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The Reactions Between Cyclopentane and Deuterium on Nickel and Nickel–Copper Alloys

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Cyclopentane–deuterium exchange has been followed on nickel and some nickel–copper alloys in the temperature range 200–430°K. In the whole range, the reaction is accompanied by self-poisoning, and on Ni at 340–430°K also by hydrogenolysis. The catalytic effect of alloying is most pronounced on hydrogenolysis and self-poisoning, but is rather small with respect to multiple exchange. In having a low activity with respect to the C–C bond fission, the Ni–Cu alloys are more reminiscent of Pt than Ni.

An important question of interest in heterogeneous catalysis is: which property of the solid should be related to its activity. In the last twenty years many suggestions have appeared in this respect. Apparently most successful are the correlations of catalytic activity with various parameters characterizing the strength of the bond between adsorbed reaction components and the catalyst (*1–4*). These correlations, volcano-shaped or antibatic (low bond strength, high activity) found for simple reactions, have also gained some support by theoretical reasoning (*1–5*). However, serious deviations from the general trend have been found, too (*4*), e.g., a surprising contrast exists in the position of Fe in hydrogenation or hydrocarbon exchange reactions. The Fischer–Tropsch reaction, as a whole, etc., could serve as another example (*4, 6*). The simple correlations are evidently insufficient to make predictions on such subtle questions as the competition of various reactions proceeding simultaneously on the same catalyst. There is, therefore, a great need for data on the selectivity effects. Some progress has been already made in catalysis by oxides (see, e.g., (*7, 8*)), but much less is known about metals and next to nothing can be found in the literature on the selectivity properties of alloys. This is very surprising, as systematic studies on alloys of well-defined surface composition should, in principle, be able to provide very relevant data with respect to some fundamental questions of catalytic selectivity by metals.

Of the effects to be expected in alloying, the most important for catalysis are presumably the following:

(1) In particular, *collective* phenomena, such as ferromagnetism, are affected by alloying. The electron distribution around *individual* nuclei depends on their environment, too. Thus, alloying may cause some bonds to become weaker (or stronger) or disappear (appear). (Indeed, the heat of hydrogen adsorption (*9*) and activation energy in benzene hydrogenation (*10, 18*) have been reported to be different for Ni and Ni–Cu alloys.)

(2) Even if the chemical properties of metal atoms (in forming chemisorption bonds) are essentially preserved also in alloys, effects of more *geometric nature* should be expected.

In VIIIc–Ib alloys, at high dilution of the VIIIc-metal, one can possibly expect presence of individual VIIIc-atoms completely surrounded by Ib-metals, pairs,

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triplets, and other combinations, the relative abundance of which depends on the degree of dilution. If for one catalytic reaction single VIIIc-atoms are sufficient as active sites, while for another reaction *ensembles* of two or more active atoms are required, dramatic selectivity effects are to be expected in alloying.

In general, the two effects—(1) changes in the chemical character of an adsorbing VIIIc-atom and (2) changes in the relative abundance of certain ensembles in the surface—will act together. In the limiting, favorable case their contribution might be derived from the temperature dependence of the catalytic reaction involved. It can be expected that (1) will show up in the exponential and (2) in the pre-exponential factor of the Arrhenius equation.

Having these questions in mind, we performed a study of the exchange reaction of cyclopentane (C.P.) with deuterium, catalyzed by nickel or nickel–copper evaporated films. It is well known (*11–13*) that this reaction is a combination of the so-called *single* and *multiple* exchange and that different intermediates play a role in both reactions. For single exchange, a simple intermediate (M stands for metal atom)

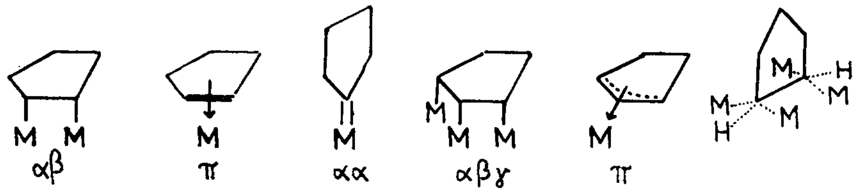
is to be expected, and for *multiple* exchange it is believed that one or two of the following intermediates exist simultaneously.

The results obtained with substituted cyclopentanes revealed that at various metals different intermediates were formed and, therefore, selectivity effects may appear with this type of reaction (*17*).

EXPERIMENTAL PART

The apparatus used was almost identical with that already described in detail (*10, 18*); only small changes have been made in order to improve the circulation of gases and to have the start of reaction better defined. The membrane manometer was placed in the volume for gas storing and handling. Before the reaction was started, in each measurement, the measured amount of C.P. had been transferred from the calibrated volume to the small trap, cooled to −193°C and placed near the reaction cell. Then the whole apparatus was filled with deuterium at a known pressure and circulation started. C.P. was then "injected" into the mixture by rapid warming up of the trap. To avoid diffusion effects, a suitable position of the trap had to be found by "trial and error" and the circulation speed had to be kept high. The standard mixture contained 0.1–0.15 Torr C.P. and 5.6–5.8 Torr D_2; the closed reaction volume was 510 cm^3. The temperatures below 0°C were kept constant by a cryostat (LAUDA Co.) and the temperatures higher than 50°C by means of an air-oven.

