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The Reactions between Cyclopentane and Deuterium on Palladium and Palladium–Nickel Alloys

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Cyclopentane–deuterium exchange has been followed on pure Pd and Pd/Ni alloy films in the temperature range 200–430 K and at hydrogen/cyclopentane ratios of ~50. Conclusions on activity changes are limited because of the self-poisoning of alloys and Ni catalysts. However, the selectivity of the catalysts is much less influenced by self-poisoning; the initial product distributions are well reproducible and independent of these side processes. The main result of alloying of Pd with Ni is the gradual disappearance of one low temperature mechanism which leads on Pd to D_{10} products. This fact can be easily understood if we assume that it is the "roll-over" mechanism which is responsible for these products.

INTRODUCTION

It is an important matter to establish which factors determine the *selectivity* of metal and alloy catalysts in hydrocarbon reactions. Our previous papers mentioned some of the possibilities in this respect (*1*, *2*) and it has also been shown that the *activity* of metal catalysts in apparently very simple reactions like benzene hydrogenation is actually determined by the *selectivity* of the catalyst (*3*). The selectivity is, in its turn, determined by the structure and composition of the intermediates of the reaction, the adsorption complexes.

Mainly due to the work of Kemball (*4*, *5*), Burwell (*6*, *7*), and others (*8*) it has become the practice to use the exchange reactions of hydrocarbons with deuterium to investigate the weakly (*4*–*9*) or the more strongly adsorbed (*10*, *11*) surface complexes. Recalling Scheme 1 given in Ref. (*2*) we shall mention below the essential difference between Ni and Pd in the cyclopentane/deuterium exchange. The main object of discussion will be the so-called initial product distribution (IPD) which is almost independent of the conversion α in the range of 0–20% and which reflects the structure of the surface complexes.

Ni favors the formation of $\alpha\beta$- (or the equivalent π-olefinic) and $\alpha\alpha$-intermediates [see Scheme 1, Ref. (*2*)]. The first complexes are held responsible for the D_2 products and for the multiple exchange in one set of hydrogen atoms (D_3–D_5), the latter for the "jump-over," of the exchange from one set of H atoms to the other (D_5–D_{10} products) and also to a less extent for the D_2 product.

Pd distinguishes itself from all other metals by an exceptionally high production of D_{10} products, even at very low temperatures. First, the π-allyl complex was supposed to be the intermediate in the process (*6*, *7*, *12*), later the so-called "roll-over" intermediate appeared (*6*, *7*, *13*) to be a much better explanation. Scheme 1 in Ref. (*2*) shows that the roll-over mechanism requires the largest ensemble of Pd atoms to be present. The $\alpha\beta$, π-olefinic and

π-allylic intermediates are usually held responsible for the multiple exchange on Pd in one set of hydrogens.

EXPERIMENTAL METHODS

The apparatus and materials used and the procedure applied to evaluate the data are almost the same as described earlier (*2*). The one change is that the evaluation procedure for the mass spectra was computerized, which made it possible to introduce also a correction for fragmentation of several (one to three) H or D atoms. For comparison (see figures below) all IPD's were interpolated to a conversion (α) of $\alpha = 15\%$ of D_0-cyclopentane. The quantitative evaluation of data follows the lines suggested by Kemball in his early papers [see, e.g., Ref. (*4*)].

Alloy films were prepared by simultaneous evaporation of both metals, directly from the respective Ni or Pd filaments. Films were condensed at 525 K and next sintered at 575 K for about 17 hr. The bulk composition was determined from the loss of weight of the respective filaments as well as by X-ray diffraction measurements (Philips diffractometer PW 1050/25) by which also the alloying was checked.

RESULTS

The procedure adopted here led indeed to the formation of alloys as can be seen from Fig. 1 where the lattice constants found for the several alloy films investigated are plotted versus the alloy composition (at.%). The line is taken from previously published data (*17*) and the bars indicate a possible uncertainty in the alloy composition or lattice constants.

