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Isomerization of Alkanes on Epitaxially Oriented (111) Pd–Cu and Pd–Ag Alloy Films

By Zbigniew Karpiński,* Wojciech Juszczyk and Jarosław Stachurski

Institute of Physical Chemistry of the Polish Academy of Sciences, Kasprzaka 44/52,
01-224 Warszawa, Poland

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The reactions of neopentane and n-butane in the presence of an excess of dihydrogen have been studied on films of Pd–Cu and Pd–Ag evaporated onto mica. The characterization of films showed that they were predominantly (111) oriented. The catalytic activity for isomerization of neopentane and n-butane was higher for *ca.* 10 at% Cu than for pure Pd, resembling the catalytic behaviour of Pd–Au(111) films. This does not, however, confirm the existence of the ligand effect in alkane isomerization over Pd–IB metal alloys. The catalytic activity of Pd–Ag(111) alloys decreases with increasing silver content, but on the basis of the inferred surface composition of these alloys this agrees with the conclusion drawn for the Pd–Cu system, *i.e.* the possible absence of the ligand effect.

Recently it has been discovered that neopentane undergoes selective isomerization over (111) oriented palladium[1] and Pd–Au(111) alloy films.[2] On the basis of the relationship between the catalytic activity and the alloy composition (the maximum for *ca.* 10 at% Au) and additional experiments with CH_4/D_2 and neopentane/D_2 exchange over Pd–Au(111) alloys (almost exclusively the stepwise mode of exchange at higher temperatures), the hypothesis was advanced[2] that neopentane isomerizes *via* an adsorbed alkyl species (not by surface carbenes) at one metal site according to the mechanism of Rooney and coworkers.[3]

On the other hand it has been suggested that the electronic ligand effect operates for the bond-shift isomerization, mainly because some Pd–Au alloys were more active than pure palladium. Even though it has been realized that the maximum on the activity against alloy composition curve is not evidence of the ligand effect,[4] so the relative importance of ensemble size as against electronic effects in the Pd–Au alloys is still unsettled.

Sachtler and Somorjai[5] have recently found that the ligand effect is absent for CO adsorption on Pt–Au(111) single-crystal surfaces. However, the enhancement of n-hexane isomerization by these alloys could follow from electronic as well as from geometric changes, and they[5] suggested the use of other Group IB elements (Cu or Ag) to prove the relative importance of the ligand effect.

Replacing Au by Cu would influence the course of the isomerization for one or more of the following reasons. (1) Changing the ligand may introduce considerable geometric changes: gold has a larger atomic radius (1.44 Å) than copper (1.28 Å) and so the distances between atoms are larger in Pd–Au than in Pd–Cu alloys, which may influence the catalytic behaviour of the Pd alloy. (2) Replacing Au by Cu has a great effect on the catalytic behaviour of platinum alloys in alkane conversion[6–9] (more hydrogenolysis occurs with copper) and other Group VIII metals (Ir, Ni and Pd) when highly diluted in copper also show increased activity for the hydrogenolysis of neopentane.[10] (3) Qualitative differences have been found in the ESCA[11] valence-band-electron spectra of the Pd–Cu and Pd–Ag systems. A tail tending toward the bottom of the valence band for the Cu-based alloys and an absence of such a tail for Pd–Ag suggests that the Pd $4d$ states are more involved in bonding in the Cu alloys than they are in the Ag alloy. Also a larger chemical shift of the Pd $3d_{5/2}$ line occurs in the copper host (0.8 eV) than in the silver host (0.5 eV). For the palladium-rich alloys, the copper *d* band hybridizes strongly with the host *d* band and loses its identity; a similar result was observed for the Pd–Au system where the $5d_{5/2}$ part (but not the $5d_{3/2}$ part) of the Au *d* band could not be identified in the spectrum for high palladium concentrations.[12] On the other hand, Hüfner *et al.*[13] showed that in the valence band of the Pd–Ag system the *d* bands of Pd and Ag are well separated.

It was decided to investigate whether these differences in the valence-band structures (and different chemical shifts) influence the catalytic behaviour of palladium atom centres.

EXPERIMENTAL

The (111) oriented films of palladium–copper and palladium–silver alloys were prepared by epitaxial growth of an evaporated layer of metals on a sheet of mica in the manner described in ref. (2). Briefly, both alloy components, palladium and copper (or silver), were evaporated simultaneously from two independent sources on the inner wall of a cylindrical reactor. The entire side wall of the reactor was covered by the freshly cleaved mica sheet. During evaporation (vacuum *ca.* 5×10^{-5} Torr, 1 Torr = 133.3 Pa) and subsequent annealing in hydrogen for 2 h (5 Torr) the reactor was maintained at 500 °C.

