition of alloy in atom per cent Pd.

TABLE 1

Activation Energies and Preexponential Factors for CH₄-D₂ Exchange over Thin Pt-Pd alloy Films^a

	Effective ^b thickness (nm)	E_A (kcal/ mol)	$\log A$ (A^c in molec/ cm ² sec)
Platinum	2.1	28.1	21.4
	6.2	28.0	21.4
	44.5	26.0	20.7
Palladium	5.4	35.5	27.0
	17.3	35.0	26.7
	60.4	37.1	27.4
60 at.% Pd	6.0	32.0	24.6
87 at.% Pd	3.2	35.6	25.9

^a Values for thicker platinum and palladium films given as references.

^b Taken as $m/\rho \cdot S$, where m is the mass of a film, ρ is the density of an alloy, and S is the geometrical film area (325 cm²).

^c Assuming the roughness factor of all films is equal to 1.

was examined by Auger Electron Spectroscopy using a retarding field analyzer with three-grid optics (Vacuum Generators). According to theoretical predictions (2) practically pure palladium should be present in the surface layer of our sample. The AES spectrum showed the presence of comparable heights of "Pt" (64 eV) and "Pd" (330 eV) peaks. An attempt was made to estimate more precisely the

outermost layers using the external calibration method, but it failed because of the reasons given in the Introduction. The average depth of material contributing to the "Pd" peak is 0.7 to 0.8 nm, as compared to only 0.4 to 0.5 nm to the "Pt" peak. Separate hydrogen and acetylene treatments at room temperature and 373 K did not cause any change in the ratio of "Pt" to "Pd" peak heights.

DISCUSSION

The experimental data for CH₄-D₂ exchange on thick Pt-Pd alloy films are in quite good agreement with those obtained on Pt-Pd powders by McKee and Norton (4). The presence of only stepwise exchange in both cases and particularly the numerical coincidence of activation energies might be accidental. It should be noticed that the above experiments on powders were performed at fairly low temperature, i.e., 356–462 K, while on sintered films methane exchange began at a measurable rate at about 573 K except on palladium. Because of the compensation effect (Fig. 2c) the sequence of activities is opposite to that found by McKee and Norton, i.e., at a higher temperature (>573 K, as in our case) passing along the series Pd, Pt-Pd, and Pt the activity diminishes. McKee and Norton (5) found the tem-

TABLE 2

Activation Energies, Frequency Factors, and Initial Product Distributions (IPD) for C₂H₆-D₂ Exchange on Pt-Pd Alloy Films

	Temp. range (K)	E_A^a (kcal/ mol)	$\log A^a$ (A in molec/ cm ² sec)	Temp. for IPD (K)	IPD						M^b
					d_1	d_2	d_3	d_4	d_5	d_6	
Platinum	573–626	26.2	23.0	573	53	—	5	18	—	24	2.12
4 at.% Pd	549–614	27.0	24.0	581	39	24	20	6	—	11	2.37
13 at.% Pd	512–580	28.5	25.2	544	12	—	15	—	33	40	4.62
80 at.% Pd	488–544	29.7	26.3	544	27	43	7	9	7	7	2.47
Palladium	472–546	29.8	26.3	546	31	20	6	16	10	20	3.23

^a Calculated from $k_\phi = A \exp(-E_A/RT)$, k_ϕ defined as by Kemball (6).

^b The mean number of H atoms exchanging initially per molecule.

perature at which the rate on all the powder samples became equal was 580 K. In our case the isokinetic temperature was lower, namely, 400 K.

Substantial contribution of a multiple $\text{CH}_4\text{-D}_2$ exchange on Pt films as found by Kemball (6) was not confirmed by our experiments. However, it should be noticed that Kemball's films were deposited onto a glass wall at about 273 K and not subjected by any further thermal treatment before the reaction, such films being polycrystalline and essentially randomly oriented (7a). The number of surface imperfections and sites of low coordination was probably much higher than for our heavily sintered films exposing predominantly (111) planes (1). We suggest that these thermally unstable sites, present in higher proportion on unsintered platinum film surface, are responsible for multiple exchange via multiply bonded intermediates. The conclusion is opposite to that proposed by Anderson and Macdonald (8) for the situation on Ni films: There the sites responsible for the formation of singly adsorbed residues from ethane and propane were associated with surface features that were thermally unstable. However, Anderson stated later (7b) that the behavior of nickel should not be extrapolated to other metals and, for example, both high and low temperature-treated platinum films gave essentially the same product distribution for ethane exchange. We can only assume that our Pt films were even more heavily sintered (773 K) than those of Anderson (rather less than 673 K). At such a high temperature (Sanders parameter $\tau \sim 0.38$) the recrystallization and grain growth become very important, leading to an almost featureless surface (7c).