The method of film preparation was the same as described in an earlier paper (*18*). However, most of the films were evaporated directly at the temperature of sintering,



	αβ (*11*)	π-olefine (*14*)	αα (*6, 11*)	αβγ (*15*)	π-allyl (*14, 16*)	roll-over (*13*)
number of diss. H-atoms	2	2	2	3	3	4
minimum number of sites	2 + 2M—H	1 + 2M—H	1 + 2M—H	3 + 3M—H	1 + 3M—H	4 + 4M—H

SCHEME 1

i.e., about 200°C. The C.P. was purified by repeated distillation, directly at the U.H.V. apparatus; deuterium and hydrogen were purified by diffusion through Ag–Pd tubes.

The usual sequence of measurements was as follows: determination of the $H_2(D_2)$ adsorption at 273°K, repeated measurements at $T = 200 \pm 5°K$, measurements at higher temperatures, measurements of the total surface area by Xe. For low temperature runs, the samples were evacuated between runs at the given low temperature, for at least 4 hr.[1] For high temperature runs, the evacuation proceeded always at a standard temperature (~430°K) for at least 2 hr (pressure achieved was $5–20 \times 10^{-9}$ Torr). In contrast to the earlier work (*18*), Xe adsorption was now measured statically and not by the flow-in method. The adsorption of C.P. on Ni was followed in separate experiments. The course of reaction was followed by a mass spectrometer MS12 (A.E.I., England). The reaction vessel was permanently connected to the mass spectrometer via a porous plug-leak (*19*) (A.E.I.) and a Granville–Phillips valve. At a chosen time, the valve was totally opened and when stationary conditions were reached (after 1½–2 min), the spectrum was recorded at high scanning speed (about 20 sec per spectrum) and the valve was closed again. In this way, the loss of reaction mixture through the leak was minimized. The spectrum of deuterated C.P.'s was measured at nominal 12 eV electron accelerating voltage and 8 kV ion-accelerating voltage (fragmentation —H was 4%). The obtained spectra were then corrected for the ^{13}C content and for the decrease in deuterium pressures. (Deuterium pressure influenced slightly the C.P. signals.) The percentage of various deuterated C.P. was calculated from the corrected spectra ($d_i = \%$ of total C.P., with i-deuterium atoms already exchanged) and the same fragmentation and ionization efficiency was assumed for all species*; at low conversions ($\Delta d_0 = 10 \pm 5\%$) initial product distributions were also calculated. Percentage of the product D_i with i-deuterium atoms was defined as: $\varphi_i = 10^2 \cdot d_i/(\Sigma_{i=1} d_i)$. Following the suggestion of Kemball (*6, 20*) the parameter Φ was calculated: $\Phi = 1 \cdot d_1 + 2d_2 + \cdot \cdot \cdot 10 \cdot d_{10}$. The mean deuterium atom content in cyclopentanes is then $\Phi \cdot 10^{-2}$.

In the wide range of conversions ($100 > d_0 > 20\%$) the kinetics are well described by equations:

$$\log[d_0(t) - d_0(\infty)] = -\frac{k_{d_0} \cdot t}{2{,}3(100 - d_0(\infty))} + \log(100 - d_0(\infty)),$$

$$\log[\Phi(\infty) - \Phi(t)] = -\frac{k_\Phi \cdot t}{2{,}3\Phi(\infty)} + \log(\Phi(\infty) - \Phi(0)),$$

with $\Phi(0) = 0$ and $d_0(\infty) \sim 0$. The relative share of the multiple exchange mechanism can be illustrated by evaluating the parameter (*20*) $M = k_\Phi/k_{d_0}$. If multiple exchange is operating, M must be higher than 1.

In order to gain more reliable kinetic data, the reactions were followed at rather low rates. Therefore, the value $\Phi(\infty)$ was not determined experimentally, but was put equal to the relative deuterium content in the mixture.

RESULTS

1. *Adsorption of Gases*

The ratio $\alpha = N_H/N_{Xe}$, where N_H is the number of H-atoms adsorbed at 273°K and about 1.10^{-2} Torr and N_{Xe} is the number of Xe-atoms adsorbed at the relative pressure $x = 0.1$ at 78°K, has a value of 2.8 (±0.6)† for pure nickel (Fig. 1). It agrees well with values found earlier on the basis of static volumetric measurements (*21, 22*). For the alloys with 15–75% Cu, α was found to have a constant value (see Fig. 1), in agreement with previous results and the two-phase model of equilibrated Cu–Ni alloys with compositions within the misci-

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[1] Pressure achieved at evacuation was $2–5.10^{-8}$ Torr.