Spectrographically standardized palladium, copper and silver wires used for evaporation were purchased from Johnson Matthey. As previously,[2] the lateral homogeneity of our films was poor. This was checked by analysing various sections of the alloy films by X-ray diffractometry (Rigaku-Denki X-ray diffractometer with Cu $K\alpha$ radiation and a scintillation counter). It was estimated from the lattice parameter that the top section of the film of nominal composition 11.3 at% Cu consisted of 10 at% Cu, whereas the middle contained 14 at% Cu. For the films of 20.0, 30.8 and 35.3 at% Cu the atomic percentages of copper in the top and middle sections were: 20 and 29, 37 and 30, and 41 and 35, respectively. Large percentage differences were also observed for the Pd–Ag alloys. 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.

The investigations of the reactions of neopentane (Fluka, puriss) or n-butane (Merck, purity of *ca.* 99.5%) with dihydrogen were conducted in a static circulation system. The whole system was made of Pyrex glass with Young's stopcocks. The main part of the apparatus was the cylindrical reactor connected to the rest of the system by two joints with Viton O rings. The progress of the reaction was followed by g.l.c. The hydrocarbons were dried and outgassed before use.

RESULTS

FILM CHARACTERIZATION

X-ray diffractometry indicated that both the Pd–Ag and Pd–Cu films had a very high degree of (111) preferred orientation with respect to the mica base. The degree of orientation was expressed as

$$\text{degree of (111) orientation} = \frac{\text{height of (111) peak} \times 100\%}{\text{height of (111) peak} + 3 \times \text{height of (200) peak}}.$$

The last columns in tables 1–4 show average degrees of orientation of films after kinetic runs. It follows from tables 3 and 4 that all Pd–Ag alloys are well oriented, whereas for Pd–Cu films (tables 1 and 2) the degree of (111) orientation diminishes with the copper content, and, as shown in tables 1 and 2, for 56.0 and 54.4 at% Cu the existence of the intermetallic compound PdCu was established. However, since both alloys were

Table 1. Reaction of neopentane on (111) oriented Pd–Cu films

film composition, Cu (at%)	reaction temperature /°C	turnover frequency[a] /molecule atom^{-1} s^{-1}	initial product distribution (%)[b]					degree of (111) orientation[c] (%)
			CH_4	C_2H_6	C_3H_8	i-C_4H_{10}	i-C_5H_{12}	
0	290	3.09×10^{-4}	10.4	2.6	6.2	25.1	55.6	100
0	286	3.31×10^{-4}	11.7	2.1	3.1	29.2	53.9	100
	299	6.61×10^{-4}	15.2	8.3	12.5	25.0	39.0	
8.6	286	3.52×10^{-4}	16.4	traces	1.5	49.2	32.9	not determined
10.7	285.5	1.38×10^{-4}	5.5	—	0.3	11.3	82.9	100
	304	8.31×10^{-4}	7.0	1.7	2.4	15.6	73.3	
10.8	284.5	1.64×10^{-4}	1.5	—	0.6	4.7	93.3	100
	309	6.17×10^{-4}	4.7	—	1.2	7.3	86.8	
11.3	292	3.12×10^{-4}	14.1	—	0.3	29.2	56.4	100
20.0	297.5	3.40×10^{-4}	1.0	—	1.9	—	97.1	100
	310	6.10×10^{-4}	2.3	—	0.5	3.9	93.3	
30.8	298.5	3.1×10^{-5}	2.3	—	traces	5.3	92.4	99
	327.5	6.24×10^{-4}	2.4	traces	0.6	5.4	91.6	
43.1	300	inactive						82
	333.5	2.51×10^{-4}	4.7	—	0.7	9.9	84.7	
	350	3.41×10^{-4}	7.3	1.5	1.6	11.6	78.0	
56.0	300	inactive						f.c.c. (*ca.* 75 at% Cu) phase + b.c.c. (PdCu) phase
	350	8.6×10^{-5}	6.1	—	4.7	7.6	81.6	
	366	1.38×10^{-4}	7.4	—	2.7	15.1	74.8	
74.0	inactive up to 400 °C		—	—	—	—	—	not determined
100	inactive up to 420 °C		—	—	—	—	—	100

[a] Assuming that the roughness factor of all films is equal to 1; geometrical surface area 400 cm^2. [b] Expressed as the percentage of a reactant consumed in the formation of a given product divided by total consumption. [c] Defined in the text.

catalytically inactive, the presence of the intermetallic compound will not be discussed further.

