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Selectivity of Ni–Cu and Pt–Au Alloys in Reactions of Butanol and Related Compounds

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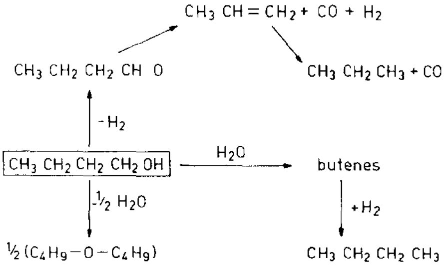
Reactions of butanal and butanol and hydrogenation of cyclopentanone have been studied in a flow apparatus in mixtures with hydrogen and at a total pressure of 1 atm. The catalysts used were Ni and Ni–Cu powders without carrier and Pt and Pt–Au on silica. Hydrogenation/dehydrogenation of the compounds is only marginally influenced by alloying, while the inter- and intramolecular dehydration (formation of olefins and ethers from alcohols) is suppressed strongly. The selectivity can be controlled by the availability of ensembles of active sites. A mechanism is suggested which can rationalize the influence of alloying, including some data from the literature.

INTRODUCTION

The main purpose of this paper is to gain information on factors responsible for the selectivity of metals and alloys in the reactions of aldehydes, ketones, and alcohols. A study with alloys can be very helpful in this respect as earlier work has shown [see, e.g., (*1–5*)]. For example, it is known that alloying of Ni with Cu has quite different effects on two different groups of reactions, namely, the reactions of the C–H and C–C bonds. Reactions of C–C bonds (hydrogenolysis, isomerization, dehydrocyclization) are always slower on Ni–Cu alloys than on Ni, usually by a factor of two or more orders of magnitude, while the reactions of C–H bonds (hydrogenation/dehydrogenation, hydrocarbon–deuterium exchange) are influenced by alloying to a much less extent. Whether the rate of the latter reactions increases or decreases with alloying depends on the extent to which the surfaces of Ni or Ni–Cu catalysts are modified by the reaction components (carbon deposition, firmly adsorbed species) (*6*).

Reactions of aldehydes, ketones, and alcohols form a very interesting object for selectivity studies. The network of possible reactions of butanal/butanol is shown in Scheme I. We can immediately see some analogy with the reactions studied previously: Hydrogenation of an aldehyde (or a ketone) reminds one of the addition of hydrogen to a $>C{=}C<$ bond, and upon formation of an ether bond (or upon de-



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hydration) one C–O bond must be broken, by analogy with the hydrogenolytic splitting of the C–C bonds in the reactions of hydrocarbons:

$$\text{C-}\boxed{\text{OHH}}\text{O-C}$$

An interesting difference is that while in the reactions of hydrocarbons the surface is modified by carbon or carbonaceous residues of reacting molecules, with aldehydes and alcohols the surface may be influenced by oxygen-containing species or even oxidized to some extent. Possible consequences of this or of alloying for the selectivity of metals were not known when this work was started.

EXPERIMENTAL

A conventional flow apparatus was used to determine the rates and to follow the product distributions of reactions occurring in the mixtures with hydrogen at the total pressure of 1 atm. A constant partial pressure of the organic reaction component was maintained by a thermostat (T_s) around the saturator filled with a particular liquid. The experiments were performed under the following conditions: cyclopentanone, saturated pressure (p_s) at $T_s = 273$ K; 1-butanol at $p_s = 20$ Torr ($T_s = 315.3$ K); butanal at $p_s = 30.4$ Torr ($T_s = 273$ K).

The catalysts were compared under the same conditions, partial pressures, and flow rates (0.5 ml/sec). The conditions (flow rate, weight of catalyst) were such that the rate measurements for the determination of the apparent activation energies were performed in a pseudo-differential reactor. Under the conditions specified, the activation energy can be then determined from the plots of log α vs T^{-1} where α is the overall conversion.

Cyclopentanone and cyclopentanol were p.a. products of Fluka and Merck, and 1-butanol and butanal were p.a. products of Baker Chem. Hydrogen was purified in the apparatus by Pd–asbestos and traps cooled at 195 K. Analysis was performed gas-chromatographically (Becker 2300 analytical gas chromatograph, flame ionization detection) under the following conditions for the particular mixtures:

Cyclopentanol/cyclopentanone: 15 wt% of OV-210 stat. phase (trifluoropropyl methyl silicone) on Chromosorb, 80 to 100 mesh; column, 6-m length, $\frac{3}{16}$-in. diameter; carrier gas, N_2; flow, 70 ml/min.