* Owing to the small extent of fragmentation, the error so induced was small.

† Here and elsewhere indicated (±) values the limits of maximum spread of values.

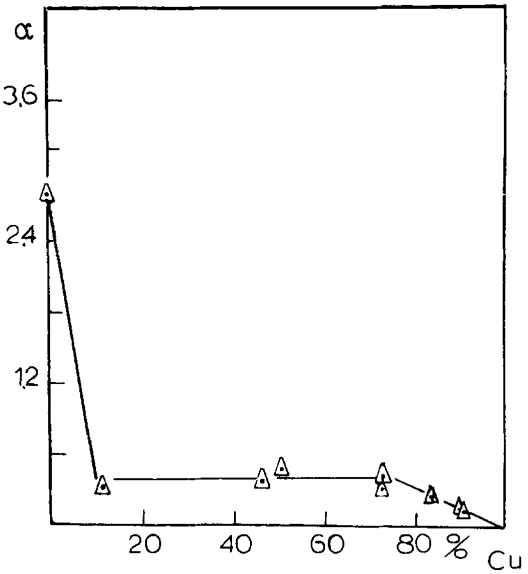


FIG. 1. Parameter α (see text) as a function of Cu content. Parameter α is under certain assumptions a measure of the Ni surface exposed in the surface. (For Ni the average value is shown, values from individual measurements for alloys.)

bility gap of this system. The numerical value for alloys used in this paper is, however, slightly lower than in the earlier work (*18*), presumably a consequence of a different way of determining Xe adsorption. If the adsorbed hydrogen is assumed to count the Ni atoms in the surface, the Ni content in the surface of two-phase alloys is 14 ± 7%, as derived from the α-values from this paper. The adsorption of C.P. on Ni at 273°K and $p \sim 10^{-2}$ Torr is very small. The background physical adsorption on the glass walls of the reaction volume is about 0.03 μmole and the adsorption with a film of Ni present 0.04–0.06 μmole. With decreasing temperature of the reaction vessel the physical adsorption of C.P. increases substantially (up to 0.12–0.2 μmole at −78°C, on the films with a surface area of about 400 cm²).

If hydrogen is admitted to Ni at 273°K after preadsorption of C.P. at 273°K and pumping off the gas phase at the same temperature, α is found to be lowered from the value for the clean surface to 1.6 (±0.1). Thus, still after C.P. preadsorption at 273°K, 50–60% of hydrogen adsorption sites remain free. The surface areas in cm² were calculated, assuming a site area for Xe of 19.4 Å at 78°K (*22*). The roughness factor *f* of pure Ni-films deposited at 200°C was about 1.2; for alloys condensed at 200°C, *f* = 2.5–3.5; for alloys condensed at 78°K and subsequently sintered, *f* decreased to about 1.6. A similar effect was observed previously for Ni (*23*). The glass vessel was used only for a small number of films as the surface area of glass increases (*24*) by the use of acids. The *r.f.* was 2.6 for the glass vessel after several experiments.

2. *Exchange Reaction at Low Temperatures* (<*300*°K)

Most of the values for M are close round $M = 1.5$. A few exceptional points deviate by as much as ±0.5 from this value. Between 195 and 300°K, M remains constant within narrow limits (see below).

In agreement with the low multiplicity factor of 1.5, the distribution curve is found to lack maxima at, e.g., D_5- or D_{10}-products. The excess values of d_2, d_3, d_4, d_5 above the binominal distribution calculated on the basis of d_0 and d_1 are also small and do not show any spectacular anomalies either (Fig. 2).

If the reaction is repeated at a constant temperature, the values of k_Φ and k_{d_0} decrease with an increasing number of runs with the same film. This decrease evidently caused by self-poisoning is more pronounced for Ni (down to 0.05–0.25 of the original value) than for the alloys (down to 0.8–0.5 of the original value). The decrease is approximately the same for both k_Φ and k_{d_0}; consequently the distribution of deuterated products remains unaltered.

