JOURNAL OF CATALYSIS 77, 118–131 (1982)

Reactions of Saturated Hydrocarbons with Hydrogen and Deuterium on Epitaxially Oriented (111) Pd and Pd–Au Alloy Films

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Received January 8, 1982; revised March 25, 1982

The reactions of neopentane, *n*-butane, propane, and *n*-pentane in the presence of an excess of hydrogen have been studied on evaporated Pd/Au-on-mica films. The characterization of films showed that they were predominantly (111) oriented. The selectivity in hydrogenolysis of all hydrocarbons decreased markedly with an increase in the content in Au. The catalytic activity for isomerization of neopentane and *n*-butane was higher for ca. 10 at.% Au alloys than for pure Pd. This finding appears to support the mechanism involving 1,2-bond shift isomerization at one metal site by McKervey *et al.* [*J. Catal.* **30**, 330 (1973)]. Additional experiments with CH_4/D_2 and neopentane/D_2 exchange over Pd–Au(111) alloys at higher temperatures showed considerable difficulties in forming carbene adspecies which could be responsible for another isomerization route. The isotopic exchange between cyclopentane and deuterium over (111) oriented Pd–Au alloys showed that the rate of multiple exchange goes through a gentle maximum for ca. 10 at.% Au. At the same time no special catalytic role of the surface sites of a low coordination number is seen. It is speculated that the rollover process may involve similar intermediate species as in alkene hydrogenation. The relative importance of ensemble size vs electronic effects in the Pd–Au alloys for various reactions is discussed.

INTRODUCTION

Recently we have found (*1*) that on a sintered palladium film on Pyrex the selectivity for neopentane isomerization is low but not negligible (ca. 3.5%). We suggested that the discrepancy between our results and those obtained by others (*2, 3*) could be attributed to an effect of the surface texture of palladium on catalyst poisoning. It has therefore become apparent that further work with more precisely controlled surface orientation of palladium was needed. Preliminary experiments with (111) oriented palladium film on mica showed that such a film was highly active in the isomerization of neopentane (selectivity of 70–80%, ref. *4*), in a distinct disagreement with the works already cited (*2, 3*). On addition, a single experiment with neopentane/D_2 exchange over Pd(111) film at a temperature only slightly lower than used for isomerization indicated that there were difficulties in forming carbene adspecies on the palladium (111) surface. Therefore, we advanced the hypothesis (*4*) that the neopentane isomerization proceeds primarily via an adsorbed alkyl species and not by a surface carbene species as employed in the other mechanisms (*2, 5*).

Extension of such studies to other alkanes would in our opinion provide information useful for the elucidation of the isomerization mechanism. Similarly, the use of a palladium alloy with an inactive metal could give an answer as to the required active ensemble size. We have chosen gold as a diluent metal because in this case one can expect rather easy (111) texturing (*6–8*) and the existing literature data allow us to estimate the surface composition (apparent absence of segregation, Refs. *9–13*).

On the other hand having well-characterized catalysts, Pd(111) and Pd–Au(111) alloys, it seemed interesting to use them as catalysts in two-set exchange of cyclopentane with deuterium and epimerization of

0021-9517/82/090118-14$02.00/0

cis-1,2-dimethylcyclohexane, a reaction mechanistically related to the former one. According to Burwell (*14, 15*) rates of these reactions on (111) planes of fcc metals would be decreased by existence of some steric hindrance in the rollover mechanism. This hindrance is presumably much less serious in the case of the rollover of cyclopentane molecule. However, Clarke and Taylor (*16*) as well as Vlasveld and Ponec (*17*) investigated the exchange of cyclopentane with deuterium over sintered palladium films and found more two-set exchange than Anderson and Kemball (*18*) on unsintered palladium film. Since sintering (especially in hydrogen) of palladium leads to its surface reconstruction, mostly to (111) planes, the quoted results seem to be in apparent disagreement with Burwell's suggestion (*14, 15*). The undertaking of such experiments with Pd(111) and Pd–Au(111) would, in our opinion, be relevant to the current debate whether the rollover process is a surface sensitive reaction or not. Rather conflicting results exist in this matter (*19–23*).

EXPERIMENTAL

Preparation of (111) oriented films of Pd and Pd–Au alloys. The (111) oriented films of palladium and palladium–gold alloys were prepared by epitaxial growth of an evaporated layer of metal on a sheet of mica in a manner similar to the way Anderson and Avery (*2*) prepared platinum (111) film. The essential part of an apparatus was a cylindrical reactor with a wide neck. The freshly cleaved mica sheet was rolled up and inserted through the neck. On unrolling inside, the mica sheet expanded to the entire side wall of the reactor. The area of the mica amounted to about 350 cm^2 (ca. 75% of the total film area, the rest was Pyrex). Palladium and gold (both spectrographically standardized, 0.2-mm-diameter wires from Johnson Matthey) were evaporated simultaneously from two independent sources (tungsten wire, 0.35 mm diameter, Luma, Sweden) following the procedure and geometry of evaporation sources elaborated by Clarke and Rafter (*24*). During evaporation (vacuum 1–5 × 10^{-5} Torr, 1 Torr = 133.3 N/m^2) and subsequent annealing in hydrogen or deuterium (before exchange reactions) for 2 hr, 3–4 Torr, the reactor was maintained at 500°C.

Because we used a cylindrical reactor rather than a spherical one (*24*) one might expect that the lateral homogeneity of our alloy films would be poor. To test the adequacy of the geometry of the evaporation sources three sections of one Pd–Au film (33.9 at.% Au, as estimated from the filament weight loss) were analyzed by the X-ray diffractometry (a Rigaku-Denki X-ray diffractometer with Cu$K\alpha$ radiation and a scintillation counter). As was estimated from the lattice parameter, the top section of the film consisted of 28 at.% Au, the middle 32, and the bottom 36 at.% Au. Further efforts were not made to develop better uniformity. Obviously, more serious nonuniformity is expected if one considers a thickness of our film. However, because the mean thickness of our films was 800–1800 Å it was concluded that they were continuous, at least on the dominant part of their surface.