1-Butanol/butanal: 20% squalene—column with Chromosorb, 80–100 mesh; 8-m length 0.25-in. diameter carrier gas, N_2; flow, 45 ml/min.

Alkanes/alkenes: Poropak; 4-m length, $\frac{1}{8}$-in. diameter; carrier gas, N_2; flow, 30 ml/min.

Data evaluation. The measured gas chromatograph magnitudes (peak heights or areas) were converted by means of a proper calibration factor into the normalized "signals" q_i (for product i), and the content of a particular compound was calculated as $q_i(\%) = 100\ q_i/(\Sigma_i q_i)$. For the reactions of 1-butanol/butanal the following parameters used were: the overall conversion α and the selectivity S_E of the ether formation. These parameters were defined as follows:

$$\alpha = \frac{C_3 + C_4 + 2C_8}{C_3 + C_4 + 2C_8 + B}$$

$$S_E = \frac{2C_8}{C_3 + C_4 + 2C_8}$$

where C_3 is $q_i(\%)$ for propane and propene, C_4 for butane and butene, and C_8 for dibutyl ether. B stands for the $q(\%)$ of 1-butanol or butanal.

Catalysts. Ni–Cu powder catalysts without a carrier were prepared according to Best and Russell (*7*) (carbonates decomposed to oxides and subsequently reduced to metals and alloys). Characterization of these catalysts is available (*2*, *8*, *9*).

Pt without carrier was prepared according to Kulifay (*10*) (reduction of H_2PtCl_4 by hydrazine chloride). Pt–Au on SiO_2, Pt on SiO_2, and Au on SiO_2 catalysts (16 wt% metal on SiO_2) were prepared as in references (*11*) and (*12*). Characterization of these catalysts is also available (*12*).

RESULTS

It is always a source of various problems that when working with metal catalysts and organic molecules the catalysts are modified by the reaction mixture itself. In the first place, this modification leads to loss of activity, but sometimes it also changes the selectivity of the catalyst [see, e.g., references (*1*), (*4*), (*6*), and (*12*)]. The extent of this self-poisoning varies in part reversibly with increasing and decreasing temperature so that the interpretation of the temperature coefficient of the reaction [$d \log (\text{rate})/d(1/T)$] is difficult. If the activation energy calculated from it is to have any meaning, at least it must be certain that the rate varies reversibly with temperature. This has been checked in all cases, and the activation energy was evaluated only when this condition was fulfilled. No detailed kinetic study was performed; all catalysts were compared under the same experimental conditions (flow, pressures), and the activation energy was determined by plotting the logarithm of the total conversion (in the region of low conversion) vs the reciprocal temperature. From these Arrhenius plots the apparent activation energy was derived, and it is shown as a function of composition in Fig. 1. For comparison, also the results for acetone (*13*) and cyclopropane (*9*) hydrogenation are shown.

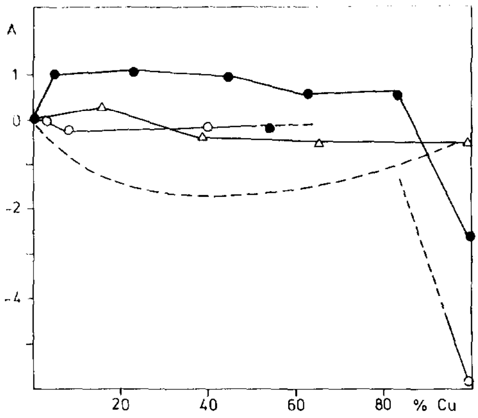

FIG. 2. Relative catalytic activity A of Ni–Cu alloys [log of the rate per unit surface area at given T; log (rate) for Ni is put equal to unity for all reactions] as a function of alloy composition. △, hydrogenation of cyclopentanone to cyclopentanol, 328 K; ○, hydrogenation of butanal to butanol at 312 K. For comparison the activity variations are also shown for cyclopropane (*9*) reactions (●, 363 K) and acetone hydrogenation (*13*) (343 K, dashed line without experimental points).