3. *Exchange Reaction at Higher Temperatures* (>*300*°K)

Figure 3 demonstrates the changes of k_{d_0} and M with temperature. The sequence of measurements is indicated by arrows. It can be seen that at this temperature interval, M changes by as much as a factor of five. The effect of self-poisoning is again observable, but the parameter M is less influenced by self-poisoning than k_{d_0}. The data in Fig. 3 are measured with one alloy

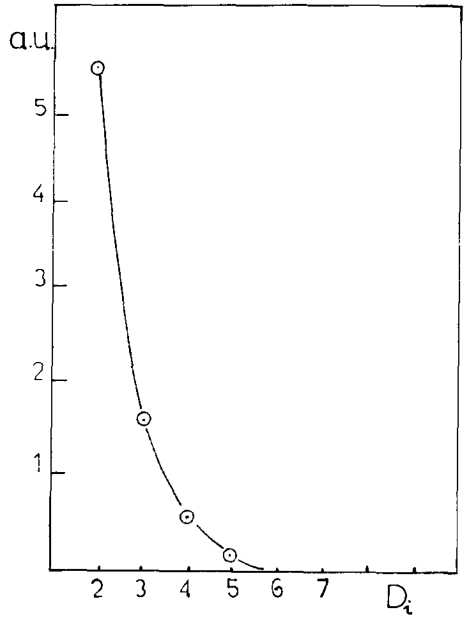


FIG. 2. Excess function for Ni film expressing the excess (in arbitrary units) of exchange over the binominal distribution calculated successively from the experimentally measured d_0 and d_1 values.

film, but the picture is much the same for nickel and other alloys.

Upon inspecting the product distributions, it appears that the influence of temperature on the selectivity is even more striking than can be seen from the M-values. Figure 4 (for further information on these data see Table 1) shows the product distributions for the same alloy as used in Fig. 3, but again the result is essentially representative for other alloys and nickel films as well. It can be easily seen that the increase of M is (in contrast to the situation at the temperature $T \sim 200°K$) specifically due to an increase of d_2 (and d_5) increase at the temperature $T < 380°K$. Quite differently at the temperature at $T > 380°K$, the high peak of d_{10} is dominant in the distributions. If for different samples (films) the value of M at the given temperature fluctuated, this was merely caused by the changes in d_1 and d_{10}, while the remaining product distribution showed only very small fluctuations. Clearly relevant information obtained in the distribution curves is partially lost in the M-values.

4. *Self-poisoning at Higher Temperatures*

Figures 5 and 6 show how M and k_Φ change with repeated measurements; their values are plotted as a function of the number of preceding runs on the same films. No points are shown for those runs performed at lower temperatures.

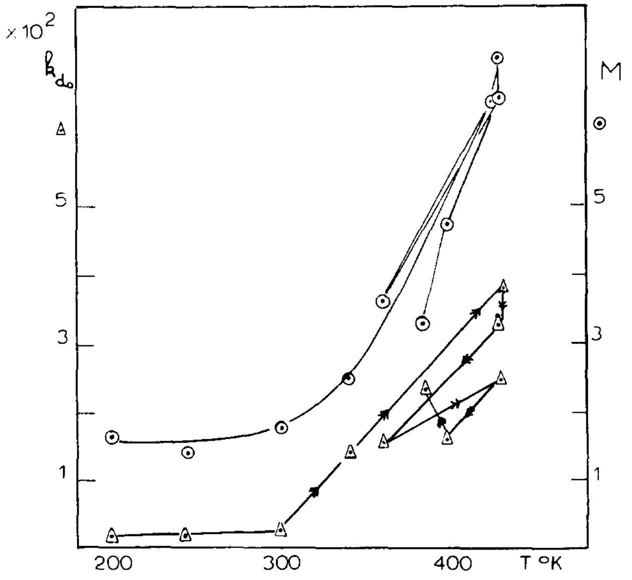


FIG. 3. Parameter M and constant k_{d_0} (%, sec^{-1}) as a function of temperature, measured for an alloy with 73% Cu. The value at 200°K was obtained after several measurements at this temperature.

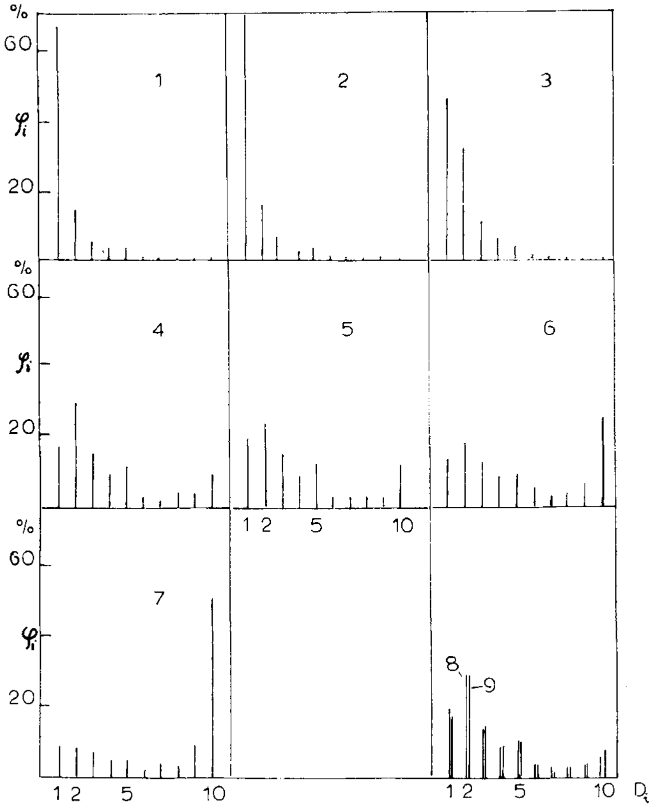


FIG. 4. Product distribution for an alloy with 73% Cu; see Table 1.

