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Exchange of Cyclopentane and Deuterium on Platinum and Platinum–Gold Alloy Films

Reactions of hydrocarbons are currently being studied in our laboratory with transition metal/Ib metal alloys as catalysts. It has appeared that alloying has a quite different effect on reactions of C–H bonds (hydro-/dehydrogenation, exchange with deuterium) and reactions on C–C bonds (isomerization, dehydrocyclization and hydrogenolysis) (*1*, *2*). In the last group, moreover, we have observed a different influence of alloying on hydrogenolysis on the one hand and on the rest of the reactions on the other. The philosophy behind this work has been explained elsewhere (*2*).

Besides the information provided with regard to the reactions of C–H bonds, the exchange reaction of cyclopentane and deuterium is also interesting as such. For this reaction various mechanisms have been suggested in the literature (*3–5*). More than one mechanism must be assumed in order to account for the variety of experimental data reported, as mentioned in our previous paper (*2*). It is interesting to investigate how the contribution of various mechanisms possibly varies when a transition metal is alloyed with a far less active Ib metal. As mentioned before (*1*, *2*), either the changes of the electronic structure of the transition metal atoms or the effect of dilution of active sites in an almost inactive matrix (Ib metal) should then be responsible for the observed changes in catalytic behavior due to alloying.

All experiments described below were performed on Pt and Pt–Au alloys evaporated under ultrahigh vacuum conditions. The technique and apparatus used were identical with that already described (*2*). Also the data evaluation followed the same procedure. The exchange process was monitored by a small bakable (MS 10) mass spectrometer connected to the reaction vessel by a Granville-Phillips valve. The partial pressures were 0.5 Torr cyclopentane and 25 Torr deuterium, higher than in Ref. (*2*). Films were equilibrated at 350°C, as in Refs. (*6* and *7*). In all experiments the reaction temperature was lower than the temperature at which reactions of C–C bonds occur. To check the possible presence of these reactions, samples were taken and analyzed by gas chromatography. For comparison with the coefficient M used in Refs. (*2*, *3*), the coefficient $\bar{M}$ was also evaluated and defined as:

$$\bar{M} = 10^{-2} \sum_{i=1}^{10} i d_i \quad (t \to 0),$$

where d_i = percentage product d_i with i D-atoms.

For platinum films, the exchange results were as follows: In the temperature range under 100°C the rate of exchange decreased with time and repeated runs. In the temperature range 100–230°C the activity of the film was more stable. Table 1 shows the initial product distributions at different temperatures.

For alloy films, as far as the activity is concerned, the same can be reported as with pure Pt. At comparable conditions the activity of alloys was about 10 times lower than that of pure Pt. The product distributions for alloys are presented in Table 2.

TABLE 1

Product Distribution on Pt Films

T (°C)	Products (%) d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	d_9	d_{10}	Conv. (%)	$k_\Phi{}^a$	$k_{d_0}{}^a$	M^a	$\bar{M}$
0	27.4	14.4	7.8	7.0	4.4	4.5	4.0	4.7	9.3	16.5	17.0	3.06	0.79	3.9	4.7
25	33.5	18.7	10.7	9.1	5.7	4.7	3.6	3.8	4.1	6.0	21.0	0.48	0.20	2.4	3.5
25[b]	18.6	5.7	3.4	7.6	32.2	6.9	3.2	4.8	3.8	13.8	12.0	0.32	0.06	5.3	5.1
110	37.7	6.5	1.1	6.1	3.3	2.3	0	1.6	3.5	37.9	7.3	0.36	0.05	7.1	5.3
159	18.0	3.9	1.8	3.8	4.7	1.7	0.9	0.7	6.7	57.7	18.9	2.18	0.30	7.3	7.3
177	15.8	7.1	3.7	5.4	5.3	2.5	1.9	1.2	7.4	49.8	19.5	6.12	0.83	7.4	6.8
195	12.6	2.7	1.2	3.8	1.5	1.6	0.8	0	7.5	68.2	19.9	7.52	0.87	8.5	8.1
229	10.1	5.1	2.6	5.0	3.1	2.7	1.6	1.1	8.3	61.7	18.1	27.1	3.45	7.8	7.9

[a] Defined as in Refs. (2–5) (%/min).
[b] Films evaporated at 0°C.

