JOURNAL OF CATALYSIS 28, 381–390 (1973)

Reactions of Methylcyclopentane on Nickel and Nickel–Copper Alloys

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Received May 8, 1972

The exchange reaction of methylcyclopentane with deuterium has been followed on Ni and Ni–Cu alloy films. Reactions of methylcyclopentane with hydrogen have been followed on Ni and Ni–Cu alloy powders. The results confirm that

1. the reactions at C–H bonds are less influenced by alloying than the reactions at C–C bonds;
2. alloying with Cu favors the nondestructive reactions (e.g., isomerization) and suppresses the hydrogenolytic cracking reactions.

The results can be rationalized assuming that the reactivity and flexibility of adsorbed molecules is inversely related to the heat of adsorption (bond strengths) and the degree of dehydrogenation.

INTRODUCTION

In the introductory words to our previous publication (*1*) we discussed the reasons which led us to the study of selectivity patterns of alloys. Briefly these reasons include the hope to arrive at a better understanding of differences in catalytic behavior of clean metals and also an attempt to solve some questions of the mechanism of hydrocarbon reactions (hydrogenolysis, isomerization, dehydrocyclization) on metals. The results published in that earlier paper (*1*) raised the question to what extent they are general or specific for the given system of cylopentane, deuterium and Ni–Cu alloys. We therefore decided to extend our work in two directions, studying not only another compound [methylcyclopentane (MCP)] on the same alloys (Ni–Cu) but also the same compound (cyclopentane) with another alloy (Pd–Ag) as the catalyst. The results for MCP are presented here; the results on Pd–Ag–cyclopentane will be published soon.

A substantial part of the present work was carried out with powders, but the significance of the results was checked by some specific experiments on films to make sure, in particular, that the different reactivities of the C–H and C–C bonds and the suppression of C–C bond fission by alloying are also characteristic for catalyst surfaces which are clean.

EXPERIMENTAL

Apparatus; Measurements and Data Evaluation

In this work two types of apparatus and two different forms of catalysts were used (*1*). The exchange reaction of deuterium with methylcyclopentane (MCP) was followed quantitatively using evaporated metal- and alloy-films in a reaction vessel connected directly to the mass spectrometer (MS12-AEI, England). Methane formation (hydrogenolytic product) could also be checked in this apparatus. Films used in these experiments were evaporated in ultrahigh vacuum ($p < 10^{-9}$ Torr). Reactions of methylcyclopentane with hydrogen were followed in an open-flow apparatus using

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metal- and alloy-powders as catalysts. Analysis of the products was performed by GLC (Becker, Delft).

The procedure of making and admitting the reaction mixture was the same as in Ref. (*1*); the standard mixture was 0.16 Torr MCP and 6 Torr D_2. The closed reaction volume where gas was circulating was 675 ml. Evaporation of films, the preparation and cleaning of H_2, MCP and Xe, the way of measuring adsorption of H_2 and Xe and of following the exchange reaction were identical with the procedure adopted earlier (*1*). Mass spectra were recorded at 20 eV (nominal) electron accelerating voltage and 8 kV positive ion accelerating voltage, at a high scanning rate (<20 sec/spectrum). With the molecular leak used (*2*) no corrections were necessary for the escape of gases out of the reaction volume. Spectra were corrected for the content of ^{13}C and for the (–H) fragmentation (3.6×10^{-2} %). Random fragmentation was assumed in these calculations and equal ionization efficiency for all species. The extent of fragmentations was small, so the error introduced in this way is probably small, too. All calculations were performed by a computer.

For each D_i-product (i.e., MCP with i-deuterium atoms) the relative concentration $d_i\%$ was calculated ($d_i\%$ is the percentage of the total MCP with i atoms already exchanged). For a low overall conversion $[-(\Delta d_0/d_0) = 10 \pm 5\%]$ the initial product distribution (IPD) in φ_i's was computed. For the D_i-product the value φ_i is defined as $\varphi_i = 10^2 d_i/\Sigma_{i=1}^{12} d_i$. Following Kemball's suggestion (*3, 4*) the parameter Φ was also evaluated; where $\Phi = 1d_1 + 2d_2 + \cdots 12d_{12}$. Usually, the extent of the multiple exchange mechanism can be estimated by evaluating the parameter M; $M = k_\Phi/k_{d_0}$ where k_Φ and k_{d_0} are the constants in the equations:

$$\log_{10}[\Phi(\infty) - \Phi(t)] = \frac{k_\Phi t}{2{,}3\Phi(\infty)} + \log[\Phi(\infty) - \Phi(0)]$$

$$\log_{10}[d_0(t) - d_0(\infty)] = -\frac{k_{d_0} t}{2{,}3[100 - d_0(\infty)]} + \log[100 - d_0(\infty)]$$

with $\Phi(0) \div d_0(\infty) \div 0$. Multiple exchange leads to $M > 1$.