After the sixth run the film was treated with 0.2 Torr C.P. (in the absence of D_2) for 20 hr. Then, the mixture was evacuated and new series of kinetic measurements was performed. It can be seen that the poisoning by C.P. is in part reversible. By treating the surface with pure D_2, the values of M and k_Φ increase even more, above the values indicated in the graph. The changes in product distribution become indeed most visible by comparing the D_1- and D_{10}-products. The production of the first mentioned species is hardly influenced (in its absolute values) by C.P. poisoning, whereas D_{10}-production decreases markedly. As a result, d_1 (%) increases, d_{10} decreases by C.P. poisoning. The rest of the distribution remains almost unchanged. The results in Figs. 5 and 6 were obtained with an alloy with 73% Cu, but the results for other alloys or for pure Ni are much the same. The poisoning by C.P. has always a more pronounced effect on the product distribution than self-poisoning by the reaction mixture.

These results imply that for this reaction, static measurements (in a closed system) are not suitable for providing kinetic data which apply to a steady state.

5. *Multiple Exchange and Reaction Kinetics*

The function $M(T)$ is, of course, influenced by the phenomena described above. Therefore, points are spread as can be seen in Fig. 6.

The values for alloys with 50–85% Cu lie between the limits given by the results for two nickel films 1 and 3 from Fig. 6. All other Ni and Ni–Cu films lie between these limits, only the alloys (not shown in this Fig.) with Cu content less than 10% have still lower values of M than the lower limit indicated. Owing to the difficulties with the steady state no reliable Arrhenius parameters can be calculated. In order to gain at least some impression of the in-

TABLE 1

a) GENERAL DATA OF SPECTRA IN FIG. 4; FOR 73% Cu ALLOY

Spectrum No.	T(°K)	Conversion of C.P. (i.e., in D_0) (in %)	M	Note
1	200	17	1.8	(*a*)
2	243	9	1.4	(*b*)
3	300	14	1.4	(*b*)
4	343	14	2.4	(*b*)
5	360	18	3.4	(*b*)
6	399	15	4.7	(*b*)
7	432	7	7.4	(*b*)
8(Ni)	343	low	($\sim$2.5)	(*c*)
9	343	14	2.4	(*d*)

b) NUMERICAL DATA OF SPECTRA IN FIG. 4

	% φ_i										Spectrum
T°K	1	2	3	4	5	6	7	8	9	10	No.
200	67.5	15.6	5.8	3.6	3.8	1.6	0.7	0.4	0.4	0.5	1
243	69.6	15.5	7.2	2.5	3.4	1.5	<0.1	<0.1	<0.1	<0.1	2
300	46.2	32.0	10.2	5.8	3.5	1.5	0.5	0.3	<0.1	<0.1	3
343	17.0	29.0	14.8	9.1	11.0	2.5	1.5	3.4	3.1	8.7	4
360	19.5	23.4	14.9	8.5	12.4	2.4	2.4	2.5	2.5	11.6	5
399	12.8	17.2	11.9	7.8	8.5	4.9	2.3	3.4	6.3	24.9	6
432	8.7	7.9	6.8	4.7	4.2	1.8	3.6	2.3	9.1	50.9	7

Note: (*a*) Run No. 1, on virgin surface.

(*b*) Measured at the first increase of T after stationary state has been attained at 200°C.

(*c*) Spectrum (8) measured by Burwell *et al.* (*13*) (for pure Ni) is normalized at D_2 of spectrum (4).

(*d*) Spectrum (9) = spectrum (4).

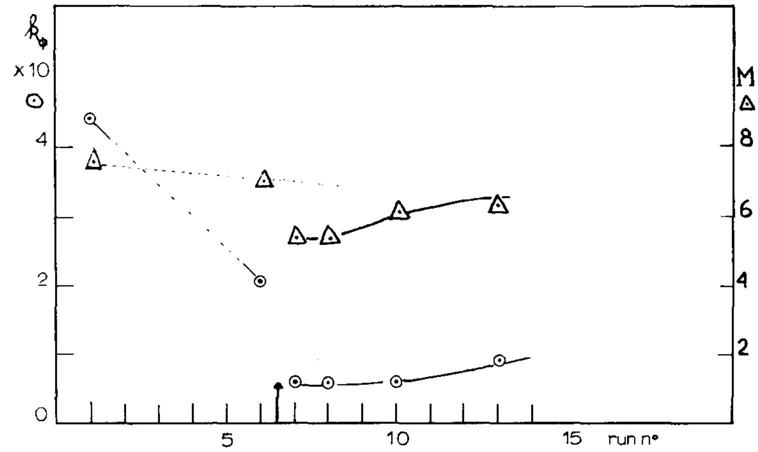


FIG. 5. Constant k_Φ (%, sec^{-1}) as a function of number of subsequent runs performed already on the film of an alloy with 73% Cu. [., left scale.] Parameter M as a function of number of runs performed already on the film of an alloy with 73% Cu. [△, right scale.] Between the run 6 and 7 poisoning by C.P. was performed.