We have followed the exchange reactions in the temperature range from 200 to 430 K. Runs with a renewed reaction mixture were performed with the same film at several temperatures, usually in the order of increasing temperatures. Generally, a part of the increase in activity due to the increasing temperature (exponential factor of the rate) is compensated by increasing self-poisoning (preexponential factor decreasing) at higher temperatures. This effect was most pronounced with Ni, less with the alloys and least with pure Pd. Because of this poisoning effect no reliable kinetic data could be obtained and moreover the activity could be estimated only roughly.

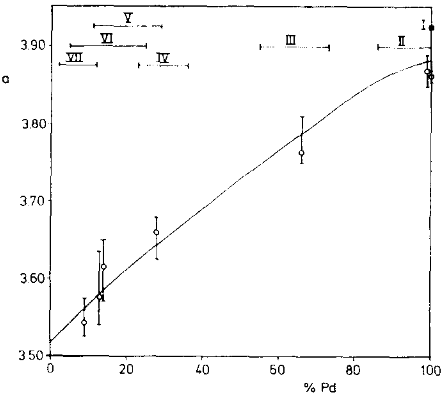

FIG. 1. Lattice constant as a function of composition. (○) The experimentally found values, while the vertical bars indicate the uncertainty in the lattice constants; (——) drawn according to the literature data (*17*). The horizontal bars represent the possible uncertainty in bulk composition. Films: I, 100% Pd; II, 95% Pd; III, 64% Pd; IV, 30% Pd; V, 20% Pd; VI, 15% Pd; VII, 7% Pd.

At temperatures of about 300 K the activity measured by the reaction rate constant k_{Φ}/cm^2 geometric surface area was within a factor 2 the same for Ni, Pd and all alloys. Above 350 K this is still true for Ni and the alloys while Pd has an activity which is clearly higher; at 400 K Pd is about 10 times more active than the average of Ni and Ni alloy catalysts.

The selectivity patterns (IPD's) are, however, rather well reproducible and they form the main subject for the discussion to follow. We have selected typical IPD's for three temperatures (273, 325, and 400 K) and these are shown in Figs. 2, 3, and 4, respectively (all data are compared at conversion $\alpha = 15\%$).

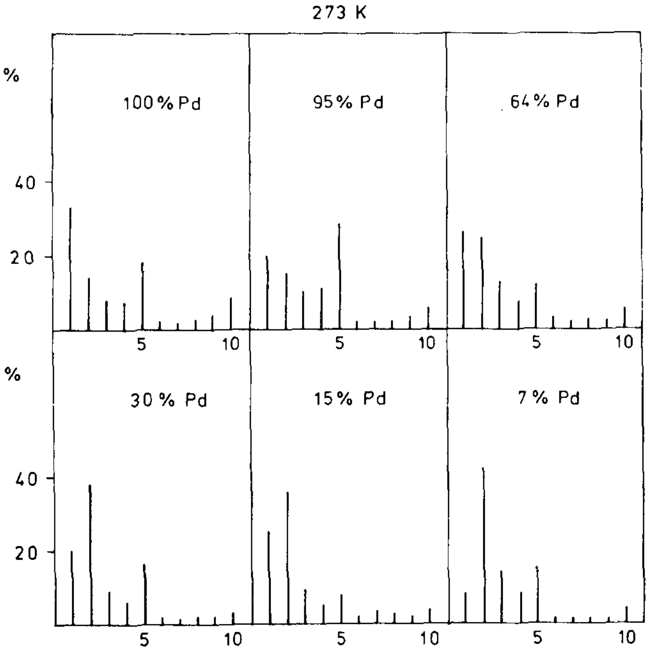

FIG. 2. Product distribution for pure Pd and the Ni–Pd alloy films at 273 K.