The X-ray diffraction study confirmed the presence of adequate phase homogeneity and gave important information as to the extent of the epitaxy of our films (see Results).

Apparatus. Investigation of the reactions of hydrocarbons with hydrogen or deuterium was conducted in a static circulation system. The main part of the apparatus was a cylindrical reactor connected to the rest of the system by a flat joint (wide neck) with an indium wire gasket and, from the bottom side, by a small diameter tubing with a Young ball joint with Viton O-ring (to effect the circulation). The whole system was made of Pyrex glass with Young stopcocks and contained no grease. The reaction procedure was described in (*1*). The reactions of hydrocarbons with hydrogen were followed by GLC. For reactions of alkanes we use a 3-m squalane/Chromosorb P column and for epimerization of *cis*-1,2-dimethylcyclohexane, a 3-m silicone SE 30/Chromosorb W. A flame ionization detector was employed.

The course of isotopic exchange between hydrocarbons and deuterium was followed with a mass spectrometer (MS10c2, AEI) via a capillary leak from the reaction system.

Most of the reactants were supplied by Fluka (*n*-butane, neopentane, *n*-pentane-puriss, *cis*-1,2-dimethylcyclohexane-purum), some by Merck (methane, purity of 99.99%; propane, ca. 99.6%). All hydrocarbons were dried and outgassed before use. Hydrogen and deuterium (CEA-CEN-Saclay, France, isotopic purity 99.75%) were purified by diffusion through a heated palladium-silver thimble.

RESULTS

Film Characterization

Transmission electron diffraction and the X-ray diffractometry both indicated that the palladium and Pd–Au alloys had a very high degree of (111) preferred orientation with respect to the mica base. In the case of pure palladium film the ratio of relative intensities of X-ray peaks 111 : 200 : 220 was 100 : 0.06 : 0.045. Similar ratios were found for three Pd–Au alloys, 11.2, 24.1, and 33.9 at.% Au. Such a high degree of orientation resulted from use of mica as a base and from high temperatures (500°C) during film growth and annealing. Christmann and Ertl (*6*) showed by LEED that a similar procedure led to the preparation of the (111) oriented single crystals of Pd–Ag. However, we did not evaporate our films in UHV conditions as Christmann and Ertl did. Therefore it seemed reasonable to employ rather higher temperatures during evaporation than did Christmann and Ertl (500°C instead of 400°C). As a matter of fact Rüdiger (*7*) and Hall and Thompson (*8*), for vacuum conditions similar to ours, reported the optimum temperatures for (111) epitaxy on mica: Pd—470°C (*7*) or 450–500°C (*8*), Au—450°C (*7*), or 270–320°C (*8*).

It should be mentioned that a single run with a Pd/mica film evaporated and annealed at 400°C showed in the reaction of neopentane with H_2 the same catalytic behavior as palladium films prepared in a standard fashion (500°C). Therefore keeping in mind the problem of alloy homogenization we chose 500°C as the standard preparation temperature.

Reaction of Neopentane, n-Butane, n-Pentane, and Propane with Hydrogen over Pd–Au (111)

These reactions were carried out in the presence of 10-fold excess of hydrogen. The alkane partial pressure in the first three reactions was 1.6–1.8 Torr whereas in the last case 2.1–2.2 Torr was used. Tables 1–4 report experimental results. Reproducibility of results (20–30%) would be estimated from the comparison between data obtained for pure palladium films or in some cases for alloys of similar composition (e.g., 32.1 vs 32.5 at.% Au, Table 2). It should be emphasized that Au-rich alloys (more than 50% Au) were generally inactive in all the reactions.

For calculation of turnover frequencies we assumed that the surface area of our films was 450 cm^2, i.e., the roughness factor was 1. Although we intended to work under very low conversion (1–2%, up to 10% for highest reaction temperatures), film deactivation occurred especially at higher temperatures. So, particularly since many experiments were carried out at two temperatures only, we did not attempt to calculate activation energies. However, to compare catalytic behavior (activity, selectivity) among different alloys it was necessary to use the temperature dependences following from data in Tables 1–4 in order to make interpolations or extrapolations (only in exceptional cases). All initial product distributions in Tables 1–4 are expressed as the carbon-percentage of a reactant consumed in the formation of a

TABLE 1

Reaction of Neopentane on (111) Oriented Pd–Au Films: Turnover Frequency and Initial Product Distribution

Film composition at.% Au	Reaction temperature (°C)	N (molec/atom sec)	Initial product distribution (%)[a]				
			CH_4	C_2H_6	C_3H_8	iC_4H_{10}	iC_5H_{12}
0	284	4.07×10^{-5}	2.5	0.8	—	3.8	92.9
	308.5	6.44×10^{-4}	4.3	1.6	2.3	7.9	83.9
0	286	3.17×10^{-5}	2.8	0.2	—	3.8	93.1
	315	8.13×10^{-4}	3.7	0.9	1.3	8.5	85.6
0	293	4.44×10^{-5}	3.7	0.7	2.3	13.7	79.6
	320	6.59×10^{-4}	2.3	0.6	0.9	4.5	91.7
0	294	5.11×10^{-5}	3.8	1.6	2.1	9.2	83.3
	323	7.81×10^{-4}	6.8	1.5	2.3	12.2	77.3
	348	1.10×10^{-3}	30.9	9.3	13.4	46.4	—
9.3	264	2.42×10^{-5}	4.1	0.3	0.4	14.9	80.3
	299	4.08×10^{-4}	5.2	0.1	0.2	18.1	76.4
	328.5	4.22×10^{-4}	11.9	1.4	3.3	24.3	59.1
12.2	314	6.02×10^{-4}	2.4	—	0.8	13.5	83.2
	345	8.13×10^{-4}	12.6	2.1	4.4	29.0	51.8
17.2	290	1.10×10^{-4}	2.1	0.2	—	15.6	82.1
	319	6.48×10^{-4}	5.1	0.2	0.2	20.1	74.5
19.7	320	5.03×10^{-4}	2.0	0.3	0.6	14.5	82.6
	346	7.15×10^{-4}	7.1	1.5	3.9	25.9	61.5
22.8	315	2.54×10^{-4}	1.8	0.6	0.8	13.6	83.2
	335	7.53×10^{-4}	5.5	1.1	2.0	24.3	67.1
28.8	302	7.36×10^{-5}	1.9	0.3	0.7	19.0	78.1
	327	4.86×10^{-4}	1.8	0.1	0.1	13.9	84.2
35.7	321	5.22×10^{-5}	3.7	—	—	19.3	77.1
	343.5	3.08×10^{-4}	5.4	0.5	1.1	14.6	78.4
36.6	317	6.08×10^{-5}	1.6	0.3	0.8	10.5	86.8
	346.5	6.17×10^{-4}	1.4	0.1	0.3	8.3	89.9
44.9	335	1.79×10^{-4}	4.3	0.5	—	13.9	81.3
	363	6.84×10^{-4}	3.9	0.3	—	11.3	84.6
57.5	338.5	1.18×10^{-5}	6.4	0.4	0.8	11.6	80.8
	361	9.19×10^{-5}	2.6	—	0.6	6.8	89.9