We used these equations for the exchange of cyclopentane and deuterium and found the indicated semilogarithmic plot always linear (*1*). With MCP, however, the data deviated systematically from the linear plot [a situation found also with some other hydrocarbons (*5*)] and M could be only determined as a ratio of derivatives of the above functions; the values of M were evaluated for $t \rightarrow 0$. During reaction, in a given run, or when comparing successive runs, the constants k_Φ and k_d were found to decrease. In contrast to our previous results with cyclopentane, no steady state could be obtained even after many runs and poisoning by MCP. Therefore, the data presented below were collected during isothermal runs, performed in order of increasing temperatures. Between the runs the apparatus was evacuated to about 10^{-8} Torr. With regard to the mentioned progressive self-poisoning no conclusion can be made on the temperature dependence of the rates.

From the initial distributions the mean content $\bar{M}$ of deuterium atoms per molecule can be calculated; this value is shown in Table 1, together with other relevant data.

Experiments with alloy- and metal-powders were performed in an open-flow reactor. The same apparatus had been used for a previous study of hexane isomerization and hydrogenolysis (*6*). The procedure for making Ni–Cu powder alloys [from coprecipitated carbonates (*7, 8*)], and for measuring the activity and evaluating the analytical data was the same as in Ref. (*6*). The following magnitudes were evaluated, using molar concentrations (determined by GLC) C_i's of hydrocarbons with i carbon atoms. Total conversion α (%):

$$\alpha = 100 \sum_{i=1}^{6} \sum_{j,j\neq k} iC_i^{(j)} \Big/ \left\{ \sum_{i=1}^{6} \sum_{j,j\neq k} iC_i^{(j)} + 6C_6^{(k)} \right\},$$

where summation over j is performed over all detected molecules (isomers and various compounds) for each i-C-atoms hydrocarbon; the index k denotes MCP. The rate of the overall reaction was determined from the measured conversion α and the flow rate (F = molecules/sec). For conversion $\alpha < 20\%$ the function $\alpha = f(F^{-1})$ was found to be linear and therefore the rate per square centimeter of the total surface (r_s) or the rate per gram of catalyst (r_w), are

$$r_s = 10^{-2} \cdot d\alpha/d(sw)/F) \div 10^{-2}(sw)^{-1}\alpha F,$$

$$r_w = 10^{-2} \cdot d\alpha/d(w/F) \div 10^{-2}w^{-1}\alpha F,$$

where the surface area of 1 g of catalyst is denoted by s and the weight of the catalyst by w. The surface areas of the catalysts were measured by a Perkin-Elmer Shell Sorptometer 2120. Activity parameters A are defined as $A_1 = \log r_w$ and $A_2 = \log r_s$, resp., and compared for the same temperature and flow rate F.

The selectivity in producing all other (than MCP) C_6-hydrocarbons is characterized by the selectivity parameter s (%) defined as:

$$S = 600 \sum_{j,j\neq k} C_6^{(j)} \Big/ \sum_{j,j\neq k} \sum_{i=1}^{6} iC_i^{(j)}.$$

In order to characterize the way of chain splitting the fission parameter M_f is used:

$$M_f = \Big(\sum_{j} \sum_{i=2}^{5} (6 - i)C_i^{(j)}\Big) \Big/ (C_1)_{\text{measured}}.$$

When $M_f \rightarrow 1$, the specific terminal splitting prevails (typical for Ni catalysts usually); when $M_f \gg 1$, random splitting plays a significant role, or the splitting is directed slightly towards the middle bonds of the molecules (typical for Pt catalyst). M_f is $\ll 1$ if multiple splitting, i.e., hydrogenolytic decomposition to C_1-fragments is dominating. Parameters M_f and S are compared for various catalysts for the same flow rate F.