The tendency to multiple exchange can be characterized roughly by the statistical multiplicity factor *M* [for definition of *M* see Refs. (*2*, *4*, or *9*)]. This factor shows a continuous increase with increasing temperatures for the pure metals as well as for the alloy films. With Pd the maximum values of *M* (*9–10*) are reached at lower

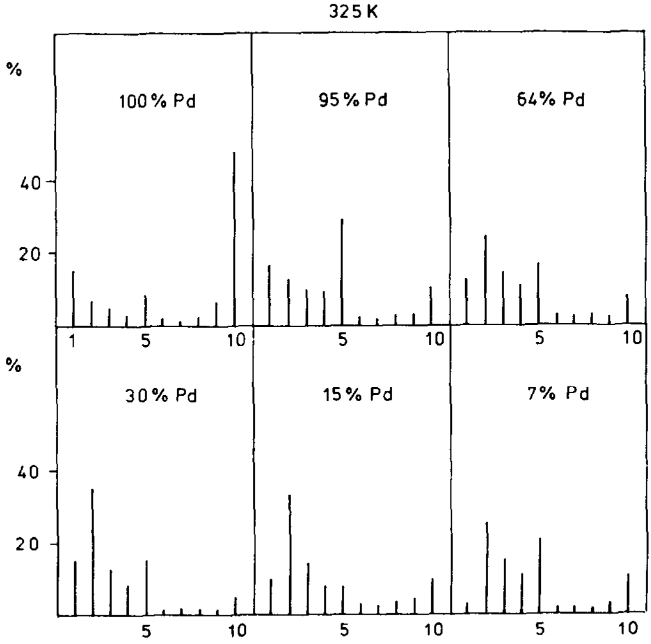

FIG. 3. Product distribution for pure Pd and the Ni–Pd alloy films at 325 K.

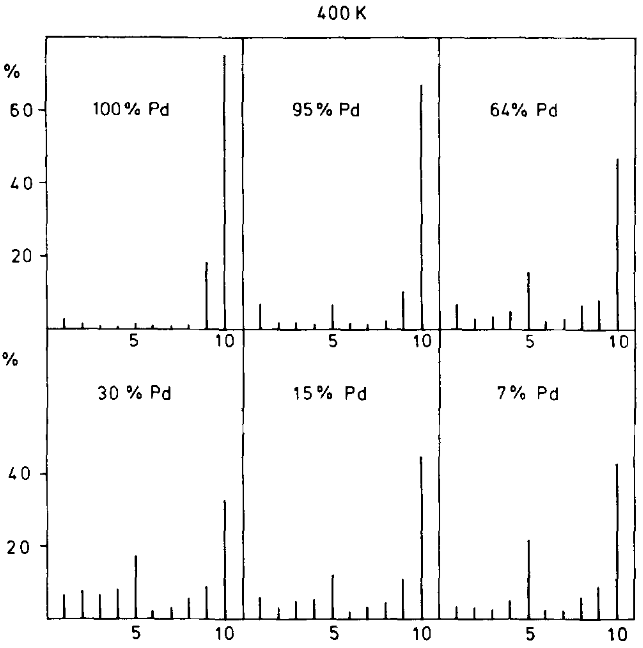

FIG. 4. Product distribution for pure Pd and the Ni–Pd alloy films at 400 K.

temperatures (about 370 K) than with Ni (about 430 K) while values for the alloy films were found to be between these two limits.

The character of changes caused by alloying can be seen better if we turn our attention from this global parameter *M* to some details of the IPD's. Mainly three peaks vary in the IPD's when the composition of alloys is changed, namely the peaks for the D_2, D_5, and D_{10} products of the exchange reaction. Figure 5 shows that as temperature increases there is an increasing contribution of D_{10} to the multiple exchange (D_2, D_5, and D_{10} products together); Pd is compared with one of the alloys (64% Pd). For the same alloy and for pure Pd the ratio D_5/D_{10} is plotted in Fig. 6 as a function of the temperature to illustrate how the "jump-over" of the exchange from one to the second set of "hydrogens" is inhibited on alloy films at low temperatures.