[a] Product distribution in Tables 1–4 is expressed as the percentage of a reactant consumed in the formation of a given product divided by total consumption.

designated product, for example mol% of methane from neopentane would be divided by 5 and normalized in deriving the initial product distribution.

Isotopic Exchange of Methane, Neopentane, and Cyclopentane with Deuterium

Rates of isotopic exchange were calculated following the procedure elaborated by Anderson and Kemball (*18*). The initial rate of a replacement of H atoms by D atoms in 100 hydrocarbon molecules (k_ϕ) was calculated from the expression:

$$-\log(\phi_\infty - \phi) = \frac{k_\phi t}{2.303\phi_\infty} - \log\phi_\infty$$

where $\phi = \Sigma_i\, ix_i$, x_i = percentage of isotopic species containing i atoms of deuterium in time t, and ϕ_∞ = equilibrium value of ϕ.

The initial rate of the substrate disappearance, k_0, (%/time)

$$-\log[X_0 - (X_0)_\infty] = \frac{k_0 t}{2.303[100 - (X_0)_\infty]} - \log[100 - (X_0)_\infty]$$

TABLE 2

Reaction of *n*-Butane on (111) Oriented Pd–Au Films: Turnover Frequency and Initial Product Distribution

Film composition at.% Au	Reaction temperature (°C)	N (molec/atom sec)	Initial product distribution (%)			
			CH_4	C_2H_6	C_3H_8	iC_4H_{10}
0	257.5	2.42×10^{-5}	16.7	—	56.3	27.1
	272	9.68×10^{-5}	23.0	6.0	50.8	20.3
	300	5.89×10^{-4}	20.1	8.8	41.9	29.2
0	265	5.07×10^{-5}	23.1	17.0	48.0	11.9
	288.5	5.77×10^{-4}	18.4	20.2	48.2	13.1
	314	2.93×10^{-3}	15.5	26.8	37.5	20.1
0	293	3.12×10^{-4}	19.2	16.6	44.3	19.9
	314	1.73×10^{-3}	16.5	22.1	38.8	22.6
11.2	273	7.06×10^{-5}	21.7	2.1	54.2	22.0
	298	3.56×10^{-4}	11.0	3.3	33.5	52.1
	324	1.83×10^{-3}	9.2	4.4	27.6	58.8
15.3	271	2.37×10^{-5}	14.0	2.9	44.2	38.9
	294.5	1.28×10^{-4}	12.1	4.9	44.2	38.8
	318.5	5.51×10^{-4}	8.7	4.1	30.3	56.9
24.1	319	1.35×10^{-4}	9.6	2.5	43.3	44.6
	343	6.62×10^{-4}	9.0	3.2	39.6	48.2
32.1	338	9.97×10^{-5}	5.0	2.4	18.7	73.9
	361	4.05×10^{-4}	5.9	1.3	26.1	66.7
32.5	323	2.74×10^{-5}	4.8	1.9	21.9	71.4
	348.5	1.92×10^{-4}	5.2	2.5	23.5	68.9

TABLE 3

Reaction of *n*-Pentane on (111) Oriented Pd–Au Films: Turnover Frequency (N) and Initial Product Distribution

Film composition (at.% Au)	Reaction temperature (°C)	N (molec/atom sec)	Initial product distribution (%)						
			CH_4	C_2H_6	C_3H_8	iC_4H_{10}	nC_4H_{10}	iC_5H_{12}	cC_5H_{12}
0	240	1.35×10^{-5}	14.0	2.8	3.6	5.7	30.5	23.0	20.4
	266.5	1.36×10^{-4}	6.0	1.1	1.1	—	29.7	6.2	55.9
	297	6.73×10^{-4}	2.8	0.9	1.3	0.1	8.7	3.3	82.9
0	240	1.48×10^{-5}	9.0	2.3	1.1	2.6	45.0	6.3	33.7
	270	1.25×10^{-4}	5.3	1.0	0.9	—	28.2	6.1	58.6
	298	7.33×10^{-4}	2.8	0.8	1.0	0.1	9.2	3.6	82.5
10.0	256	2.20×10^{-5}	1.5	0.5	0.7	1.0	3.0	7.3	86.0
	288	1.72×10^{-4}	1.0	0.6	0.1	0.1	4.8	5.9	87.5
	332	6.68×10^{-4}	0.8	0.4	0.5	0.1	3.9	5.2	89.0
16.8	269	4.17×10^{-5}	0.5	0.7	0.5	0.9	5.3	5.7	86.4
	295	1.88×10^{-4}	0.3	0.2	0.3	0.6	3.1	5.0	90.5
	317	4.03×10^{-4}	0.2	0.1	0.3	0.1	2.5	4.0	92.9
34.7	261	9.85×10^{-6}	0.5	0.8	1.2	1.8	10.2	5.5	80.0
	298	1.09×10^{-4}	0.5	0.6	0.5	0.2	6.3	7.5	84.4
	328	4.18×10^{-4}	0.2	0.1	0.2	0.2	3.2	3.5	92.6