It can be seen immediately that they do not differ essentially from the Pt distributions, but there are some interesting differences of detail. The multiplicity coefficient $\bar{M}$ reveals a temperature dependence similar to other metals and alloys. However, by alloying, this function is shifted to higher temperatures. It means that at a given temperature $\bar{M}$ is lower on alloys and in the product distributions there is a shift from the d_{10} to the d_1 product (at all alloy compositions these are the main products!).

TABLE 2

Product Distribution on Pt–Au Alloys

Pt %	T (°C)	Products (%) d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	d_9	d_{10}	Conv. (%)	$k_\Phi{}^a$	$k_d{}^a$	M^a	$\bar{M}$
52	120[b]	36.5	9.6	5.9	6.9	13.1	2.8	1.6	1.6	3.4	18.7	12.2	—	—	—	3.6
	160	21.0	6.5	2.9	6.0	7.3	2.6	—	1.9	2.9	48.9	7.0	0.36	0.05	7.2	6.5
	181	17.5	6.3	1.7	5.4	6.0	1.5	0.8	1.5	4.3	55.1	9.0	1.20	0.17	7.1	7.0
41	0[b]	16.0	10.2	6.0	5.5	3.8	3.9	3.9	4.5	14.3	32.0	16.1	—	—	—	6.3
	174	20.1	8.7	4.8	7.1	6.9	4.5	2.2	5.2	4.5	36.2	4.2	—	—	—	6.0
	247	11.7	3.8	1.5	2.7	1.5	1.6	0.5	—	10.4	66.3	22.9	1.40	0.16	8.7	8.1
26	165	23.8	6.8	2.6	5.3	6.0	2.4	0.8	2.0	5.2	45.1	6.9	0.21	1.03	7.0	6.3
	187	18.9	6.4	1.4	5.9	5.6	2.7	1.3	3.1	4.1	50.5	6.8	0.46	0.07	6.6	6.8
	208	17.1	5.1	1.9	5.0	3.8	1.8	0.9	0.8	5.9	57.6	8.8	0.79	0.11	7.2	7.2
20	166	29.6	13.0	6.7	7.0	6.3	3.9	2.2	2.9	4.7	23.6	15.5	0.56	0.11	5.1	4.8
	224	18.5	7.4	3.3	4.6	3.9	2.2	1.7	1.3	6.4	50.7	17.6	1.56	0.22	7.1	6.8
11[c]	200	43.0	11.2	3.5	11.5	1.3	3.8	0.8	2.8	2.7	19.4	6.4	—	—	—	4.0
	226	27.5	7.0	4.9	16.9	1.9	6.3	1.1	4.2	3.2	27.0	7.1	—	—	—	5.1

[a] Defined as in Refs. (*2–5*) (%/min).
[b] Strong decrease in the rate due to self-poisoning.
[c] Film has very low activity.

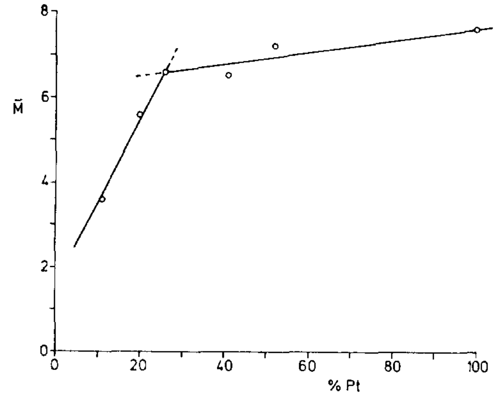

FIG. 1. $\bar{M}$ as a function of alloy composition (190°C).

This is shown in Figs. 1 and 2 (the data were either extrapolated or interpolated to the same temperature).

First, we should make a remark on the surface composition of the films. According to all available literature (*8*) at 350°C sintered films are composed of two phases: a Pt-rich phase (~97% Pt) and a Au-rich phase (~18% Pt). The surface of the films is formed by the Au-rich phase for all concentrations within the miscibility gap (97–17% Pt). For higher Pt dilutions the Pt content in the surface decreases below that of the Au-rich phase (*6, 7*). This Pt–Au system strongly resembles the Ni–Cu alloys; both alloys have a negative heat of formation. For Ni–Cu alloys the formation of Ni clusters was experimentally proven and we can expect that clustering occurs in Pt–Au alloys as well.