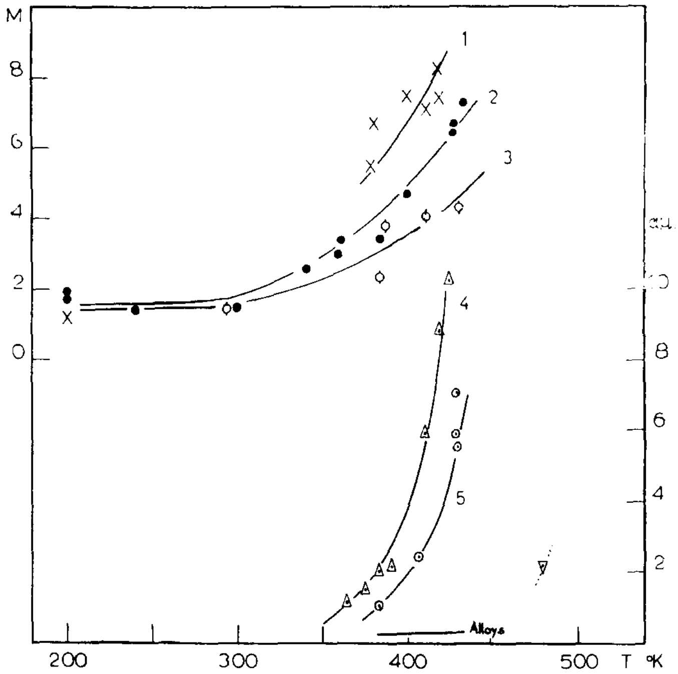


FIG. 6. Upper part: $M(T)$ function for Ni films (1, 3) and an alloy film (2) with 73% Cu. Lower part: Production of CD_4, in arbitrary units (amounts produced per time interval of 100 min) over Ni films (4, 5). Production of CD_4 was for all alloys lower than the indicated limit. The single point ▽ was obtained for an alloy with 73% Cu.

fluence of the temperature, a measuring progress was chosen of the type T_sT_1, T_sT_2, T_sT_3, etc., when the standard temperature T_s was higher than any other used (usually about 430°K). In this way, measurements at T_s then show the changes in kinetics due to self-poisoning. This "cycling" was started at surfaces which themselves were already nearing the "stable" state. The values $E(d_0)$ found in this way were very low for some films, particularly for Ni ($\sim 0 - 1$ kcal), likely as a consequence of reversible self-poisoning. The $\Delta E = E(\Phi) - E(d_0)$, governing the increase of M with temperature was roughly estimated as being 4 ± 2 kcal.

Figure 7 shows the k_Φ values per cm² of Ni surface ("titrated" by H_2-adsorption) determined at 430 ± 2°K on the surfaces nearing the steady state (after several repeated runs). No dramatic change is visible at 60% Cu content, i.e., the catalytic efficiency is essentially the same for a Ni-atom in the surface of Ni and of alloy films. All that has been said about the experimental determination of Arrhenius plots holds likewise for the determination of the orders of reaction. On surfaces nearing the steady state, the following picture was obtained by "cycling" between different and standard pressures at 430 ± 2°K. If $k = Ap_{D_2}^{m}p_{C.P.}^{n}$, then for both k_Φ and k_{d_0}, m is small and positive (and increasing with decreasing temperature) while n is small and negative.

6. *Side Reactions*

At temperatures above 360°K, hydrocracking becomes visible. It is best seen on the mass 20 (CD_4) which does not coincide with any fragmentation peak in the mass spectrum. The production of CD_4 (number of mols of products after 100 min of reaction) on different films is shown (in arbitrary units) in Fig. 6. It is remarkable that the rate of production of CD_4 on alloys is dramatically below that of nickel. This effect is much greater than would correspond with the decrease in Ni surface content, i.e., the efficiency of Ni-atoms to