We could not measure the surface composition of our Pd–Cu and Pd–Ag alloy films. Therefore for further interpretation of kinetic data it is necessary to use literature data on surface segregation in both alloy systems.[14–19]

REACTION OF NEOPENTANE AND n-BUTANE WITH HYDROGEN OVER Pd–Cu(111) AND Pd–Ag(111) ALLOY FILMS

These reactions were carried out in the presence of a ten-fold excess of hydrogen. The alkane partial pressure was *ca.* 1.85 Torr. Tables 1–4 report the results; the reproducibility of the results is estimated to be 20–30%.

The calculation of turnover frequencies and initial product distributions selectivities was performed in the way described in ref. (2). Usually it was intended to work under very low conversion (1–3%) and so most of the experiments were carried out at only two temperatures (conversion at the third temperature was too high). In order to compare the catalytic behaviour of different alloys at one temperature it was necessary to make interpolations or even, in exceptional cases, extrapolations.

Table 2. Reaction of n-butane on (111) oriented Pd–Cu films

film composition, Cu (at%)	reaction temperature /°C	turnover frequency[a] /molecule atom^{-1} s^{-1}	initial product distribution (%)[b]				degree of (111) orientation[c] (%)
			CH_4	C_2H_6	C_3H_8	i-C_4H_{10}	
0	272	2.28×10^{-4}	32.6	13.6	43.0	10.9	100
	294.5	6.54×10^{-4}	26.6	24.6	40.5	8.3	
9.6	289	1.23×10^{-4}	19.6	4.6	34.2	41.7	100
	312	7.38×10^{-4}	18.4	8.4	34.6	38.6	
15.5	302.5	2.35×10^{-4}	27.1	6.6	39.9	26.4	100
17.8	316	2.39×10^{-4}	21.0	6.3	42.6	30.1	95
	331.5	5.34×10^{-4}	20.6	9.1	41.4	28.9	
35.3	305	9.4×10^{-5}	26.5	5.5	29.3	38.7	100
	324	2.50×10^{-4}	23.1	6.6	29.0	40.9	
54.4	354	6.9×10^{-5}	5.8	13.5	18.4	62.3	mainly PdCu (b.c.c. phase)[d]
	368	9.1×10^{-5}	10.4	12.6	24.8	52.2	
73.5	388	5×10^{-6}	25.4	25.4	49.3	—	85[e]
	425	7.9×10^{-5}	17.8	36.4	38.5	7.3	
100	inactive up to 420 °C		—	—	—	—	100

[a–c] As in table 1. [d] Slightly marked superstructure lines. [e] Most probably the f.c.c. alloy (not $PdCu_3$), no superstructure lines.

DISCUSSION

Pd–Cu ALLOYS

Table 1 shows the results for neopentane conversion over Pd–Cu(111) films. As in the case of Pd–Au(111) alloys,[2] selectivity towards isomerization is high but it now increases with copper content. These results do not confirm the existence of the 'hydrogenolytic' effect of copper in mixed Pd–Cu ensembles, as has been reported for copper-rich Pt–Cu alloys.[6–9] Unfortunately, the activity of the 74.0 at% Cu alloy was far below the detection limit.

The fact that the degree of (111) orientation was worse with copper-rich alloys (table 1) does not seem to affect the catalytic properties. The isomerization activity for alloys having > 30 at% Cu is very low. Fig. 1 shows the rate of isomerization of neopentane on Pd–Cu(111) alloys at 300 °C. It is clear that the rate is similar to the rate of neopentane isomerization over Pd–Au(111).[2] Again, palladium alloys with *ca.* 10 at% of a diluent metal (now Cu) are more active than pure Pd. It was argued previously[2] that there is no serious surface segregation of the Pd–Au system and the same situation seems to exist for the Pd–Cu system. Van Langeveld *et al.*[14] have studied the surface composition of Pd–Cu alloy films by A.e.s. and photoelectric work-function measurements. Their experimental results were in good agreement with the calculated values (assuming a broken-bond model) and showed only slight surface enrichment in copper. Assuming in the present case the absence of surface segregation (as in the case of Pd–Au alloys[2]) we conclude that there is no change in the catalytic activity of the palladium sites surrounded by copper atoms as compared with palladium adjacent to Au atoms.