Materials Used

Films were evaporated and sintered (at least 20 hours) at 200°C in the UHV apparatus, as described previously (*1*). Ni–Cu and Ni powders were reduced in the flow apparatus, *in situ*, for at least 24 hr at 350–400°C (*6*). All hydrocarbons used for measurements and calibrations were GLC or puriss-grade (ex. Fluka, Switzerland).

In this paper all alloy compositions are expressed in atomic %. Pressures are expressed in Torr (1 Torr = 133.3 N m^{-2}), and activation energies in kcal/mol (1 kcal/mol = 4.184 kJ/mol).

RESULTS

1. Exchange Reaction of Deuterium with MCP on Films

The most important results are collected in Table 1 and in Fig. 1, where the initial product distributions (IPD) are shown. As can be immediately seen from these data the multiplicity of the exchange ($M > 1$) manifests itself at low temperatures by a small peak of the D_{12}-product and its contribution is, in general, low. The pronounced maxima at D_4 and D_8 found by other authors for Pd catalysts (*9*) were not

TABLE 1

MULTIPLICITY OF THE EXCHANGE REACTION OF D_2 WITH MCP ON Ni–Cu FILMS

Cu (%)	T (°C)	$\Delta d_0/d_0$^{a}	M	$\bar{M}$
0	0^b	15.4	3.3	3.67
	80	9.9	8.6	4.67
	80^b	24.7	8.6	6.83
	130	8.1	11.5	7.41
	130^b	18.2	11.5	10.10
5	0^b	2.0	5.2	4.90
	100^b	19.3	8.5	7.76
	150	5.0	11.8	10.49
	150^b	25.8	11.8	10.42
29	0	6.2	2.5	2.50
	130	6.5	8.1	8.01
	180	67.0	10.1	8.24
	180	14.6	10.1	9.43
83	100	6.4	6.8	5.27
	100^b	10.2	6.8	5.86
	150^b	9.7	8.1	7.95
	200^b	9.5	10.0	9.85

[a] $\Delta d_0/d_0$ = measure of total conversion of the light hydrocarbon; $M = k_\Phi/k_{d_0}$; $\bar{M}$ = mean deuterium content calculated from the product distribution.

[b] Product distributions for these measurements are shown in Fig. 1.

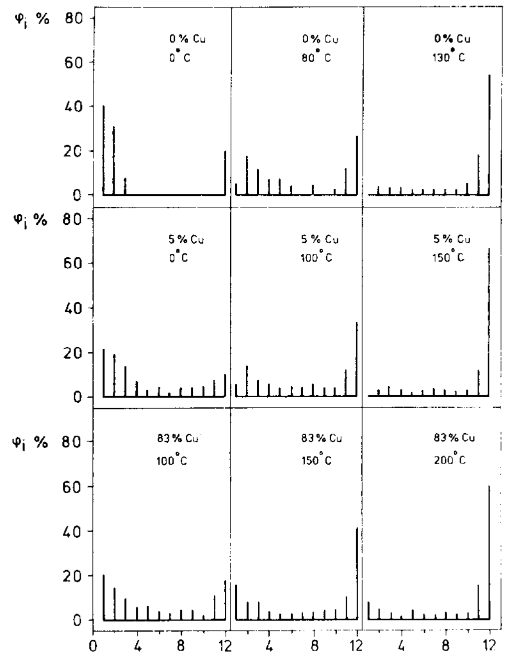

FIG. 1. Initial product distribution in the exchange reaction of MCP with deuterium on films. The temperature and film composition are indicated; for other data see Table 1.

found here, although there is a little enhancement above the binominal distribution at these peaks at higher temperatures.

With increasing temperature the parameters M and $\bar{M}$ increase and they reach their maximum values at 130–180°C for all films, including clean Ni. Also the IPD pattern does not reveal any remarkable difference between Ni and Ni–Cu alloys as is immediately seen from Fig. 1. In all cases the D_{12}-product is responsible for the observed multiplicity. Poisoning by MCP (admitted without H_2, at $P = 0.16$ Torr) leads to a slight decrease in M; subsequent static reduction by H_2 regenerates the catalyst only partially.