Information on the changes in the electronic structure of Pt–Au alloy is scarce. The magnetic susceptibility has been measured on quenched one-phase alloys (*9, 10*). One can conclude from it that the density of states at the Fermi level $[N(E_F)]$ undergoes the most pronounced changes at low concentrations of Au. In very diluted alloys the changes in electronic structure are much more moderate.

The exchange results presented here remind one very strongly of the results obtained with Ni–Cu alloys (*2*). This is not surprising because the phase diagram of Ni–Cu is similar to that of Pt–Au alloys. Also, there seem to be no grounds for believing that there is a substantial difference in electronic structure between these two alloys. The shift of $\bar{M}$ to lower values (at a given temperature) and the selective increase in d_1 (and a decrease in d_{10}) products occur at the highest dilution appplied here. There is much less effect of dilution in the range 100–18% Pt than in the range <18% Pt. If we recall in which region the most essential changes in electronic (= magnetic) behavior and in surface composition occur, then we must conclude that the shift in $\bar{M}$ (and the ratio d_{10}/d_1) must be related with the variation in number of available active sites and the size of the ensembles involved in the catalytic reaction studied. The question arises as to the consequences.

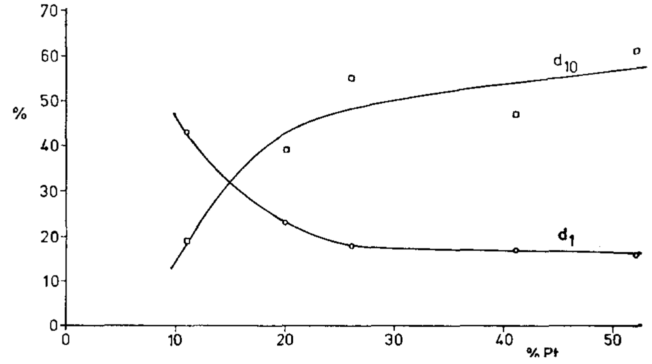

FIG. 2. Percentage d_1, d_{10} as a function of alloy composition (200°C).

From other experiments performed in our laboratory we know that alloying of Pt with Au leads to a decrease in the average bond strength (average heat of adsorption) of hydrogen on Pt (*6*, *7*). The results obtained from the thermal desorption study were explained by an assumption that hydrogen can be bound to ensembles of varying dimensions, larger ensembles being responsible for a stronger bonding. Alloying changes the distribution of ensembles according to their size: in the surface alloys have relatively more smaller ensembles (*7*).

What are the necessary conditions for a multiple exchange to occur at a low temperature?

1. Dissociation of more than one C–H bond and the formation of an $\alpha\beta$, $\alpha\alpha$, π-olefinic and similar intermediates [see Refs. (*2–5*)].
2. A concentration of D_{ads} at the surface which is sufficient to supply deuterium to the adsorbed species.

According to our results we conclude that these factors remain approximately unaltered if Pt is diluted up to a concentration of about 20% Pt (in the bulk). Only further dilution leads to important changes in the exchange picture. Because there is no continuous shift from, say, d_{10} as main product to d_9, d_8, etc. but a discontinuous leap to d_1, we believe that factor 1 above is more important for the shift in the product distribution than factor 2. So a rather high dilution (Pt < 20%) is necessary to reveal any effect of alloying on the distribution of various intermediates involved in exchange reactions.[1]

It is very difficult to arrive at definite conclusions about the decrease of activity of films due to alloying because the activity is not stable. However, comparing the alloy and Pt films at the same conditions we conclude that the activity decreases on alloys by up to one tenth of that of pure Pt films. This is in contrast with the views expressed in the catalytic literature some years ago. According to these, alloys such as those with 18% Pt (and less) should have *no* activity because the *d*-band of Pt should be filled completely at this concentration of Au.

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[1] As can be seen from Tables 1 and 2, at higher temperatures the proportion of the d_2 and d_4 product (less apparent but also noticeable at d_6 and d_8 products) is rather high in comparison with the amounts of d_3 and d_5 products. A referee of this paper suggested that this could be arising from a contribution from α,α-diadsorbed species. If this explanation, with which we do not dissent, is true, this would be another piece of evidence for the fact that even a strong dilution does not eliminate the ability of platinum to form multiple metal–carbon bonds.

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