TABLE 4

Reaction of Propane on (111) Oriented Pd–Au Films: Turnover Frequency (N) and Initial Product Distribution

Film composition (at.% Au)	Reaction temperature (°C)	N (molec/atom sec)	Initial product distribution (%)	
			CH_4	C_2H_6
0	280	1.88×10^{-5}	40.7	59.3
	309	9.45×10^{-4}	36.2	63.8
	345	1.15×10^{-2}	38.6	61.4
9.8	312	4.49×10^{-4}	39.5	60.5
	340	3.20×10^{-3}	41.9	58.1
	366	7.07×10^{-3}	44.0	56.0
23.5	311.5	2.98×10^{-4}	34.9	65.1
	334	1.77×10^{-3}	37.1	62.9
	370	6.36×10^{-3}	39.0	61.0
34.3	337	9.35×10^{-6}	69	31
	377	1.93×10^{-4}	37.3	62.7
	405	1.95×10^{-3}	32.2	67.8
47.9	371	3.29×10^{-5}	38.3	61.7
	398.5	2.62×10^{-4}	34.4	65.6
	430	2.24×10^{-3}	35.4	64.6

where X_0 and $(X_0)_\infty$ are percentages of light hydrocarbon during reaction and in equilibrium.

The rate constants k_ϕ and k_0 are related: $k_\phi/k_0 = M_k$, where M_k is the mean number of H atoms exchanging initially per molecule.

At very low conversions of light hydrocarbon (isotopic dilution of deuterium by protium negligible) $M_k = M_d$, where $M_d = \Sigma_i \, id_1/100$ and d_i's = the initial distribution of exchange products.

The usual corrections where applied for natural isotopic abundance and fragmentation (electron energy 15–20 eV).

In the case of CH_4/D_2 exchange (p_{CH_4} = 4.0–4.2 Torr, sevenfold excess of deuterium) on Pd and Pd–Au films we observed only simple exchange, i.e., only CH_3D was an initial product. Figure 4 shows the Arrhenius plots of k_ϕ for Pd and three Pd-rich alloys.

In the case of neopentane/D_2 exchange ($p_{neopentane}$ = 1.6–1.8 Torr, 10-fold excess D_2) the results are shown in Table 5 (the analysis of t-butyl ions). Again the simple (stepwise) exchange seems to dominate, however, at higher temperatures the situation is more complex. A single experiment with neopentane/D_2 exchange on a (111) Pt/mica film showed a maximum for the d_3 product and distinctly a higher value of M_k than in the case of palladium.

Generally, fairly good agreement between M_k and M_d was found for lower reac-

TABLE 5

Neopentane–D_2 Exchange over (111) Oriented Pd–Au Films: Reaction Rate and Initial Distribution of t-Butyl Ions

Film composition (at.% Au)	Reaction temperature (°C)	k_ϕ (%/min)	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	d_9	M_k	M_d
0	228	2.008	93.8	5.2	0.5	0.5	0.01	—	—	—	—	0.986	1.078
	252	6.035	63.4	28.4	6.6	0.5	1.1	—	0.001	—	—	1.058	1.476
9.3	244	3.600	87.7	11.0	1.3	—	0.001	—	—	—	—	1.005	1.136
	264	7.699	47.4	34.5	12.7	4.5	0.9	—	0.001	—	—	1.071	1.770
17.2	245	1.241	92.5	6.8	0.7	0.02	0.001	—	—	—	—	1.018	1.083
	265	2.511	62.9	29.7	6.8	0.06	0.01	0.001	—	—	—	1.038	1.452
	288	5.641	36.8	37.8	20.0	4.4	1.0	0.02	0.001	—	—	1.046	1.951
28.8	254.5	0.578	95.6	4.4	—	0.01	—	—	—	—	—	1.011	1.044
	277	1.200	84.7	13.7	1.6	—	0.002	—	—	—	—	0.997	1.169
	297.5	1.523	62.6	31.7	4.4	1.3	0.004	0.001	—	—	—	0.976	1.445
44.9	286	0.338	99.98	—	0.02	0.002	—	—	—	—	—	0.958	1.000
	305	0.623	90.0	8.4	1.6	—	0.002	—	—	—	—	1.015	1.116
	332	1.342	68.6	26.1	5.3	—	0.005	—	—	—	—	1.058	1.367
Pt/mica	258	8.246	56.4	8.8	19.0	3.5	1.7	1.8	1.3	1.9	5.6	2.418	2.393

TABLE 6

Cyclopentane–D_2 Exchange over (111) Oriented Pd–Au Films: Reaction Rate and Distribution of Initial Deuterium Exchange Products