Owing to the strong self-poisoning by MCP the functions $k^{\Phi}(T)$ and $k_{d_0}(T)$ revealed a maximum. Above a certain temperature, the self-poisoning effect is stronger than the Arrhenius temperature dependence. Because no steady state could be reached no reliable comparison of activities of Ni and alloys was possible. A very rough estimate shows (see Fig. 5) that the possible decrease in the total exchange activity does not decline very much from the decrease expected according to the decrease in the extent of hydrogen adsorption, which can be used in turn as a certain measure of the number of Ni atoms in the surface (*1*, *10*). However, the values are more spread here than they were in the case of cyclopentane (*1*).

2. *Hydrogenolytic Reaction of MCP with D_2 on Films*

The mass spectrum of cyclopentane is rather complicated in the region of lower fragments, so it is difficult to use this region for analytical purposes generally. However,

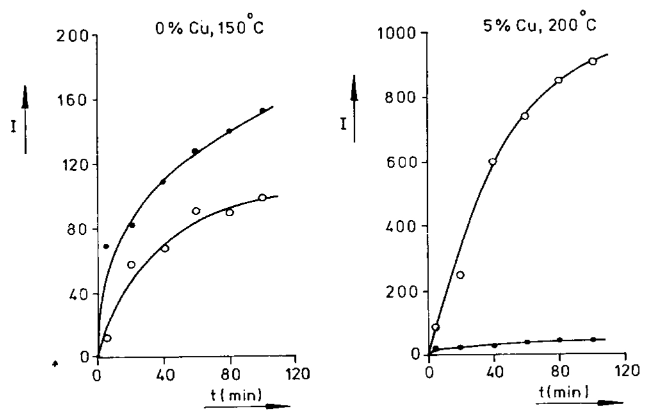

FIG. 2. Production of C_6H_{12} (○) compared with CD_4 (●) production for clean Ni film (T = 150°C) and film with 5% Cu (T = 200°C). Comparison is shown in arbitrary but directly comparable units.

TABLE 2
ACTIVITY AND SELECTIVITY OF Ni–Cu ALLOYS IN MCP REACTIONS[a]

Cu (%)	T (°C)	M_f	S (%)[b]	2-MP/3-MP	A_1 (555°K)	A_2 (555°K)	E_{act} (kcal)
0	210–250	1.0	70–55	0.7	19.25	15.04	42
5	290–330	1.0	57–62	1.4–1.7[b]	17.44	12.42	46
17	280–320	1.1–1.3[b]	81–75	1.6–1.1[b]	16.67	—	55
40	265–305	0.8–1.8[b]	89	2.6–2.0[b]	17.27	—	58
46[c]	300–320	—	>90	About 2.5	—	—	—

[a] M_f, S%, A_1, A_2 are defined in the text, evaluated for the same flow F; MP means methylpentane.

[b] The parameter is temperature dependent and varies in the range indicated.

[c] Unstable catalyst with low conversion; only rough estimates of parameters were possible.

mass 20 (CD_4) and 16 (CH_4) can well be used as a measure of the methane formation. The currents I (CD_4^+) and I ($C_6D_{12}^+$) are compared in Fig. 2 (CD_4 is characteristic for hydrogenolytic reactions, C_6D_{12} for multiple exchange). The currents are corrected for different sensitivities of the mass spectrometer for these two compounds. It can easily be seen that, under the conditions where the D_{12}-formation has a comparable rate on clean Ni and Ni–Cu alloys, a marked difference exists in the CD_4 formation rate on these catalysts. The decrease of the rate of hydrogenolysis, or, more precisely, cracking to methane, upon adding Cu to Ni as compared to smaller changes of the multiple exchange reaction rate was previously also found for cyclopentane (*1*) and seems to be a general phenomenon. The selective decrease of the rate of a given reaction can be studied in a more quantitative way on powders but it is worth noting that qualitatively the same difference between Ni and Ni–Cu alloys in hydrogenolytic reactions is found for films prepared in UHV.

3. *Reaction of MCP with H_2 on Powders*

After an initial period of slow decreasing activity (selectivity pattern remained substantially unchanged and this period lasted about 1 day) the performance of the catalyst was fairly stable if the temperature was kept lower than about 320°C. The catalysts are evidently much more sensitive to the self-poisoning by MCP than by hexane (*1*) or cyclopentane (*6*).* This is also clear from the following fact. While for the reactions of hexane a continuous decay in activity was observed only with catalysts containing >65% Cu, a similar decay was observed with MCP already for alloys containing >40% Cu.