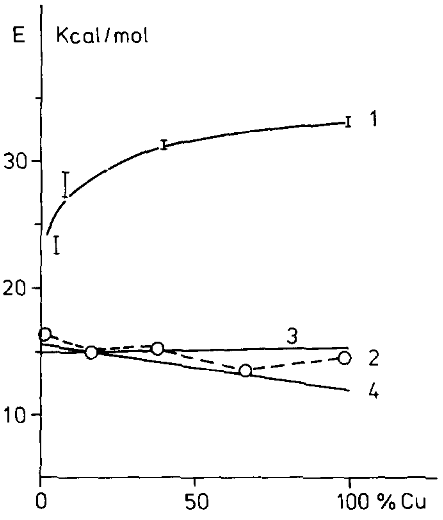

FIG. 1. Apparent activation energy E as a function of Ni–Cu alloy composition. (1) Hydrogenation of butanal to butanol, (2) hydrogenation of cyclopentanone to cyclopentanol. For comparison the variations of E are also shown (without experimental points) for acetone hydrogenation (3) (*13*) and cyclopropane conversion (4) (*9*) (conversion of cyclopropane comprises hydrogenation and hydrogenolysis).

The relative (areal) activity of various catalysts defined as log [rate(cat)/rate (Ni)] under standard conditions (constant flow; T = 328 K for cyclopentanone, 312 K for butanal, 363 K for cyclopropane, and 343 K for acetone; with rates related to

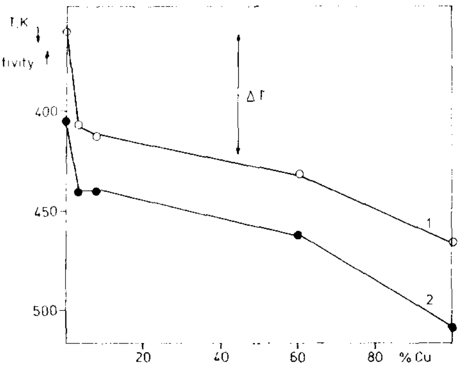

FIG. 3. Activity in the total conversion of butanol (see Scheme I) as a function of Ni–Cu alloy composition. As a measure of activity is taken the temperature T necessary to reach the same areal activity under standard experimental conditions. Curve 1 is for $\alpha = 5\%$, Curve 2 for $\alpha = 20\%$, where α is the overall conversion.

unit surface area), is shown in Fig. 2. For comparison, again the results are shown for acetone (*13*) and cyclopropane (*9*). The activation energy was obtained at temperatures around those used in the comparison of activities. It should be noted that in Figs. 1 and 2 it is the main reaction which is stated; the main reaction, however, is accompanied by side reactions of small extent at higher temperatures. At low temperatures hydrogenation prevails. With cyclopentanone and a hydrogen pressure of 1 atm, conversion into cyclopentanol is $\alpha > 90\%$ for all temperature $T < 350$ K and for butanal $\alpha > 95\%$ for $T < 450$ K. Low temperatures are also more favorable for ether formation; at 350 K, $\alpha > 99\%$ and at 500 K, $\alpha \simeq 95\%$. These equilibrium conversions were estimated by using the data in references (*14–16*).

When a certain temperature is passed, the changes in α are no longer reversible. This is the case with cyclopentanone and butanal if the reaction temperature is increased to such a value that dehydrogenation becomes observable. In this temperature region (i.e., from this temperature upward) the products are the same as when starting from the respective alcohols.

There is a rather broad region of temperature where the hydrogenation of, e.g., butanal to butanol overlaps with the reactions of butanol into other products. With 1-butanol as starting compound, measurable conversions ($\alpha > 1\%$) into di-*n*-butyl ether were observed at $T > 340$ K with pure Ni (2.5 g of catalyst) and Pt/SiO$_2$ (0.7 g of catalyst with 16 wt% Pt) and with 3% or 8% Cu in Ni catalysts (2 g of catalyst) at $T > 390$ K.

The activity toward ether formation was reasonably stable on all catalysts, but nevertheless the variations of the activity with temperature were less reversible than hydrogenations at low temperatures with butanal or cyclopentanone. Therefore, no reliable values could be obtained of the activation energy. To gain at least some information on the activity of various alloys, comparison was made of the temperature at which the same rate per unit of the alloy surface area was observed with different catalysts upon measurements performed under otherwise similar conditions. The result of this comparison is shown in Fig. 3.