Film composition (at.% Au)	Reaction temperature (°C)	k_0 (%/min)	Initial product distribution d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	d_9	d_{10}	M_d	M_k
0	20.5	0.00084	—	—	11.5	17.9	14.2	8.2	13.2	10.3	—	24.7	6.5	6.5
	48	0.00573	—	—	—	1.5	7.7	1.2	0.9	3.6	4.7	80.4	9.3	9.4
	22.5[a]	0.00123	—	—	15.5	19.8	13.4	6.1	9.1	13.8	8.7	13.7	6.2	6.2
	42[a]	0.00246	—	—	4.6	5.6	5.4	1.6	1.3	3.5	5.7	72.4	8.9	8.9
0	59[a]	0.01345	—	—	—	3.4	6.3	0.9	0.2	1.4	4.0	83.7	9.4	9.7
	42.8[b]	0.01351	—	—	2.1	1.8	9.1	1.3	1.1	6.7	7.2	70.7	9.0	9.4
	42.8[c]	0.00245	—	—	4.1	7.3	8.5	5.2	Traces	6.9	7.3	60.7	8.4	8.6
	24	0.00102	—	—	6.8	0.3	15.7	9.9	—	14.2	1.9	51.2	8.0	8.2
0	49	0.00896	—	—	1.2	2.3	4.2	1.6	0.7	1.3	6.5	82.2	9.4	9.6
	70	0.10808	—	—	0.3	1.0	4.5	0.9	0.1	1.6	8.8	82.7	9.5	9.7
11.3	56.8	0.23117	—	—	10.9	1.4	24.0	0.4	0.4	6.9	6.4	49.6	7.7	8.1
17.0	43	0.04919	—	—	0.7	2.3	59.0	—	0.2	9.9	3.7	24.4	6.6	6.7
	62	0.43568	0.3	—	Traces	3.3	47.5	0.6	0.8	8.5	3.0	36.1	7.2	7.2
	21.3	0.00294	—	3.8	0.2	3.2	58.5	—	3.0	5.3	6.4	19.6	6.3	6.3
21.2	44	0.01879	4.5	—	—	0.4	54.9	0.3	—	6.6	0.4	33.0	6.7	6.9
	75	0.56758	1.7	0.1	0.1	4.9	26.8	—	0.9	7.6	9.5	48.4	7.9	8.0
32.2	58.5	0.02270	—	—	1.1	3.1	40.0	1.9	0.4	9.5	3.3	40.7	7.4	7.5
	82	0.25248	0.7	—	—	3.5	31.7	1.3	1.0	7.4	6.7	47.7	7.9	8.0
33.9	72	0.02469	—	—	0.4	2.6	16.8	1.9	1.0	6.5	6.4	64.4	8.7	8.8
	88	0.14127	0.3	—	Traces	0.7	10.3	Traces	0.2	4.1	8.0	76.3	9.2	9.3
41.3	69	0.00346	3.5	—	2.1	3.9	21.2	2.9	0.2	2.2	4.3	59.7	8.0	8.0
	94	0.09114	—	0.1	—	0.1	11.2	0.4	0.5	4.2	5.8	77.7	9.3	9.8

[a] Typical (111) oriented Pd film.

[b] Film a after decomposition of PdD phase at 50°C.

[c] Film b after subsequent annealing in D_2 at 500°C.

tion temperatures. At higher temperatures the extent of conversion was too high to enable us to use the results of mechanistic considerations.

Table 6 and Fig. 5 show results obtained for exchange between cyclopentane and deuterium [$p_{\text{cyclopentane}} = 1.5$ Torr, 10-fold excess D_2, no formation of β-PdD phase (*38*)]. The M_d and M_k are very high, usually between 8 and 10. The amount of d_1 and d_2 product is probably underestimated because of relatively large correction for the isotopic abundance.

TABLE 7

Epimerization of *cis*-1,2-Dimethylcyclohexane on (111) Oriented Pd–Au Films

Film composition (at.% Au)	Reaction temperature (°C)	Turnover frequency (molec/atom sec)
	90	5.1×10^{-5}
0	114	1.25×10^{-4}
	140	2.81×10^{-4}
10.0	97	8.73×10^{-4}
	88	5.4×10^{-5}
16.1	111.5	1.35×10^{-4}
	137.5	3.63×10^{-4}
34.9	119	2.15×10^{-4}
	141	4.61×10^{-4}
41.9	110	4.0×10^{-5}
	135	1.80×10^{-4}

Epimerization of cis-1,2-Dimethylcyclohexane

The reaction rate was calculated from the increase of the concentration of *trans*-product (Table 7, Fig. 6). The partial pressure of hydrocarbon was 1.7–1.9 Torr (10-fold excess H_2).

DISCUSSION

Alkane Hydrogenolysis on (111) Oriented Pd–Au Alloys

Figure 3 shows the results obtained for hydrogenolysis of *n*-butane (317°C) and propane (351°C). As had been expected, an increase in the gold content resulted in a rather sharp drop in the hydrogenolysis activity. Similar results have been reported by other workers for hydrogenolysis of various hydrocarbons: Clarke and Taylor (*16*) for deuteriolysis of cyclopentane on highly sintered Pd–Au films; O Cinneide and Gault (*26*) for the hydrogenolysis of *n*-hexane over Pd–Au/Al_2O_3 catalysts; and Visser *et al.* (*27*) for hydrogenolysis of *n*-hexane on Pd–Au powders. Somewhat similar dependences were found for other alloy systems, e.g., Ni–Cu (*42*) or Ir–Au (*28*). Since there is some evidence that the electronic structure of Pd–Au alloys differs from that of Ni–Cu alloys in that with an increase of IB metal content the number of d holes remains constant for Ni–Cu whereas it drops for the Pd–Au alloy system (*27*), similar relation of catalytic activity vs alloy composition again seems to show (*28, 29, 42*) that the geometry and size of the active ensemble is responsible for the hydrogenolysis activity, namely, the presence of Pd–Pd doublets seems to be essential. It should be noticed that generally Pd(111) is not very active in alkane hydrogenolyses. Most probably the reaction occurs via tri- or tetraadsorbed radicals (α, α, β or α, α, β, β) which form on Pd(111) and Pd–Au(111) with some difficulty (see the following section). Initial distributions of hydrogenolysis products (Tables 1–4) show that the reaction is rather selective (mostly demethylation) for both palladium and Pd–Au alloys. This is in general accordance with the literature (*26, 27, 46*).

Isotopic Exchange between Methane and Deuterium, and Neopentane and Deuterium over Pd–Au(111)

Stepwise exchange dominates in both reactions, i.e., only one atom of hydrogen exchanges in one period of adsorption. This is in agreement with earlier results for Pd film (CH_4/D_2, Refs. (*25, 29*); neopentane/D_2, Refs. (*4, 30*)) and Pd–Au powders (CH_4/D_2, Ref. (*31*)). It must be emphasized that the aim of this part of the work was to study the exchange reaction at rather higher temperatures (>228°C), i.e., only slightly lower than for alkane conversion. In the case of CH_4/D_2 exchange such a high temperature was necessary to follow the reaction course, whereas in the case of neopentane/D_2 exchange the reaction rates in this temperature region were very high (even several percent per minute, Table 5). Therefore in some cases initial product distributions might be subjected to a serious error (isotopic dilution). However, for the lowest reaction temperature the initial product distributions are very close to those calculated from the binomial distribution (*4*). On the other hand, the experiment with one Pt(111)/mica film (Table 5) at 258°C showed a much higher extent of multiple exchange than in the case of Pd(111) or Pd–Au(111) alloys. The Pt(111) film exhibited a fairly distinct maximum at d_3. At the same time the conversion of neopentane to isopentane was less than 0.5%. This suggests that in the case of platinum the adsorbed species might be more highly dissociated than in the case of Pd or Pd–Au alloys. It appears then that formation of carbene radicals is not a very fast process on palladium.