Table 2 presents data obtained on the reactions of MCP with hydrogen on Ni and Ni–Cu powder alloys. Figures 3 and 4 show data obtained for one of the alloys used, viz, 17% Cu. For other alloys, as well as for Ni, a similar picture is obtained. Figure 5

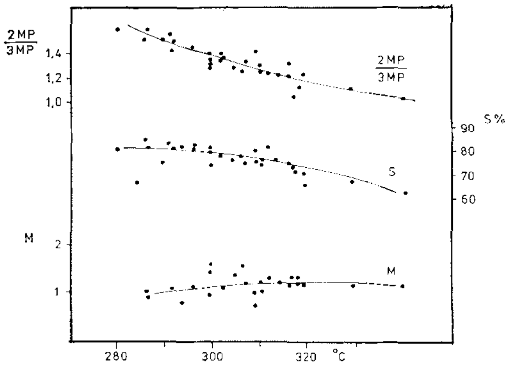

FIG. 3. Reactions of MCP with hydrogen on 71% Cu alloy powder. Dependence of S, M and 2-MP/3-MP ratio on the temperature of reaction (for S and M, see text).

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* It should be mentioned that, when working with hexane and 3-methylpentane and the same type of catalysts, the self-poisoning of catalysts was also particularly rapid at temperatures when a rather high percentage of MCP and benzene was found among the products.

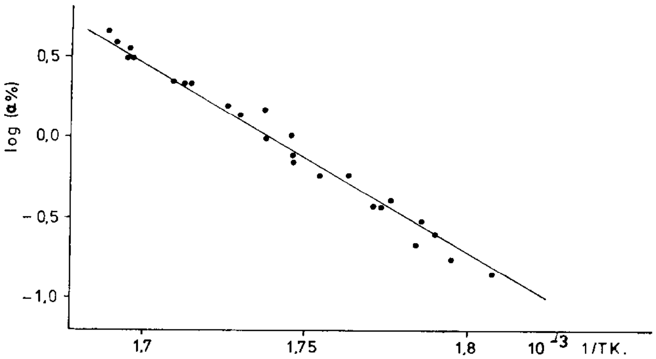

FIG. 4. Reaction of MCP with hydrogen on 17% Cu alloy powder. Arrhenius plot for the overall conversion (for the reactor working as "differential reactor").

shows the results on activity parallel to the data obtained with hexane on the same type of catalysts (*6*).

Typical product distributions obtained with MCP are shown in Table 3. The main reaction is the ring opening, which is accompanied by hydrogenolytic cracking to lower hydrocarbons and by dehydrogenation–isomerization reactions leading to benzene. As can also be seen from Table 3, the production of benzene can be enhanced (at higher reaction temperatures) but, as already mentioned, the catalyst is then progressively poisoned (see column for α; conversion α is direct proportional to the activity of the catalyst).

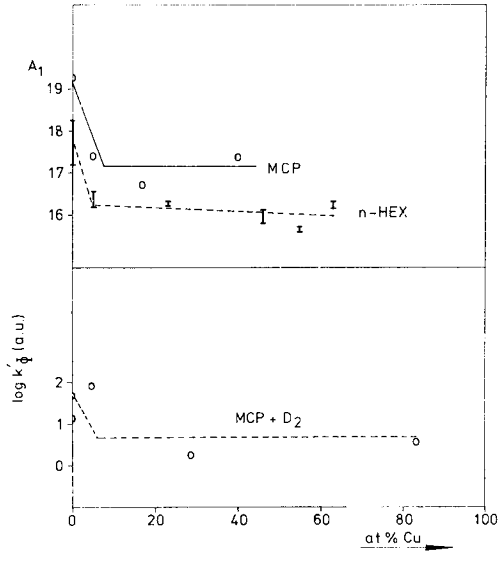

FIG. 5. Activity parameters for reaction of MCP on powders and films, and reaction of *n*-hexane [from Ref. (*6*)] on powders (for *A*, used for powders, see text).

k'_{Φ} = specific reaction rate for MCP + D_2 exchange per unit of the total film surface area (at 100°C in arbitrary units). Dashed line = nickel surface area, as measured by hydrogen adsorption. Relative changes in nickel surface with alloy composition, as found in Refs. (*1*) and (*10*), are plotted in the graph in the logarithmic scale.