For n-butane isomerization, fig. 2 shows a similar relationship, suggesting the same mechanism for the isomerization of neopentane and n-butane. Again, alloys with *ca.* 10 at% Cu are more active than pure Pd and the relationship resembles the catalytic

Table 3. Reaction of neopentane on (111) oriented Pd–Ag films

film composition, Ag (at%)	reaction temperature °C	turnover frequency[a] /molecule atom^{-1} s^{-1}	initial product distribution (%)[b]					degree of (111) orientation[c] (%)
			CH_4	C_2H_6	C_3H_8	i-C_4H_{10}	i-C_5H_{12}	
0.8	317.5	2.90×10^{-4}	3.0	—	0.2	8.6	88.2	100
	335	4.42×10^{-4}	9.0	3.6	5.7	18.2	62.6	
1.9	316.5	8.2×10^{-5}	1.7	—	0.6	6.1	91.6	99.5
	337.5	3.40×10^{-4}	1.7	—	traces	8.6	89.7	
6.1	338	9.3×10^{-5}	1.9	—	traces	8.7	89.4	100
	359.5	1.75×10^{-4}	3.1	traces	0.6	17.7	78.6	
9.2	360	1.1×10^{-5}	5.1	—	6.2	14.5	74.3	99.5
	392	6.2×10^{-5}	7.3	—	traces	25.1	67.6	
12.8	333.5	2.5×10^{-5}	5.9	—	5.9	17.1	70.9	not determined
	365	1.18×10^{-4}	7.4	—	0.4	22.2	70.0	

[a–c] As in table 1.

Table 4. Reaction of n-butane on (111) oriented Pd–Ag films

film composition, Ag (at%)	reaction temperature /°C	turnover frequency[a] /molecule atom^{-1} s^{-1}	initial product distribution (%)[b]				degree of (111) orientation[c] (%)
			CH_4	C_2H_6	C_3H_8	i-C_4H_{10}	
2.5	319	5.2×10^{-5}	17.0	2.8	32.1	48.0	100
	339	2.61×10^{-4}	6.0	6.0	48.4	39.4	
7.2	347	5.2×10^{-5}	7.7	0.9	16.1	75.3	100
	369	2.36×10^{-4}	4.7	2.0	28.0	65.3	
8.6	361	7.9×10^{-5}	10.4	4.3	44.9	40.3	not determined
	386	5.50×10^{-4}	2.0	5.9	62.6	29.4	
15.0	362	5.4×10^{-5}	7.9	2.4	48.2	41.2	99.5
	386	4.26×10^{-4}	2.1	3.8	56.4	37.8	

[a–c] As in table 1.

behaviour of Pd–Au(111) films in n-butane reaction [fig. 2 in ref. (2)]. Similarly the selectivity for isomerization increases with the content of inactive metal (table 2).

Therefore replacing one ligand (Au) by another (Cu) in the alloy does not alter the catalytic behaviour of palladium very much. Whether this is proof of the absence of the ligand effect is still uncertain, but it is possible that by changing the ligand only minor changes in the electronic structure of the palladium alloy have been introduced. Uncertainty in the assessment of the surface composition and the lack of control of defect density do not allow small quantitative changes to be considered. Note that for one Cu-rich alloy (75.5 at% Cu) it was possible to observe predominant hydrogenolysis of n-butane (table 2). The result is in good agreement with the results published by Ponec and coworkers for Pt–Cu[6–9] and Pd–Cu[10] alloy catalysts, where they argued against the ligand effect. It is possible that their arguments may be strengthened by the results obtained in this work, *i.e.* the same catalytic behaviour of Pd–Au and Pd–Cu alloys. However, the presence of the maximum in the isomerization activity against alloy composition curve still has to be explained. It is

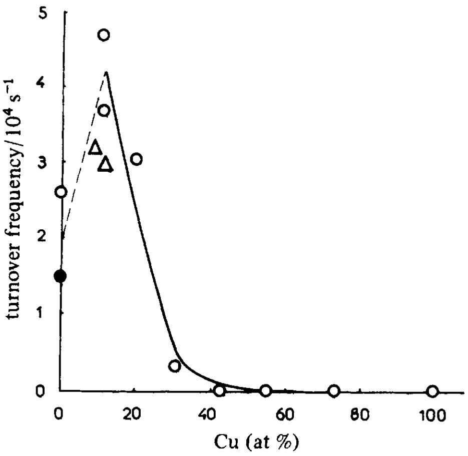

Fig. 1. Catalytic activity of Pd–Cu(111) alloys for the isomerization of neopentane at 300 °C: ○, this work; ●, from ref. (2); △, rough estimates from the activity at other temperatures (see table 1).