Exchange reactions are accompanied at high temperatures by side-reactions, mostly of hydrogenolytic splitting. The main product is methane, most of which is in the form of CD_4. If we compare the catalysts studied in this paper with regard to the CD_4 formation we arrive at the following conclusion. At 400–450 K the hydrogenolytic activity of Pd is negligible, while on Ni about 1% of cyclopentane is split hydrogenolytically at 425 K in about 1 hr. The alloys have an activity for CD_4 formation lower than Ni but the slowing down of the

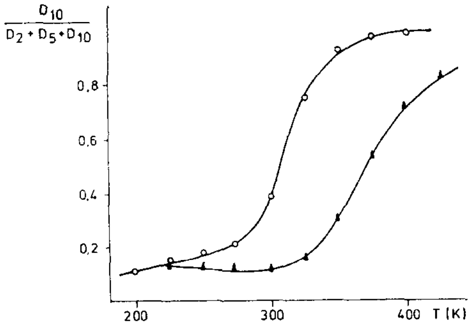

FIG. 5. The ratio $D_{10}/(D_2+D_5+D_{10})$ found with a pure Pd film (○) and a 64% Pd alloy film (▲) plotted as a function of the temperature (conversion in D_0 is $\alpha = 15\%$).

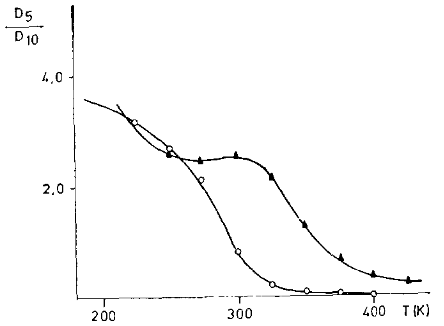

FIG. 6. The ratio D_5/D_{10} found with a pure Pd film (○) and a 64% Pd alloy film (▲) plotted as a function of the temperature (conversion in D_0 is $\alpha = 15\%$).

hydrogenolysis is less than when alloying Ni with Cu.

DISCUSSION

Table 1 summarizes some physical data for Ni and Pd relevant for this discussion. On the basis of these data we can expect the surface composition of the alloys to be about identical to the bulk composition.

Pd has a slightly larger atomic radius, lower heat of sublimation and a lower surface tension so that if any surface enrichment occurs it would be Pd enrichment. Recent papers (*18*) where Auger spectroscopy has been applied showed that the average composition of the two or three upmost layers is indeed equal to the bulk composition. The IPD's presented by Figs. 2, 3, and 4 contain some indirect qualitative information on the surface composition as well. We can see that the D_2 peaks are relatively high with respect to D_1, and other products (see, e.g., Fig. 2 for 273 K) typical only for Ni are present at a bulk concentration of only 5% Ni, witnessing that already at this level Ni is present in the surface. On the other hand, the low temperature IPD's on a film with 7% Pd contain already a relatively high D_5 concentration (with respect to the D_4 and D_6 products) which is a feature of IPD more characteristic for Pd than for Ni. Thus, both elements are apparently present in the surface in the whole range of concentrations studied.

Figure 3 is a representative illustration for changes caused by alloying. With Pd at 325 K the D_{10} product is clearly dominating but an addition of only 5% Ni causes most of the exchange to proceed only to the D_5 product (one set of hydrogen atoms) and does not continue up to D_{10} products to the same extent as with pure Pd. A relative increase of the D_5, and a relative decrease of the D_{10}, product is also observed with other alloys. At higher dilutions of Pd this is also observed at higher temperatures. For example, at 400 K we can see this consequence of alloying with the 64–7% Pd alloys. On Pd at 400 K practically only D_{10} is observable, not the D_5 product. At sufficiently high temperatures all films, also pure Ni (*2*), reveal D_{10} as the main product; this is also demonstrated by Figs. 5 and 6.