Summarizing the results presented in Tables 2 and 3 it can be said that alloying with Cu lowers the activity for the overall conversion of MCP, leads to a higher selectivity for C_6-hydrocarbons (slowing down hydrogenolytic cracking reactions) and to a higher activation energy. Simultaneously the ratio 2-methyl-/3-methylpentane and the contribution of random splitting both increase.

DISCUSSION

The present results confirm and implement our conclusions from papers published earlier (*1*, *6*) on cyclopentane reactions with deuterium on Ni and Ni–Cu films and on hexane reactions on Ni and Ni–Cu powders. They are, briefly summarized:

i. Upon alloying Cu with Ni, reactions of C–H bonds are influenced to a lesser extent than the reactions on C–C bonds (isomerization, cracking, etc.) (see, e.g., Fig. 5). The exchange reaction retains its high multiplicity also on alloys with high Cu

TABLE 3

EXAMPLES OF PRODUCT DISTRIBUTIONS IN MCP-H_2 REACTION ON POWDERS[a]

Cu (%)	T (°C)	α	C_1	C_2	C_3	iso-C_4	n-C_4	iso-C_5	n-C_5	Cyclo-C_5	2-MP	3-MP	n-C_6	Be + CH
0	239	6.9	36.4	1.4	1.7	2.4	3.2	11.4	2.3	2.6	14.8	20.9	2.9	—
5	310	8.2	36.8	1.1	2.1	2.1	2.9	9.9	2.9	4.1	20.7	14.2	2.0	1.3
17	316 stationary	3.1	21.7	0.6	0.3	1.5	0.8	7.5	1.5	11.0	25.0	23.4	1.9	4.8
	340 unstable	2.7	28.8	0.4	0.9	2.4	1.4	8.9	1.7	12.2	13.8	12.7	0.5	16.2

[a] α = total overall conversion (%), measured at the same flow F; C_i = hydrocarbons with i carbon atoms; 2-MP = 2-methylpentane (not separated from 2,3-dimethylbutane); 3-MP = 3-methylpentane; Be = benzene; CH = cyclohexane.

content while cracking is strongly suppressed.

ii. Alloying changes the selectivity pattern of reactions on C–C bonds in favor of nondestructive reactions (e.g., isomerization).

Some other recent papers (*14–17*) also offer the same picture as summarized under (i); (i) applies not only to the reactions of cyclopentane and hexane but also to cyclohexane dehydrogenations and cracking (*16*), cyclopropane reactions (*17*) and cracking of ethane (*15*) and propane (*17*).

McMahon, Carr and Clarke (*14*) suggested that the D_4 and D_6 maxima in the IPD of the cyclopentane–deuterium reaction, which they found at 200–290°C, represent a proof of the existence of multiply bonded cyclopentane species. However, in our experiments rather extensive ring opening and cracking occurred already at 150°C with cyclopentane and at 180–200°C with methylcyclopentane. This makes a straightforward interpretation of mass spectra obtained at still higher temperatures impossible and we were therefore unable to confirm the conclusions of McMahon, Carr and Clarke (*14*).

In comparison with molecules used previously (*1*, *6*), the molecule of MCP also offers a possibility to see specificity (or nonspecificity) in the ring opening. Fission of $C^{(1)}$–$C^{(2)}$ and $C^{(1)}$–$C^{(5)}$ bonds leads to hexane, of $C^{(2)}$–$C^{(3)}$ and $C^{(4)}$–$C^{(5)}$ bonds to 2-methylpentane and of $C^{(3)}$–$C^{(4)}$ to 3-methylpentane. Considering these possibilities, purely kinetically controlled and statistically random splitting would lead to the ratio n-HEX:2-MP:3-MP = 2:2:1. (The thermodynamic ratio 2-MP/3-MP is in the range of temperatures used 2.1–1.9, that of n-HEX/3-MP is 1–1.2) (*11*). For all catalysts studied, Ni as well as Ni–Cu alloys, the hexane content is remarkably lower than predicted in this way. For Ni the observed ratio 2-MP/3-MP is clearly in contradiction to the random fission mechanism, testifying to specificity in splitting, and alloying with Cu leads to higher values of this ratio (even above the value for random splitting). An increase of the 2-MP/3-MP ratio is accompanied by an increase of the fission parameter M_f, which grows from a value $M_f \sim 1$ as characteristic of specific terminal splitting for Ni to values $M_f > 1$. It also shows a change towards a more "random" splitting mechanism. Similar results in this respect are thus found for both MCP and n-hexane (*6*).