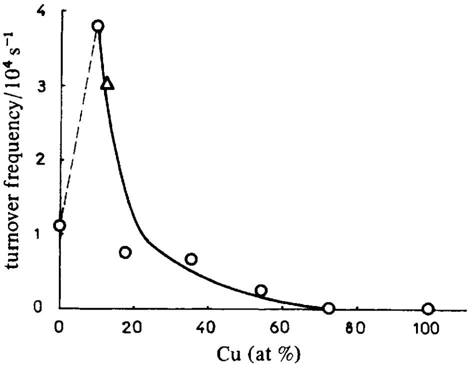

Fig. 2. Catalytic activity of Pd–Cu(111) alloys for the isomerization of n-butane at 317 °C: ○, this work; △, rough estimates from the activity at other temperatures (see table 2).

doubtful as to whether progress will be made without careful surface control in the sense of the surface composition, surface defects and the extent of surface carburization.

Pd–Ag ALLOYS

The situation with regard to the results for the Pd–Ag(111) system is not as good, as we were limited to Pd-rich alloys (up to 10–15 at% Ag in the bulk) because larger amounts of silver deactivated palladium completely (tables 3 and 4 and fig. 3 and 4). No maximum for the isomerization rate was found, but a rather dramatic decrease of the activity with the Ag content was noticed. The situation is more complicated than with Pd–Cu alloys because surface enrichment in silver is predicted by theory[15] and has been confirmed by the majority of experimental studies.[16–19] From recent work by Kuijers and Ponec[19] it follows that the alloy of *ca.* 10 at% Ag in the bulk should

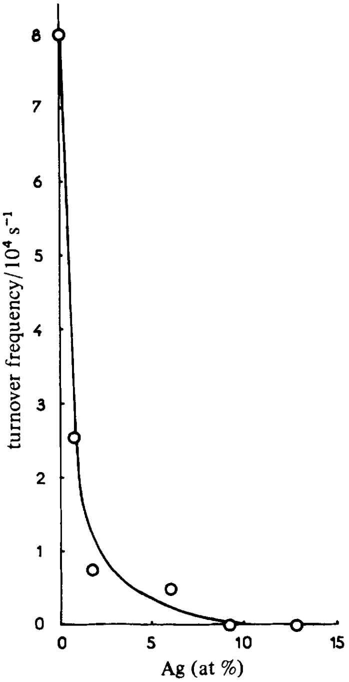

Fig. 3. Catalytic activity of Pd–Ag(111) alloys for the isomerization on neopentane at 317 °C.

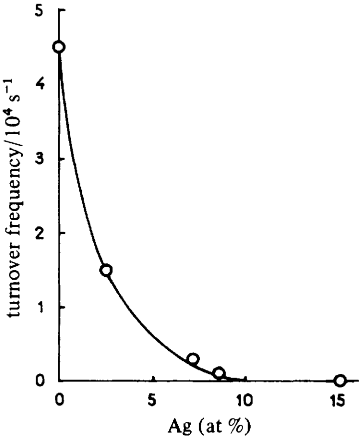

Fig. 4. Catalytic activity of Pd–Ag(111) alloys for the isomerization of n-butane at 344 °C.

have 40–80 at% Ag in the surface layer, depending on whether the alloy is equilibrated *in vacuo* (*ca.* 80%) or after interaction with CO (*ca.* 40%). Therefore one should not be surprised by the steep decrease in the isomerization activity with increasing silver content. The absence of a maximum in fig. 3 or 4 (*cf.* Pd–Cu and Pd–Au alloys) does not necessarily confirm the existence of the ligand effect. Such a maximum, if it exists, would be difficult to find (probably somewhere between 0 and 1% Ag in the bulk). If we do suppose that a maximum exists for *ca.* 1 at% Ag, then, remembering that the lateral homogeneity of our films was not very good, we must consider the activity of the film as the average value of the 'integrated' activity, *i.e.* measured over the film with a reasonable concentration gradient (say between 0 and 2 at% Ag). Thus the activity maximum could be easily overlooked for the Pd–Ag system.

Furthermore, no changes were found in the selectivity for isomerization for all three of the palladium systems: Pd–Au[2] and Pd–Cu and Pd–Ag. This suggests that the ligand effect does not occur for alkane isomerization over palladium alloys. However, more careful study (with a good surface control, especially for Pd–Ag alloys) is needed in order to establish the origin of the synergistic effect in the isomerization of alkanes on alloys.

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