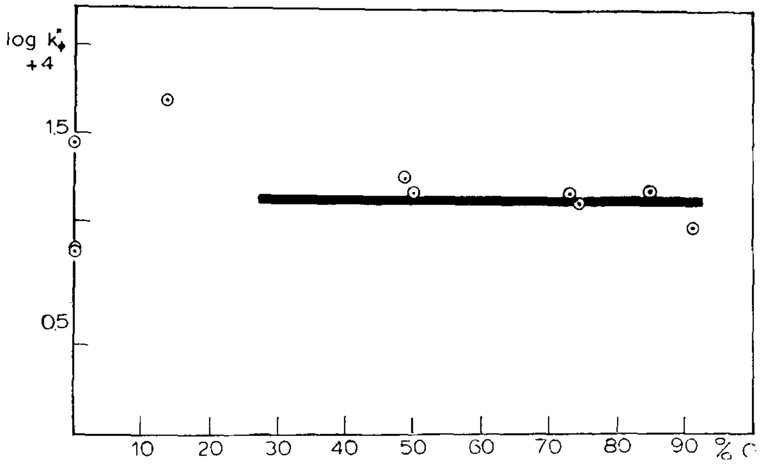


FIG. 7. Constant k_Φ^* (i.e., k_Φ (%, sec^{-1}) per cm^2 of Ni surface measured by H_2 adsorption) as a function of Cu content in alloys.

catalyze hydrogenolysis is strongly lowered by alloying with copper. The measurements were performed under such conditions that the total extent of the side reaction was always low; roughly estimated a few % of C.P. decomposed in the course of the followed exchange reaction, thus the exchange kinetics were not disturbed.

Some preliminary experiments have been done on Ni-powders at 240–280°C in hydrogen stream with a pulse reactor apparatus connected to a gas chromatograph. It has been found that C.P. decomposes more easily on the same sample than *n*-pentane under the same temperature and other conditions. Appearance of methane is mainly a result of *multiple* hydrocracking of C.P. in the adsorbed state.

DISCUSSION

On the basis of experience reported in the literature (*6*, *11–17*) some conclusions from the present results emerge immediately. Besides the single-exchange intermediate, more than one intermediate for multiple exchange is necessary. One of them (A) must be responsible for the multiple exchange, temperature independent in the range of temperature $T = 200$–300°K. At temperatures of about 340°K, the $M(T)$ increases with temperature, and we see that at least two intermediates must be responsible for this increase: one leading to the maximum (in product distributions) at $D_{(2)}$-product (B) and one (C) at $D_{(10)}$-product (resp. $D_{(5)}$). Whether each of these differs from (A) is not yet clear.

From the time course of $D_{(9)}$ and $D_{(10)}$, it may be concluded that they arise through the same process, i.e., via the same intermediate. Further, there are no maxima at $D_{(8)}$ (minima have actually been found instead at D_8), so that the present data do not support the idea of a "roll-over" intermediate (suggested (*13*) for Pd) at Ni and Ni–Cu surfaces.

The self-poisoning by the reaction mixture and, to a greater extent, poisoning by C.P. in the absence of D_2 suppress the multiple exchange mechanisms mainly by changing the relative production of D_1 and D_{10}. The very strong dilution of Ni in Cu leads to the same effect.

The question arises whether we can rationalize the data obtained in this research on the basis of our present knowledge on the reaction mechanisms and on the system Cu–Ni.

According to the predictions made on the thermodynamics of Cu–Ni alloys (*25*) and the photoelectric research on these alloys (*26*), as well as according to the CO (*25*) and H_2-titration (*18*) experiments, all films equilibrated at 200°C and having the bulk composition about 10–80%, should have the same surface composition, viz., about 80% Cu.

According to the more recent measurement and thermodynamic calculations (*27*), the outer phase should have a bulk composition of 70% Cu under the same conditions. Should the surface composition be directly reflected by the extent of H_2 adsorption, then according to the present H_2-titration measurements the surface content should be about 79–93% Cu.

In any case the Cu-content of the outer phase and of its surface is higher than necessary to fill all holes in the *d*-band, according to the rigid band theory of Mott and Jones (*28*). In terms of the original electron theory of catalysis (*6, 29*), a very low, or even zero, activity is predicted for reactions of hydorgen on these alloys. However, it is well possible that in spite of the spin interactions between Cu- and Ni-electrons, the Ni-atom behaves with respect to the strong perturbations (which chemisorption certainly is) as an atom of the pure nickel surface (*30*), or even as an essentially isolated atom.

It is not without interest that the "single atom" approach proved to be useful in explaining other experimental data on chemisorption (*31*) and field ionization (*32*), too.

The relatively small effect of alloying on the selectivity for multiple exchange (see Fig. 6) can be explained on the basis of one of the following assumptions.

(i) The multiple exchange reaction proceeds via one of the one-site intermediates (α, $\alpha\alpha$, π-complexed, π-allylic, see scheme 1). The hydrogen splits off on the same site as in the case of mononuclear complex homogeneous catalysts (see, e.g., 33) and then migrates away from the place of dissociation (the spill-over (*34*) effect).