From the present work it can be concluded that the intermediates leading to D_2 (on Ni) or D_5 (on Pd) products are not very sensitive to alloying. Further, we know from our previous work (*2*) that also the mechanism leading to the high-temperature production of D_{10} on Ni is not very strongly influenced by dilution of Ni in a much less active metal as, e.g., Cu. Evidently, the *low-temperature mechanism* leading to D_{10} on Pd is the only one sensitive to alloying.

The question arises as to which of the

TABLE 1

Some Properties of Nickel and Palladium

	Ni	Pd
Lattice type	fcc	fcc
Lattice constant (Å)	3.52	3.88
Atomic radius (Å) (*19*)	1.25	1.37
Heat of sublimation (kcal/mole)	102.8	91
Surface tension (at the melting point) (dyn/cm)	1778	1500
Work function (evaporated films) (eV) (*15*, *16*)	5.0	5.2

TABLE 2

Mechanisms and Reaction Intermediates in Cyclopentane/Deuterium Exchange

Type of exchange	Temperatures at which present	Products	Intermediates possibly responsible for IPD's[a]
Single exchange	All T	D_1	α
Multiple exchange			
Mechanism I	Low T	D_2(Ni)	$\alpha\beta$, π-Olefinic, $(\alpha\alpha)$
	Low T	D_5(Pd)	$\alpha\beta$, π-Olefinic
II	Low T	D_{10}(Pd)	"Roll-over"
III	High T	D_{10}(Ni)(Pd?)	As for Mech. I, combined with $\alpha\alpha$'s

[a] See, e.g., Ref. (2) for the nomenclature and structures of the intermediates.

mechanisms suggested in the literature to be responsible for the D_{10} products at low temperatures can be influenced by alloying in the way observed. Is it the π-allyl (one-site) mechanism with Ni then modifying the electronic properties of the individual Pd atoms to reduce the ability of atoms to form π-allyl complexes, or is it the so-called roll-over (multisite) mechanism which requires at least two equivalent Pd atoms in the right geometry to occur and with Ni, unsuitable for this mechanism, then operating mainly by lowering the chance of finding proper ensembles of Pd sites and by producing intermediates not suitable for the roll-over mechanism? There is no definite answer possible at this moment but the following arguments make the second possibility, i.e., elimination of the roll-over mechanism by Ni, more attractive as a possible explanation.

First, the recent literature (*13*) generally finds the roll-over mechanism more likely than the π-allyl mechanism. Second, if the π-allyl mechanism were really responsible for the D_{10} products, then this should be because of the (hypothetical) ability of the allyl to accept D from "under" the ring (up to D_5) as well as from "above" the ring (up to D_{10}). Because the D_5 production is not particularly slowed down by alloying, the results obtained would mean that not the formation of the allyl complex itself was significantly altered by addition of Ni to Pd but the ability to accept D from "above." Third, we have to consider the information available on the electronic structure of alloys. UPS and XPS valence band spectroscopy shows (*14*) that Ni and Pd are rather similar metals and, therefore, there are no grounds to expect substantial changes in the electronic structure of Pd atoms by alloying with Ni. Various data (*20*) indicate mutual spin-polarization and localization effects in alloys, but in some respects the behavior is almost additive. In any case, there are no signs of substantial charge transfer between the components of the alloy (the work function of pure components differ by only 0.2 eV, see Table 1) and this is to be compared with the fact that allyl complexes are known for various oxidation states of the ion (atom). For these reasons we prefer the explanation in geometric terms: by alloying Pd with Ni the roll-over mechanism leading to the D_{10} products is dramatically reduced, because there are less Pd ensembles of the necessary size available on alloys than on pure Pd. Ni influences the exchange by diluting Pd sites and by forming intermediates (for example, multiply bound intermediates) which eliminate a roll-over mechanism also on the neighboring Pd ensembles in the case when they are present. Table 2 summarizes the present knowledge on cyclopentane exchange and our conclusions based on this and the previous paper (*2*).