As mentioned, the least frequent product of the ring opening is n-hexane. At first sight, a steric reason might be considered. However, when the reaction was followed at very low temperatures using a larger amount of Ni (see Fig. 6), the n-hexane yield was markedly higher. Because n-hexane itself reacts on the same catalyst at higher temperatures than MCP, we conclude that an intermediate of MCP con-

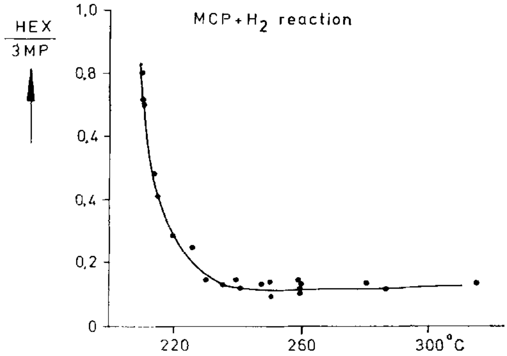

FIG. 6. n-Hexane to 3-methylpentane ratio as a function of temperature for Ni powder.

version leads to hexane at low temperature but to fission products at higher temperature. In other words, C–C bond rupture is easier in this adsorbed reaction intermediate than in intermediates which have a structure leading to other products, as, e.g., 2-MP and 3-MP.

Before we make an attempt to rationalize our results on the basis of the present knowledge of electronic and structural properties of Ni/Cu alloys, we would like to mention some unpublished results on n-hexane conversion which are relevant for the following discussion. As can be seen from Table 4, the distributions of C_6-products of n-hexane conversion on various alloys show clear patterns in the dehydrogenation activity of these catalysts. Nickel is little active in the production of C_6-hydrocarbons but among the C_6-products the dehydrogenated ones are more prevalent than among the products on Cu-rich alloys, which are otherwise more active in the overall C_6-production.

It has repeatedly been suggested in the literature that the Ni–Cu system is an ideal example where the so-called rigid band model holds, and that the catalytic properties of alloys are controlled by the assumed electron transfer from Cu to Ni. Also, forming of an ideal solution by alloying was usually assumed. However, the recent results of the literature lead us to the following conclusions.

1. These alloys are not described by a rigid band model and there is no measurable transfer of electrons from Cu to Ni atoms (*18*, *19*). However, certain changes in electronic properties of atoms in the alloy occur, as is manifested by variation of magnetic, electric and mechanical properties upon alloying.

2. These alloys have a tendency to clustering (*20*) at higher temperatures, above the miscibility gap, and because the sublimation heat of Cu and Ni is different and lower for Cu, Cu will be enriched in the surface of an equilibrated alloy; also in a one-phase system. Such an enrichment has been experimentally found in systems such as Pd/Ag and Pt/Sn (*21*, *22*).

3. Ni–Cu alloys have a miscibility gap at low temperatures and they accumulate in the surface the Cu-rich equilibrated alloy (*23*).

TABLE 4

DISTRIBUTION OF C_6-PRODUCTS IN REACTIONS OF HEXANE

Cu (%)	T (°C)	α[a]	S[a]	2-MP	3-MP	MCP	Be	MCP + Be (dehydrog.)
0[b]	315	11.6	5.3	50	19.1	8.7	22.3	31.0
	335	13.2[c]	3.8	41.3	18.8	6.9	33.1	40.0
23	334	10.0	11.8	49.4	25.0	17.9	7.7	25.6
46	334	3.9	69	71.4	17.4	8.7	2.5	11.2
63	333	1.4	62	72.2	19.6	7.1	1.2	8.3

[a] For parameters S and α, see text; for other symbols see Table 3.

[b] Ni (0.1 g) diluted in 1 g of an inert SiO_2.

[c] After prolonged work at higher temperatures, conversion is lower. However, self-poisoning suppresses the total conversion, but leaves selectivity patterns unchanged.

4. Hydrogen adsorption, perhaps a good counter of Ni-sites, shows the same function of the Cu content for powders equilibrated at temperatures higher than the temperatures of the miscibility gap (*8, 16*) and for films equilibrated at temperatures lower than the gap-limiting temperatures (*1, 23*).