(ii) More than one Ni-atom is necessary to form an active center for the multiple exchange, but the alloy contains segregated islands of Ni with 2, 3 or more nickel atoms. ΔH_f of alloy formation is positive and corrosive chemisorption may help in forming such islands (*35*). In this model, the alloy should act like Ni, but with a smaller surface area. Evidently, this model cannot explain that in hydrogenolytic reactions alloys behave qualitatively different from Ni.

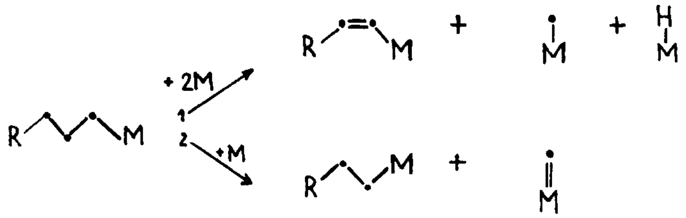
The effect of C.P. poisoning and of strong dilution of Ni on $M(T)$ can be then understood on basis of (i) as, e.g., an effect on C—H splitting and on H-migration; with the help of the assumption of (ii) as a simple blocking effect and decrease of probability of the formation of islands in highly diluted Cu-alloys.

It is remarkable that alloying influences the other two processes much more strongly, viz., it suppresses

(a) the self-poisoning effect at low temperatures and
(b) CD_4 formation (hydrogenolysis).

The latter process shows a stronger temperature dependence than multiplicity, i.e., $M(T)$, but begins to be visible at the same temperature where the increase in $M(T)$ sets in. However, in each particular run, hydrogenolysis and D_{10}-production do not proceed in parallel; CD_4 formation is highest in the first stages of the reaction. Thus, the mere presence of the dehydrogenation processes responsible for π-complexed, π-allylic or $\alpha\alpha$-intermediates leading to D_{10} is not a *sufficient* condition for the appearance of the hydrogenolytic products although dehydrogenation may well be a *necessary* condition for hydrogenolysis to proceed.

The following suggestions may help to understand the effect of Cu on hydrogenolysis. The simplest way of C–C splitting is schematically the route 1 or 2;



or an equivalent of it, with a formation of Me=C bond in the longer rest of the molecule, etc. The C–C fission on scheme 2 starts with the simplest possible intermediate, α-single adsorbed molecule. However, it can also start from $(\alpha\beta)$, $(\alpha\beta\gamma)$, $(\alpha\gamma)$, $(\alpha\alpha,\gamma)$ or similar intermediates, already suggested to this end (*6*, *36*).

It remains the common feature for all these schemes that (i) at least 2 Me–C bonds per original molecule are necessary (thus 2 sites necessary) and (ii) it is also necessary to accommodate somehow the electron from the broken bond. It all can proceed via one of the steps similar to that of scheme 2*. Where are now the sources for the different influences of Cu on multiple exchange and on hydrogenolysis? One possibility is as follows. The exchange is a one-site mechanism, while the hydrogenolysis is a multiple-sites mechanism (at least two sites!). Or, both of them are multiple-site mechanisms, but the number of necessary Ni sites is different and higher for hydrogenolysis. Besides this, in principle, "geometrical" effects, also a "chemical" or "electronic" effect may be expected (see Introduction). One may assume that the formation of certain bonds necessary for the multiple exchange (e.g., α, $\alpha\beta$, π-complexed, π-allylic) is not influenced (or the bonds are slightly influenced in their strength only) by alloying, while those for hydrogenolysis are influenced strongly (these could be, e.g., $(\alpha\alpha)$, $(\alpha\beta\gamma)$, $(\alpha\alpha,\gamma)$, etc.). In principle, both the mentioned effects—"geometrical, electronic"—can rationalize the results obtained and at the moment no definite conclusion can be made. The big contrast between the reactivity in C–H and C–C splitting is not restricted to Cu–Ni alloys but also encountered when groups of metals of similar behavior can be found, see e.g. Pt, Pd on the one hand and Ni, Rh on the other hand in hydrogenolysis (*36*, *37*). Here we are certainly inclined to believe in some "electronic" effect rather than in a "geometrical" effect in the sense used above.

The preliminary experiments with hydrogenolysis of methyl cyclopentane on Cu–Ni alloys bring essentially the same results; the suppressing of the hydrogenolytic power of Ni by Cu seems to be general. It is hoped that suppressing of the hydrogenolysis by Cu can make other reactions observable on Ni/Cu alloys which on pure nickel are masked by extensive C–C splitting. This view is also strongly supported by the recent results of Reman, Ali, and Schuit (*38*).

Note on units used: Torr has been used as pressure unit throughout; 1 Torr = 133,32 Nm^{-2}. The composition of alloys is in wt%.

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* There is always a problem what to do with H-atoms split off from the hydrocarbon. However, with the exchange reaction the same problem exists and as we now want to discuss the difference between multiple exchange and hydrogenolysis processes, we may forget it for a moment.

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