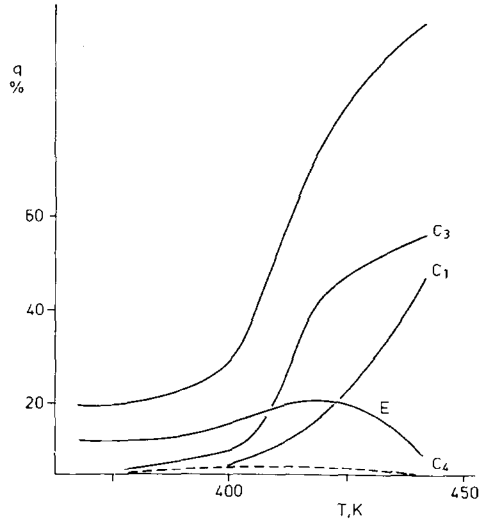

FIG. 4. Reactions of butanol on pure Ni. Product distribution as a function of temperature. C_1, methane; C_3, propane; C_4, butane; E, di-*n*-butyl ether; uppermost curve, total conversion of butanol.

TABLE 1

Product Distributions: Catalysts without Carrier

Catalyst	T(°K)	C_1[a]	C_3[a]	C_4[a]	*di-n*-butyl ether	1-Butanol	Butanol	α(%)
Butanol in the feed								
Ni	388	2.15	2.77	0.04	8.25	86.8		18[b]
	443	43.15	51.85	0.42	2.28	2.3		—[c]
3% Cu	421		4.45		2.9	92.3	0.3	10.3
8% Cu	421		5.2	0.02	0.9	93.75	0.12	7.1
60% Cu	459		6.0		0.35	93.2	0.45	7.1
Butanal in the feed								
Cu	420		0.67			4.03	95.3	4.7
	431		1.1			12.5	86.4	13.6
Ni	317		0.01		0.24	17.46	82.1	17.9
Pt	430		0.12	0.56	2.32	97.0		5.3

[a] C_1 = percentage of methane, C_3 = percentage of propane and propene together, C_4 = butane and butene, all as percentages; for α see text.

[b] Total conversion, except into methane.

[c] Not evaluated.

A comparison of Fig. 3 with Fig. 2 is also interesting. While the activity in hydrogenation of butanal or cyclopentanone varies only marginally with alloy composition, the activity in the overall conversion of butanol (main reaction on Ni is ether formation) is clearly slowed down by addition of Cu to Ni. With an assumed activation energy of the overall conversion $E = 20$ kcal/mol (a rough estimate from the temperature dependence of the butanol conversion gives $E = 20 \pm 5$ kcal/mol) an increase ΔT (as indicated in Fig. 3) of 60°C in temperature necessary to maintain the same activity corresponds to a decrease in the rate, due to alloying, by a factor of 50.

The product patterns of 1-butanol reactions vary with temperature. An example is shown in Fig. 4 for a pure Ni catalyst and butanol/H_2 as a feed. Some product distributions are collected in Table 1. The selectivity of various Ni–Cu catalysts is compared in Fig. 5 in two ways. First, at a constant temperature (T_E = 423 K) for all catalysts, this temperature being one at which all catalysts revealed a readily measurable activity, and second, by plotting a maximum selectivity achieved with a given catalyst, at different temperatures. At T_E = 423 K Ni catalyzes a number of side reactions to a too large extent: Propene

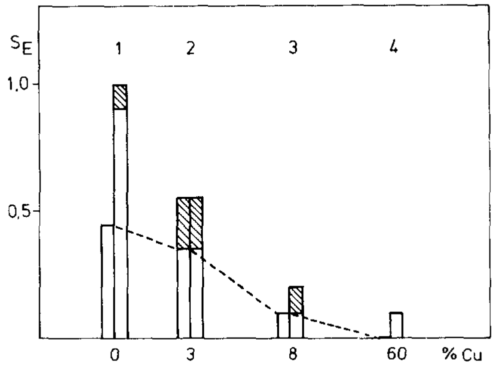

FIG. 5. Selectivity S_E for di-*n*-butyl ether formation in the butanol/hydrogen mixture. Dashed line connects values of S_E at 423°C. At this T, conversion on Ni is too high ($\alpha \approx \sim 60\%$), and the low S_E of Ni is a consequence of consecutive reactions (see Fig. 4). For comparison also the maximum selectivities achieved are shown; these values were obtained at the following temperatures: 1–363 K, 2–423 K, 3–413 K, 4–433 K. Cu content (as a percentage) in the catalyst is indicated (shadowed areas, limits of uncertainty).