The catalytic activity of Pd–Au alloy in CH_4/D_2 exchange drops drastically with increase in the gold content, as may be estimated from Fig. 4 (Arrhenius plots). A similar result was reported by McKee (*31*) for Pd–Au powders (temperature > 130°C). Accordingly, Allison and Bond (*32*) suggest that if both reactants (CH_4 and D_2) possess only σ electrons, the decline in catalytic activity in the region of d-band filling may be dramatic. Somewhat similar, although less drastic character, is found for neopentane/D_2 exchange on Pd–Au(111).[1] This small difference might be due to some specific character of neopentane molecule (methyl

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[1] As may be estimated from Table 5, the alloy of 9.3 at.% Au is only slightly less active than pure palladium.

substituents as electron donors, neopentane always more reactive than methane in the deuterium exchange). Besides, the relation between catalytic activity and Pd–Au alloy composition for both exchange reactions supports the view that we dealt with alloys for which the surface concentration changed rather smoothly with bulk content (no serious surface segregation). This view is in line with the majority of work on the surface composition of Pd–Au alloy (*9–13*).

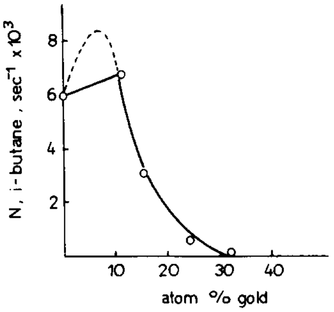


FIG. 2. Catalytic activity of Pd–Au(111) alloys in isomerization of *n*-butane at 317°C.

Isomerization of Alkanes over Pd(111) and Pd–Au(111) Alloys

Table 1 and Fig. 1 show results obtained for neopentane conversion over Pd–Au(111) alloy films. Selectivity toward isomerization is always high and almost constant (ca. 70–90%) for all catalysts. Thus, the rate of overall conversion (Fig. 1) presents approximately the same character as the rate of isomerization. In this figure a distinct maximum in the catalytic activity for ca. 10 at.% Au is seen. The dependence of isomerization rate vs alloy composition for the conversion of *n*-butane (Fig. 2, broken line) is similar although less pronounced. However, in the latter case the increase in the selectivity for isomerization from ca. 20% for pure Pd up to 60–70% for alloys is observed. Now it is clear that in the isomerization of neopentane and *n*-butane the Pd(111) is more active than unoriented Pd film (*2, 4*).

The maximum in the isomerization activity for Pd–Au alloys allows us to discuss some aspects of the reaction mechanism. First, the similar dependence of activity vs alloy composition for the isomerization of both neopentane and *n*-butane suggests that the mechanism is the same in both cases. Second, the presence of a distinct maximum for ca. 10 at.% Au cannot be easily explained by the geometry and size of active ensembles only (in contrast to the hydrogenolysis activity). We believe that the initial process of d-band filling by s electrons of gold must be of some importance here. Boudart and Ptak (*3*) attempted to

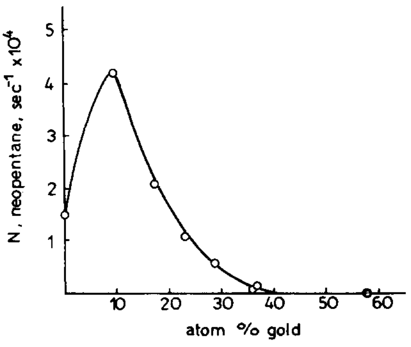


FIG. 1. Catalytic activity of Pd–Au(111) alloys in isomerization of neopentane at 300°C.

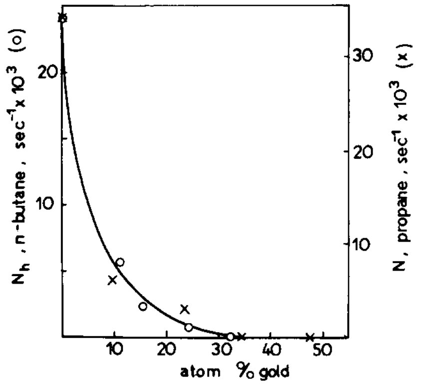


FIG. 3. Catalytic activity of Pd–Au(111) alloys in hydrogenolysis of *n*-butane at 317°C (O), and propane at 351°C (×).

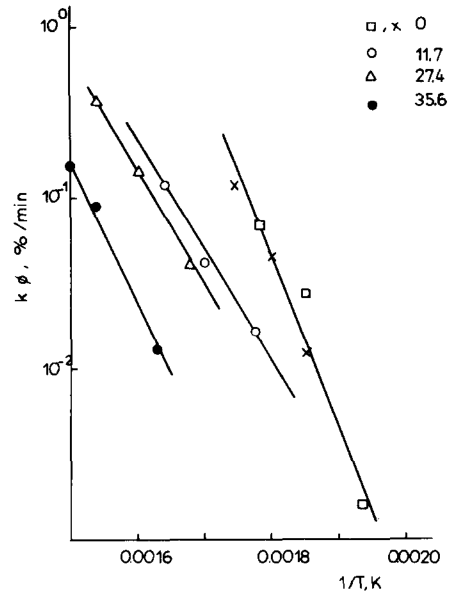
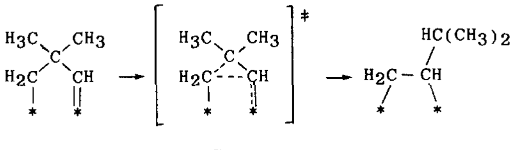