On the basis of these pieces of information, a safe statement with regard to the surface of these alloys would be: All alloys used have less Ni-sites in the surface than pure Ni and the surface is enriched in Cu in comparison with the bulk. Possibly, the Ni-sites form ensembles of a site varying with varying Cu content.

Several attempts have been made in the literature to characterize the electronic structure of metals by the so-called *d*%-character (*24*) of the metallic bond [for a review see Refs. (*25–27*)]. However, detailed considerations show (*25, 28*) that the calculation of *d*%-character does not have a very exact physical meaning and for alloys it is even more questionable. All empirical formulas used by Pauling for calculations are suggested for pure elements with homopolar bonds, but alloys are mostly formed from components with different electronegativities. As far as Ni–Cu alloys are concerned, there is no "filling of the *d*-orbitals" and the magnetic moment can hardly be used to estimate the contribution of different resonance structures, in the sense of Pauling (*24*). For all these reasons we find the parameter *d*%-character unsuitable for the discussion of the catalytic properties of alloys.

Upon reviewing the totality of results on the catalytic and adsorption activity of Ni–Cu alloys an interesting picture emerges. For a number of phenomena where Ni is distinctly different from Pt, the Ni–Cu alloys display a behavior more similar to Pt than to Ni. This trend is visible in the following observations. Addition of Cu to Ni leads to (i) an increase in isomerization/cracking ratio, (ii) an increased randomicity in cracking (M_f increases), (iii) an increase in 2-MP/3-MP ratio, (iv) a decrease in the heat of adsorption (*12*) of hydrogen (not strictly proven but likely, because of a decrease in the metal–hydrogen bond strength), (v) a decrease (*13*) in the adsorption heat of CO_2 (also likely because of a decrease in the metal–carbon bond strength), (vi) a decrease in the activity for dehydrogenation (Table 4).

For any discussion of the mechanistic causes of the typical selectivity changes observed upon adding Cu to Ni it seems justified, therefore, to use the basic assumption that the metal–adsorbate bond strength is weakened by alloying. For pure nickel a specific terminal fission of hexane or specific $C^{(3)}$–$C^{(4)}$ splitting of MCP are typical. It seems reasonable to assume that just in these places the molecules are preferentially chemisorbed and dehydrogenated by a dissociative chemisorption. In this way the C–C bond in question becomes accessible to further reactions. We now have to assume that molecules are in this way less strongly chemisorbed and dehydrogenated on Ni–Cu-rich alloys and Pt than on pure Ni. If the metal–carbon bond is very strong and the chemisorbed group is strongly dehydrogenated, a nonreactive rigid species arises and further reactions are mainly confined to the place of primary adsorption, for example, the terminal groups. Lowering of the heat of chemisorption and of the degree of dehydrogenation will consequently increase the activity and flexibility of the adsorbate, i.e., the place of attacking the molecule to the surface can be shifted to the center of the molecule. In this way the random splitting characteristic for Pt- and Ni–Cu-rich alloys can be understood. This model would also explain why more flexible and reactive groups, expected for the less strongly adsorbing surfaces, are more prone to form intermediates, for example cyclic ones (*29–31*), necessary for isomerization and dehydrocyclization. This is observed on Pt- and Ni–Cu-rich alloys.

The electronic effect (leading to the lowering of bond strengths) is also assisted by a geometric effect. The size of Ni ensembles is smaller in alloys than it is in pure Ni and this fact favors the reactions which need less sites (e.g., isomerization reactions) and makes the reactions which make use of more sites (e.g., cracking) less probable. However, a geometric effect alone cannot elucidate the great difference which exists in catalytic behavior of Ni and Pt and, therefore, the electronic effect cannot be ignored in the discussion of the behavior of alloys.

Although the model discussed above is far from conclusive, we have the impression that a wide range of phenomena observed on transition metals and their alloys might be consistently explained starting with the postulate that the flexibility and reactivity of chemisorbed molecules is inversely related to the heat of adsorption.

ACKNOWLEDGMENTS

The investigations were supported by the Netherlands Foundation for Chemical Research (S.O.N.) with financial aid from the Netherlands Organization for the Advancement of Pure Research (Z.W.O.). The authors are indebted to Mr. F. C. Kauffeld whose skill in constructing the apparatus was essential for this work.

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