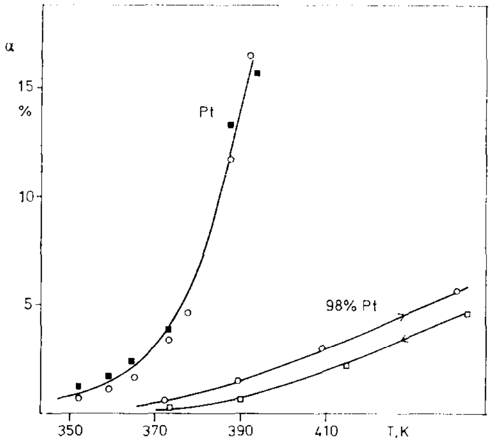

FIG. 6. Butanol reaction on Pt and on Pt–Au alloy, 0.7 g of catalyst, 16 wt% metal. Variation of the total conversion with temperature. ○, measurements in the sequence of increasing temperature; ■, decreasing temperatures. Composition of catalysts indicated.

and propane are formed by CO elimination from the dehydrogenation product butanal, methane is formed by hydrogenolysis of various products, etc. Therefore, the apparent selectivity S_E of Ni is very low at 423 K. On the other hand, no activity is measurable with alloys at low temperatures such as those at which Ni is already active in ether formation. Nevertheless, the data of Fig. 5, together with those of Fig. 3 and the information just added, clearly show that the activity for ether formation is strongly depressed by alloying of Ni with Cu.

The problem of surface modification by the reaction mixture has already been mentioned. This question is particularly important in relation to ether formation. For a long time the prevailing opinion in the literature was that ethers were formed from alcohols mainly by oxides, and metal catalysts were actually never suggested as efficient catalysts for ether formation [see, e.g., reference (*17*)]. Pines and co-workers (*18*), however, published a series of papers where it was shown that metals like Ni or Pd can be very efficient in ether formation from various alcohols (including higher, secondary, or cyclic), the authors speculating that this activity was only due to the presence of unreduced Ni or Pd ions in the surface of the metal catalysts.

Platinum has been found inactive (*18*) which was explained by the assumption that platinum oxide is much more easily reducible than palladium oxide. While it is certain that Pt oxides can be reduced more readily than NiO, a substantial difference between Pd and Pt is suspected. Therefore, it seemed appropriate to reinvestigate the Pt behavior and to extend the experiments to Pt–Au alloys. It has already been indicated by the data in Table 1 that pure Pt (without carrier) is an active catalyst with a rather high selectivity for ether formation. Further information was obtained by studying Pt, Au, and Pt–Au on SiO_2 catalysts (16 wt% metal). Figure 6 shows the total conversion α as a function of temperature for Pt/SiO_2 and (2% Au/98% Pt)/SiO_2 catalysts. The activation energy E_a estimated from these data was $E_a = 16 \pm 3$ kcal/mol for Pt and $E_a \sim 14$ kcal/mol for 2% Au/98% Pt catalysts, respectively. Other catalysts investigated, viz., 86% Au/14% Pt and 96% Au/4% Pt were active only at a higher temperature, at which a reliable estimate of E_a was impossible. Product distributions for several temperatures and various catalysts are shown in Table 2. As can be seen from Fig. 7, the selectivity in ether formation decreases only marginally with alloying (Au itself reveals a slow but measurable formation of ether), in contrast to Ni–Cu alloys. The activity in ether formation, however, decreases very much after addition of Au to Pt (see, e.g., Fig. 6).

Because the activity of Pt–Au dilute alloys is very low and does not vary reversibly with temperature, an exact comparison of Pt and its alloys (which requires a reliable extrapolation over a certain temperature gap) is not possible. The following, however, can be said.