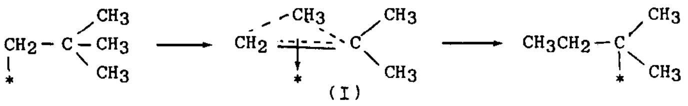
FIG. 4. Arrhenius plots for CH_4/D_2 exchange on Pd–Au(111) alloys. Identifying symbols indicate composition of film in atom percent Au.

correlate the catalytic activity in isomerization of neopentane of various metals with Pauling percentage d-character (σ). They succeeded only in the cases of Pt, Ir, and Au. The fact that the rest of the metals did not fit into the correlation (lack of activity) was caused, according to Boudart and Ptak (*3*), by the relative difficulty in shifting surface valencies necessary for Anderson–Avery mechanism of isomerization (*2*):



SCHEME I

Further work showed, however, that the catalytic activity of gold (*28*) and perhaps of iridium (*2, 28, 33*) in the neopentane isomerization is questionable. Only platinum seems to be a unique catalyst in this reaction. Therefore the replacement of platinum by other efficient catalysts might be realized by preparation of materials which had some physical properties resembling platinum. Such trials have been done in the past with tungsten carbide (*34*). In this respect it should be noted that a 10 at.% Au alloy has the same lattice parameter as platinum (ca. 3.91 Å) and the same percentage d-character $\sigma_{10\%/\mathrm{Au}} \cong \sigma_{\mathrm{Pt}} \cong 46\%$. These facts suggest that we should consider that the reaction is catalyzed by all surface atoms (Pd and Au) rather than by palladium atoms only. However, this does not prove that the attachment of neopentane has a multiple character (Scheme I). As a matter of fact, the Anderson–Avery mechanism has not been proved unequivocally. The existence of sp^2 hybridization for one C atom in the transition complex in the Anderson–Avery mechanism seems a key factor. Studies with CH_4/D_2 and neopentane/D_2 exchange over Pd(111) and Pd–Au(111) alloys show surface carbene species are not formed easily (see the preceding section). O'Donohoe *et al.* (*43*) in their studies on the mechanism of alkane homologation over transition metals reach a similar conclusion. They showed that when surface carbenes are plentiful homologation is fast but isomerization does not take place at all. Besides, CH_2 seems to "homologate" in a linear fashion only (no branching). Therefore it is difficult to apply for isomerization any mechanism with carbene participation, e.g., Anderson–Avery (*2*), Gault (*5*), etc. On the other hand Figs. 1 and 2 very much resemble the catalytic behavior of Pd-rich Pd–Au alloys in many hydrogenation reactions (*32, 35*), where activity is either constant or exhibits a distinct maximum for Pd-rich alloys. Bonding of unsaturated hydrocarbon can involve back-donation of electrons from metal to vacant (antibonding) orbitals in the adsorbed molecules and this may be a key factor in the hydrogenation. A similar situation is proposed by McKervey *et al.* (*44*) in their 1,2-bond shift isomerization mechanism, where bonding between the hydrocarbon intermediate (I) and the surface is very similar to that in olefin–metal complexes:



SCHEME II

Incidentally, the fact that gold improves the isomerization activity of palladium has already been patented (*36, 37*). However, because in catalytic reforming the catalyst has a dual function character, it is difficult to assess whether this improvement is due to better hydrogenation–dehydrogenation action only. At last we should emphasize that all results presented concern (111) oriented palladium and palladium–gold alloys.

The formation of cyclopentane was the dominant reaction (Table 3) in the reaction of *n*-pentane on all Pd–Au films. It seems that in the temperature range 260–270°C, the selectivity for 1,5-cyclization rises from 50–60% for pure Pd to ca. 80% for alloys, in good agreement with the earlier finding of Visser *et al.* (*27*) for methylcyclopentane formation from *n*-hexane over Pd–Au powders.

Isotopic Exchange between Cyclopentane and Deuterium, and Epimerization of cis-1,2-Dimethylcyclohexane on Pd(111) and Pd–Au(111) Alloys

There is a general agreement that cyclopentane/D_2 exchange on palladium gives maxima in the initial product distribution for deuterium atom numbers 5 and 10 (sometimes also 8). The multiple rollover process (*45*) results in the formation of a C_5D_{10} product. Some years ago Burwell (*14, 15*) suggested that on densely packed planes of fcc metals steric hindrance would make ring rollover difficult. This hindrance is even more serious in the rollover of some substituted cyclanes, so the formation of epimerized product would be suppressed. Consequently the importance of various active centers such as defects was emphasized (*45*). To examine this hypothesis much work was done in the past. There is still controversy as to whether the rollover process is a structure sensitive reaction. Some workers found little change in the absolute turnover frequency for rollover (i.e., for $\Sigma_{i=6}^{10} d_i$) of palladium or platinum catalysts with the percentage exposed (*19–21*) whereas others found either distinct (*22*) or less marked (*23*) dependence on the metal particle size. On the other hand the results obtained on sintered palladium films (a roughness factor ca. 1, mostly (111) planes) showed a rather unexpected result: the amount of d_{10} product was not less than in the case of unsintered films (*18*) although strict comparison is not possible because of slightly different reaction conditions (different partial pressures, a presence of β-PdD phase or not).

Our results for cyclopentane/D_2 exchange are in good agreement with those by Clarke and Taylor (*16*) obtained on highly sintered Pd–Au-on-Pyrex films. First, for similar reaction conditions there is a distinctly lower contribution of two-set exchange for alloys of 10–20 at.% Au (Table 6). Second, there seems to be good agreement if one considers the overall rollover activity (defined as $k_0 x \Sigma_{i=6}^{i=10} d_i$) as a function of Pd–Au alloy composition (Fig. 5). Clarke and Taylor (*16*) stated that their rate constants were approximately the same for alloys of 0–40 at.% Au, interest attaching more particularly in their reduction in activity of 3–4 orders of magnitude observed at 30–40 at.% Au. However, a closer internal comparison with their results is possible. Thus, from Fig. 1 of their paper (*16*) it follows that the alloy of 12.2 at.% Au is clearly more active than palladium (for log k_0 = 0, reaction temperature $t_{r(\mathrm{Pd})}$ = 340 K