From the experiments presented it is not yet clear whether at high temperatures Pd contributes to the D_{10} production by formation of intermediates which are not present on Pd at low temperatures (e.g., the $\alpha\alpha$ intermediates). Alloys of Pd with a virtually inactive component should give an answer to this question because the high temperature behavior of Pd is masked here by the reaction on Ni.

REFERENCES

1. Ponec, V., *Catal. Rev.* **11**, 45 (1975).

2. Ponec, V., and Sachtler, W. M. H., *J. Catal.* **24**, 250 (1972).

3. Van Barneveld, W. A. A., and Ponec, V., *Recl. Trav. Chim.* **93**, 240 (1974).

4. Kemball, C., *in* "Advances in Catalysis" (D. D. Eley, W. G. Frankenburg, V. I. Komarewsky and P. B. Weisz, Eds.), Vol. 11, p. 223. Academic Press, New York, 1959.

5. Kemball, C., *Catal. Rev.* **5**, 33 (1971).

6. Burwell, R. L., *Accounts Chem. Res.* **2**, 289 (1969).

7. Burwell, R. L., *Catal. Rev.* **7** (1) 25 (1972).

8. Bond, G. C., and Turkevich, J., *Trans. Faraday Soc.* **50**, 1335 (1954); Addy, J., and Bond, G. C., *Trans. Faraday Soc.* **53**, 368, 383, 388 (1957).

9. Bond, G. C., "Catalysis by Metals." Academic Press, London, 1962.

10. Dowie, R. S., Gray, M. C., Whan, D. A., and Kemball, C., *Chem. Commun.* 883 (1971).

11. Frennet, A., *Catal. Rev. Sci. Eng.* **10**, 37 (1974).

12. Rooney, J. J., *Chem. Brit.* **1966**, 242.

13. Quinn, H. A., Graham, J. H., McKervey, M. A., and Rooney, J. J., *J. Catal.* **22**, 35 (1971); Clarke, J. K. A., and O'Cinneide, A., *J. Catal.* **24**, 181 (1972).

14. Smith, N. V., Wertheim, G. K., Hüfner, S., and Traum, M. M., *Phys. Rev. B* **10**, 3197 (1974); Hüfner, S., Wertheim, G. K., and Wernicke, J. H., *Phys. Rev. B* **8**, 4511 (1973); Cable, J. W., Wollan, E. O., Felcher, Y. P., Brun, T. O., and Hornfeldt, S. P., *Phys. Rev.* **34**, 278 (1975).

15. Sachtler, W. M. H., and Dorgelo, G. J. H., *J. Catal.* **4**, 654 (1965).

16. Bouwman, R., Lippits, G. J. M., and Sachtler, W. M. H., *J. Catal.* **25**, 350 (1972).

17. Hultgren, R., and Zapffe, C. A., *Trans. AIMME* **133**, 58 (1939).

18. Mathieu, H. J., and Landolt, D., *Surface Sci.*, **53**, 228 (1975); Stoddart, C. T. H., Moss, R. L., and Pope, D., *Surface Sci.* **53**, 241 (1975).

19. Pauling, L., "Nature of the Chemical Bond," p. 319. Cornell Univ. Press, Ithaca, N. Y., 1929.

20. Ferrando, W. A., Segnan, R., and Schindler, A. I., *Phys. Rev. B* **5**, 4657 (1972); Tansil, J. E., Obenshain, F. E., and Czjzek, G., *Phys. Rev. B* **6**, 2796 (1972); Cable, J. W., and Child, H. R., *Phys. Rev. B* **1**, 3809 (1970); Fischer, G., Henry, A., and Meijer, A. J. P., *J. Appl. Phys.* **39**, 354 (1968).