Within the limits of error all C_4 and C_3 hydrocarbons produced with Pt and 98%Pt are saturated hydrocarbons; on the 14.5 and 4% Pt catalysts a mixture of olefins and alkanes [Z-(*cis*) and E-(*trans*) butenes are in a nonequilibrium ratio] is found, while with the Au catalysts pure propene is formed. This means that even the 4% Pt catalyst does still contain some Pt in the surface. The areal activity for ether formation by Pt is at least about 10^3 times higher than that by Au so that if only 1% of the surface atoms were Pt atoms, the activity of such catalysts should be at least 10-fold higher than that of Au catalysts. If the available information on the surface area of the catalysts used is considered [a rough estimate was made according to reference (*12*)], however, we come to the conclusion that the activity of the 4 and 14% Pt catalyst does not essentially differ from the activity of Au (within a factor of about 2). In other words, in ether formation a very diluted Pt no longer behaves as Pt.

DISCUSSION

Let us start the discussion by indicating the relationship of the data just presented to those in the literature. Our results fully confirm (*18*) that metals are active in ether formation also from higher alcohols, contrary to earlier statements (*17*). It is also confirmed that ether formation is very sensitive to the content of alkali ions, as pointed out by Pines and co-workers (*18*). The catalysts for which results are presented in this paper contained $2\cdot10^{-4}$–$2\cdot10^{-3}$ wt% Na as determined by atomic absorption spectrometry.[2] When the Na content was as high as 0.2 wt%, however, ether formation was completely eliminated, and the catalysts were only active in hydrogenation/dehydrogenation and CO-elimination reactions. This too could be one of the reasons why in earlier papers no ether formation was observed. Another reason could be the self poisoning.

TABLE 2

Product distributions: Reactions of 1-Butanol on SiO_2 Support and on Au/SiO_2, Pt/SiO_2, and Pt–Au/SiO_2 Catalysts

Catalyst	*T*(°K)	C_3 (%)	C_4 (%)	Butanal (%)	Dibutyl ether (%)
SiO_2	464		0.1	0.2	0.0
(2 g of catalyst)	501		4.0	0.2	0.0
Au	446		0.1	0.6	0.4
(2 g of catalyst)	504		5.3	5.4	2.4
14% Pt	443			0.6	0.6
(2 g of catalyst)	503	0.9	0.6	4.1	3.3
98% Pt	409		0.4	0.2	1.6
(0.7 g of catalyst)	506	14.7	12.9	5.0	18.7
Pt	393		3.9		8.7
(0.7 g of catalyst)	444	0.5	9.1	2.1	11.8

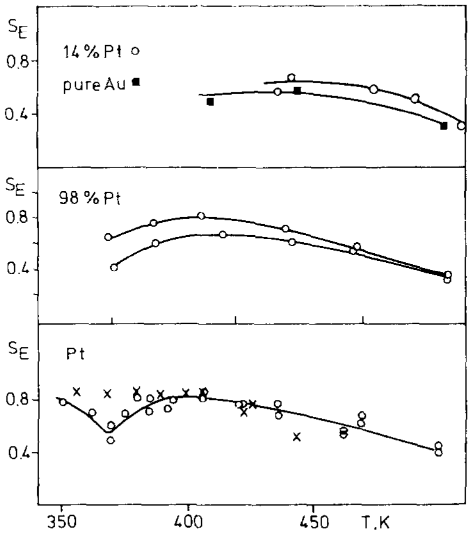

FIG. 7. Selectivity S_E for di-*n*-butyl ether formation on Pt, Au, and Pt–Au alloys, as a function of temperature. 98% Pt: upper curve for the sequence of increasing temperatures; lower curve for decreasing temperatures. Pt, pure: ○, measured in the sequence of increasing *T*; ×, decreasing *T*.

A decrease of activity, accompanied by a modification of the surface caused by the

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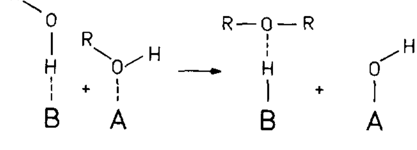
[2] For analysis the authors are very grateful to Mr. J. Stephan (Mineralogical Institute, Rijksuniversiteit Leiden).

reaction mixture itself, can significantly change the metal selectivity. Some earlier papers mentioned such an effect with regard to the reactions of alkanes (*1*, *4*, *12*), and in this paper similar effects with alcohols were also observed. More pronounced were the effects with Ni and Ni–Cu catalysts. If the catalysts were pretreated by the reaction mixture at a higher temperature their selectivity for ether formation at lower temperatures was then lower. Hemidy and Gault (*19*) described that such effects occurred with Pd films and with butanol/butanal even in a more dramatic way: Pd films were very active in ether formation at 273 K, but the activity was quickly suppressed to zero by self-poisoning; surfaces nearing the steady state were active only at temperatures higher than 273 K and revealed an activity only in hydrogenation/dehydrogenation reactions, no ether being formed at all. In the less recent literature [see reference (*17*)], reactions of alcohols were often followed at too high temperatures, and it was in some cases possible that the catalytic activity for ether formation was poisoned by such surface modification.