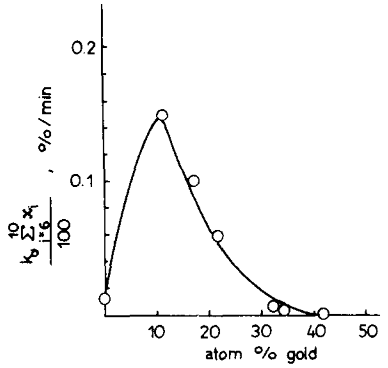


FIG. 5. The overall rollover activity in cyclopentane/D_2 exchange on Pd–Au(111) alloys at 57°C.

whereas $t_{r(12.2\%Au)} = 310$ K). Assuming the activation energy for the rollover process is ca. 20 kcal/mol (*45*) it is easy to show that the 12.2 at.% Au alloy is one order of magnitude more active than palladium. Now, if one considers even less of a contribution from the two-set exchange to the whole process for alloys (Fig. 2 from Ref. (*16*)), the relation $k_0 \; x \; \Sigma_{i=6}^{i=10} \; d_i = f(x_{Au})$ must give a maximum just for 12.2 at.% Au, in a good agreement with our Fig. 5.

In order to examine the relative importance of (111) planes in the rollover process we attempted to compare catalytic activities of different palladium surfaces. We therefore performed a simple experiment marked in Table 6 as *a*, *b*, and *c*. After performing one typical experiment with Pd(111) (film a), the film was treated in deuterium (ca. 300 Torr) at room temperature overnight. Such a treatment should enable the β-PdD phase to be formed (*38*). After the β-PdD phase decomposition by a long pumping at 50°C we found that our film (now b) became about five times more active than the original one, however, the initial product distribution was not very much changed. Subsequent annealing of the film at 500°C in 3–4 Torr of D_2 (film c) gave a good return to the initial catalytic behavior (film a). Since some increase in a roughness factor of Pd film is expected after PdD decomposition (*39*, *40*)—the specific activity of palladium might be almost the same for all palladium films. If this is so, it is possible to conclude that, at least for cyclopentane rollover, there is no special role of such sites as corner or edge atoms. This implies that the cyclopentane molecule may roll over on the (111) face of palladium without serious steric hindrance.

Recent results by Barbier *et al.* (*22*) may imply actually that only plane metal atoms of supported platinum play the main role in the rollover process. The authors found a very strong activity dependence on the percentage exposed in the range of ca. 16–32 Å of metal particle size. This dependence resembles very much the relation of number of plane atoms (or their ensembles) vs metal particle size (*41*).

Unfortunately we were not able to observe any epimerization of *cis*-1,2-dimethylcyclohexane at temperatures as low as in the case of cyclopentane/D_2 exchange (Table 7). This fact seems to support Burwell's view as to the relative difficulty in the rollover of substituted cyclanes. A similar result, i.e., a much lower rate of epimerization of *cis*-1,2-dimethylcyclohexane (vs cyclopentane/D_2 exchange) over Pt/Al_2O_3 catalysts was reported by Barbier *et al.* (*22*).

In Fig. 5 (cyclopentane/D_2 exchange) and in Fig. 6 (epimerization) one can see somewhat higher activity of alloys than pure pal-

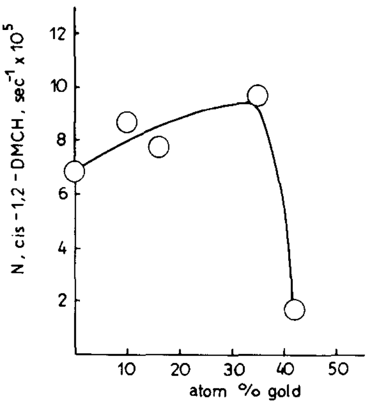


FIG. 6. Catalytic activity of Pd–Au(111) alloys in epimerization of *cis*-1,2-dimethylcyclohexane at 97°C.

ladium. Combining this fact with the similar relation found for many hydrogenation reactions over Pd–Au (*32, 35*) one can conclude that the rollover process might involve similar intermediate species as in alkene hydrogenations. It must be noted that in the case of epimerization the relatively high reaction temperature (usually ≥100°C) would rather easily produce dehydrogenated species. As a matter of fact at about 130°C we observed ca. 0.3% of orthoxylene in the reaction mixture.

CONCLUSIONS

The skeletal isomerization of neopentane and *n*-butane is catalyzed by (111) Pd and Pd–Au alloys. In the case of the neopentane reaction the selectivity toward isomerization is very high, ~70–90%. The rates of neopentane and *n*-butane both go through a maximum at ca. 10 at.% Au. This fact as well as the fact that isotopic exchange between deuterium and methane and neopentane on (111) Pd–Au alloys gives almost exclusively alkane-d_1 at temperatures only slightly lower than used for isomerization is compatible with the Rooney mechanism of 1,2-bond shift isomerization (*44*) involving a transition complex similar to that involved in olefin hydrogenation.

The two-set isotopic exchange between cyclopentane and deuterium over (111) Pd–Au alloys goes through a gentle maximum again for ca. 10 at.% Au.

The relative importance of ensemble size vs electronic effects in the Pd–Au alloys seems to be as follows:

(1) alkane hydrogenolysis—the ensemble effect (the concentration of Pd–Pd doublets) predominates over the electronic effect;

(2) CH_4/D_2, neopentane/D_2 exchange—strong electronic effect, the decline in activity in the region of d-band filling is dramatic (*32*), all reactants possess only σ electrons;

(3) alkane bond shift isomerization—the electronic effect must be of some importance, the reaction may not involve any special surface ensembles;

(4) cyclane rollover—no special role of sites of a low coordination number, the electronic effect seems to prevail over the ensemble effect.

ACKNOWLEDGMENTS

The author is indebted to Prof. W. Palczewska for helpful discussions during the course of this research. I also acknowledge Mr. J. Stachurski for performing the X-ray diffraction examinations of Pd–Au films. I thank Prof. R. L. Burwell for a critical reading of the manuscript.

This work was carried out within Research Project 03.10.

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