Another interesting point arises from the analysis of the compensation effect. The monotonic dependence of both the activation energy and the frequency factor on the alloy composition has led us to the suggestion that the compensation effect is

probably due to individual contributions from "platinum" and "palladium" surface centers in such a way (9) that

$$\begin{aligned} A_{\text{Pt}_{1-x}\text{Pd}_x} \exp(-E_{\text{Pt}_{1-x}\text{Pd}_x}/RT) \\ = (1-x)A_{\text{Pt}}^* \exp(-E_{\text{Pt}}^*/RT) \\ + xA_{\text{Pd}}^* \exp(-E_{\text{Pd}}^*/RT), \end{aligned}$$

where x is the atom fraction of palladium in the surface layer, and A_{Pt}^* , A_{Pd}^* , E_{Pt}^* , and E_{Pd}^* are hypothetical Arrhenius parameters of "platinum" and "palladium" centers in $\text{Pt}_{1-x}\text{Pd}_x$ alloy, respectively.

Substitution of A_{Pt}^* , A_{Pd}^* , E_{Pt}^* , and E_{Pd}^* by values characteristic for pure metals gives unreasonably low values of x which could suggest very strong surface enrichment in platinum. The incorrectness of such an approximation for the surface composition diagnosis probably results from some electron transfer between palladium and platinum in the alloy "ligand effect," (10)).

Having still in mind the solution of the problem of estimating alloy surface composition we turned our attention to the experimental data for thin films. As shown in Table 1 the thickness of the film does not influence the catalytic behavior of Pt and Pd films very much, so the same may hold for Pt-Pd alloys of the same surface concentration. According to the theory of alloy segregation (2) there might be none or very little surface enrichment in palladium for very thin films resulting from the mass balance for small alloy particles. Thus either from Fig. 2a [$E_A = f(x)$] for thick and thin films or from Fig. 2b [$\log A = f(x)$] it is easy to construct another graph (Fig. 3) presenting "inferred" surface composition vs bulk composition. In Fig. 3 the data foreseen by the Williams-Nason model (2) for Pt-Pd alloy system are also shown. To compute the Ω parameter the thermodynamic data on Pt-Pd alloys furnished by Darby and Myles (11) were used. The substantial difference between "inferred" and theoretical data can be easily seen. We think

that the former are more characteristic for our samples. We do not claim that we have solved the general problem of the thermodynamically stable situation for Pt-Pd alloy surface. We only suggest that it might be possible to apply the surface reaction as a diagnostic tool in relation to apparent surface composition. The virtue of our approach relies on the fact that we have selected the conditions (temperature, nature of reaction mixture) of the diagnostic reaction as being very similar to those in which Pt-Pd alloy films were kept during the neopentane isomerization described in Part I (1). We now have the feeling that our conclusion on the mechanism of isomerization is more rational.

Our AES experiment, for reasons given in the Introduction, is only of rather qualitative value. It shows that there is not as serious a surface enrichment in palladium as theory predicts, but it does not say anything about the accurate value of Pd surface content. Obviously it is not in contradiction with the conclusion drawn from the exchange experiments.

Arrhenius parameters of catalytic exchange of ethane with deuterium on Pt-Pd alloy films (Table 2) were found to be less sensitive to the alloy composition than those of CH₄-D₂ exchange, although again the compensation effect seems to exist. Also in this case, i.e., for the temperature range well above the isokinetic temperature, palladium was more active than platinum. Arrhenius parameters and, particularly, initial distributions of deuterioethanes differ slightly from those reported by Anderson and Kemball (12) for unsintered Pt and Pd films. Less multiple exchange is seen in our experiments both of Pt and Pd films than in Anderson and Kemball's work (12), where the mean number of H atoms exchanging initially per molecule was 3.5 for Pt and 4.8 for Pd. Again the reasoning involving the featureless surface state of our heavily sintered

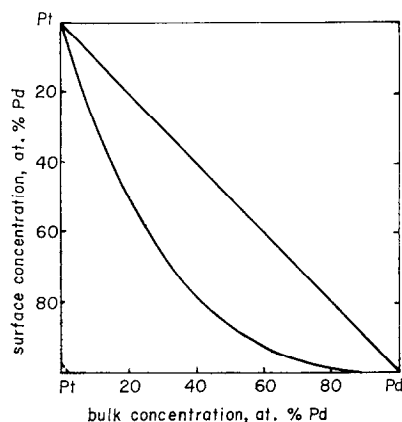
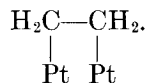


FIG. 3. Surface composition of Pt-Pd alloy: "inferred" (from CH₄-D₂) surface composition (solid line) and theoretically predicted (2) surface content (broken line).

films in relation to randomly polycrystalline films of Anderson (7a) may be valid. We can only assume that now the compensation effect may be explained by the possible existence of such surface species as



However, in this case, where surface doublets are involved, the entropy of activation may increase with the energy of activation due to the collective action of Pt-Pd "mixed" ensembles. It is worth stressing that in the case of methane exchange, where only singly adsorbed methyl species were formed, the compensation effect would result just from the changing the proportion of different active centers.

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