There is one point from the papers by Pines and co-workers (*18*) which is difficult to reconcile with the data now available. Following the ideas of Jain and Pillai (*20*), Pines *et al.* (*18*) suggested that for ether formation ensembles (doublets) of two active sites are required, one with basic and another with acid properties. The two alcohol molecules react in the following way (*18*):



According to the authors (*18*) doublets are created by an incomplete reduction of the metal (B = O^{2-}, A = Ni^{2+}), a factor which is therefore very essential for ether formation. This is the point which makes it difficult to accept the mechanism of Pines *et al.* (*18*). We could not confirm any relation between the reducibility of catalysts and their selectivity in ether formation. First, we found that Pt could also be active in ether formation and even Au showed a very low but measurable activity in ether production. Second, it is improbable that under the reaction conditions Pt, Au, or Ni (or Pd) would have comparable amounts of oxygen on their surfaces.

One aspect of the mechanism suggested by Pines and co-workers (*18*), however, seems to be a good starting point for the discussion of any other suggestion, namely, that *an ensemble of several sites is necessary* for the reaction to occur. An analysis (*18*) of the kinetic data revealed that the number of sites in one ensemble is about 4. Let us keep this in mind for the discussion to follow.

Conclusions made in this paper with regard to the mechanism rely very much on the interpretation of the alloying effects. Let us therefore briefly summarize what is known about Ni–Cu and Pt–Au alloys [for more details, see reference (*5*)]. Both alloys are formed endothermically; under the reaction conditions Ni–Cu exists as a one-phase and Pt–Au as a two-phase alloy (miscibility gap between about 2 and 83% Au). For both systems, in a broad range of bulk composition (10–80%), the surface composition *in vacuo* is almost constant, and surfaces are enriched in the Ib metal (transition metal content is estimated as 10 ± 8%). Ni forms clusters in Cu as has been proved experimentally (*5*), and for Pt the same behavior can be expected. It has also been shown experimentally that the electronic structure of Ni atoms is practically the same in pure Ni and Ni–Cu alloys. For Pt–Au, thermal programmed desorption data are available for hydrogen. From all these data one can conclude (*5*) that the character of individual Ni or Pt atoms does not change substantially, but by alloying with increasing content of the Ib metal Ni or Pt becomes better dispersed; fewer of the big ensembles of active sites (Pt, Ni) are available in dilute alloys than in pure Ni or Pt metals.

With both alloy systems studied, the activity for ether formation was substantially suppressed when Ni or Pt were alloyed with Cu or Au, respectively. Bearing in mind the information presented in the last paragraph, we suggest that this is because a fast ether formation requires ensembles of several transition metal atoms, and there are fewer of these ensembles in alloy surfaces. The conclusions from kinetics support this view (*18*).

The selectivity for ether formation S_E is suppressed to almost zero on Ni–Cu alloys but remains rather high on Pt–Au alloys. The reason for this is obvious when the data in Tables 1 and 2 are compared. In dehydrogenation and CO elimination Cu is a better catalyst than Au, which has a very low activity but a selectivity rather similar to that of Pt; Ni and Cu differ much more. This explains the different behavior of S_E with Ni–Cu and Pt–Au alloys (Figs. 5 and 7).

Figure 2 shows that the activity in the $>C{=}O + H_2$ addition is not suppressed to the same extent as ether formation, although the same groups $>C{-}O{-}H$ are involved as in alcohol reactions (the activity per surface Ni atom is even higher on alloys than on pure Ni). Thus the suppression of the ether formation by alloying is not due to this group and the presence of a heteroatom in the reacting molecule but rather is due to some particular reaction step which this molecule has to undergo. The splitting or formation of the O–H bond cannot be that step (see Fig. 2). Upon ether formation, however, one of the C–OH bonds must be split, and evidently this fission is suppressed by alloying. According to what has been said above, this means that the fission of a C–OH bond requires an ensemble of several transition metal atoms. On the other hand, addition of H_2 to $>C{=}C<$ bonds [even small amounts of Pt in Au convert the primarily formed olefines into alkanes; see also reference (*21*)], addition of H_2 to $>C{=}O$ bonds (see Fig. 2), and probably elimination of CO can all occur rapidly even on very diluted Ni and Pt alloys.

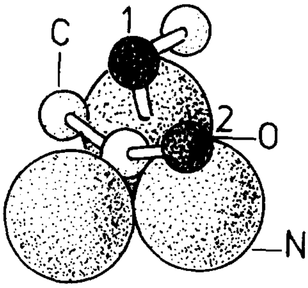


FIG. 8. Scheme of ether formation, –C–O– skeletons shown only. The C–O bond is switched over from oxygen atom 2 to oxygen atom 1.

A model which can help us to understand the data is shown in Fig. 8. The scheme is made for the (111) fcc plane; however, this is not essential, as similar schemes can be suggested for other planes as well. Two alcohol molecules which have both lost the H atoms of their OH group are placed on the surface as shown. The C atom of the first molecule is in the valley and has lost one or both of its H atoms. The second alcohol molecule is bound only via its O atom to the top of a Ni (Pt) atom; the O atom of the first molecule is also near to the top of the surface metal atom. Upon formation of an ether a bond is merely switched over from one oxygen atom to the other. What is the role of Cu in Ni or of a sodium ion poison, etc.? Copper makes the binding of C atoms in the valleys less favored as indeed many data have already indicated (*22–25*). A sodium ion or a sodium salt microcrystal is most probably blocking the valley position as well and thus eliminates ether formation. If the surface modification by the reaction mixture is mainly due to C atoms deposited on the surface, the suppression of ether formation by self-poisoning is another support for the mechanism suggested; viz., the carbon deposited on the surface is known to prefer the positions in the valleys (*22*). In compliance with the evidence from the kinetic (*18*), the mechanism suggested above makes use of several surface atoms [three on a (111) f.c.c. plane, or four on a (100) f.c.c. plane, etc.].

Let us now summarize. The influence of alloying on the $\rangle C{=}O + H_2$ addition is similar to the case of hydrogenation/dehydrogenation reactions of multiple carbon–carbon bonds and hydrocarbon/deuterium exchange of the C–H bonds (*5*). This group of reactions can also be catalyzed by mononuclear homogeneous complexes and they are known as "structure-insensitive" reactions (*26*). In contrast to this, the influence of alloying on ether formation reminds us of the case of reactions on the C–C bonds (mainly hydrogenolysis) and methanation of CO (*27*) in which reaction fission of the carbon–carbon or carbon–oxygen bond is involved. To our knowledge no mononuclear homogeneous complexes are known as catalysts for these reactions and some of these reactions were already found to be "structure sensitive" (*26*). We predict all this will also apply to ether formation.

The last question which has to be answered is that of where the difference originates. Why, for example, is the fission of a C–H or O–H bond structure-insensitive and able to occur also on single catalytic active atoms (ions) while the fission of C–C or C–O bonds requires an ensemble of several active sites? We suggest the reason is as follows. Before a C–C bond of a hydrocarbon or a C–O bond of an alcohol can be opened, it must first be made "accessible"; i.e., some of the hydrogen atoms must be split off from the C or O atoms, and these C (or O) atoms must be attached to one of the metal surface atoms. At the moment of the C–C or C–O bond dissociation the surface has to saturate another formal valency on each of the two atoms involved. Upon fission of a C≡O bond, it is quite evident that more formal valencies have to be saturated by the surface simultaneously when CO dissociates (*27*). In all three cases just mentioned the reactions can only occur when an ensemble of several active sites is available. The two phenomena are most probably related: Reactions upon which a multiple bond with the metal surface have to be formed with at least two particles simultaneously require ensembles of several active sites and these reactions are "structure sensitive."

Note added in proof: Professor Y. Schächter (Israel) communicated to us he also observed ether formation on Pt. The authors acknowledge with pleasure the benefit they had from the discussion with Prof. Y. Schächter during his visit to Leiden.

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