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Hydrogenolysis of C_2H_6, C_3H_8, and n-C_4H_{10} over Silica-Supported Nickel–Copper Catalysts

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Rates of C_2H_6, C_3H_8, and n-C_4H_{10} hydrogenolysis are measured on homogeneous, SiO_2-supported Ni–Cu alloys for which surface and bulk compositions were shown to be very similar. Kinetic parameters (apparent energy of activation, orders) are copper concentration independent, suggesting that the observed variations in the activities when adding Cu to Ni are due to changes in the number of active sites. Activities seem indeed to vary as the probability of finding ensembles of N adjacent nickel atoms at the surface of the alloy and are fully acounted for by purely geometric effects of dilution. Values of N vary between 12 and 20 according to the reaction. These values of N are in good agreement with results of magnetic studies of hydrocarbon chemisorption and with kinetic studies of hydrocarbon hydrogenolysis over Ni/SiO_2 catalysts.

INTRODUCTION

A crucial point in catalytic studies over bimetallic systems is the knowledge of the surface composition of the metallic phase. Experimental studies (*1*) and theoretical calculations (*2*) suggest indeed that the surface and bulk compositions of alloys may differ, making rather difficult the interpretation of alloying effects on the catalytic activities.

In the field of catalysis, the nickel–copper system is one of the most studied bimetallic catalysts. Ni–Cu catalysts were principally studied as films (*1, 3*), single crystals (*4, 5*), and unsupported powders (*6, 7*), and show in these cases surface enrichment in copper with a fixed surface composition which remains independent of the bulk composition over a wide range of composition. This enrichment which was observed by various techniques, such as work function (*1, 3*), AES (*4, 5*), chemisorption (*6, 8*), and catalysis measurements (*7, 9, 10*), gives rise to some difficulties in the quantitative interpretation of the effects of adding Cu to Ni from the catalytic viewpoint; both electronic and geometric effects were proposed (*7, 11–13*) to account for the observed data.

Supported Ni–Cu catalysts were less investigated and a previous study of Ni–Cu alloys supported on silica suggested to us that surface and bulk compositions of these supported alloys were very close (*14*). For these conditions it seemed possible to try to correlate quantitatively catalytic activities with the composition and hence with the electronic state of alloyed nickel or with geometric effects of dilution of active Ni atoms by inactive Cu atoms. Some preliminary results (*15*) obtained on ethane hydrogenolysis on $Ni–Cu/SiO_2$ catalysts have suggested to us the importance of such dilution effects. They have prompted us to develop new studies on hydrogenolysis of heavier hydrocarbons where, besides the activity, the selectivity in C–C bond rupture can be followed when alloying Cu with Ni. The results of these studies are reported here.

EXPERIMENTAL

The preparation and morphology of the catalysts are described elsewhere (*14*). We shall merely recall that reduction by hydrogen at relatively high temperatures (up to 1300 K) of the precursors ($Ni(OH)_2$ + $Cu(OH)_2/SiO_2$) gives homogeneous Ni–Cu alloys supported on silica (metal loading lies between 10 and 20%). The surface composition, as studied by H_2 adsorption

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and magnetic study of H_2 and O_2 chemisorption, appears to be very near the bulk composition. Magnetic granulometry indicates that the average metallic particle size is near 6 nm when reduction is performed at 950 K; this diameter is nearly copper content independent.

For the kinetic studies, catalysts were reduced in a quartz reactor by flowing hydrogen (4 liters/hr) at 950 K for 15 hr, then cooled under H_2 to the temperature of reaction. Kinetic experiments were carried out in a quasidifferential flow reactor at atmospheric pressure. The total flow was 120 ml/min. Helium was used as a diluent, the partial pressure of hydrocarbon, P_{HC}, was always kept low in comparison with the H_2 pressure, P_H ($P_{HC}/P_H < 0.16$), and total conversions were always kept smaller than a few percent; for these conditions no catalyst-aging phenomena were observed.

In ethane, propane, and butane hydrogenolysis, the formation of reaction products can be considered as resulting from the reactions:

$$C_2H_6 + H_2 \rightarrow 2\ CH_4, \quad (1)$$

$$C_3H_8 + H_2 \rightarrow CH_4 + C_2H_6, \quad (2)$$

$$C_3H_8 + 2\ H_2 \rightarrow 3\ CH_4, \quad (3)$$

$$C_4H_{10} + H_2 \rightarrow CH_4 + C_3H_8, \quad (4)$$

$$C_4H_{10} + H_2 \rightarrow 2\ C_2H_6, \quad (5)$$

$$C_4H_{10} + 2\ H_2 \rightarrow C_2H_6 + 2\ CH_4, \quad (6)$$

$$C_4H_{10} + 3\ H_2 \rightarrow 4\ CH_4. \quad (7)$$

Specific rates (per unit area of metallic surface) are referred to as r_n for reaction (n).

RESULTS

Ethane Hydrogenolysis

Kinetic parameters (apparent energy of activation, orders with respect to reactants) are reported in Table 1; orders were determined over the partial pressure range of 100 to 600 Torr for H_2 and 2 to 25 Torr for C_2H_6. Specific activities measured in standard conditions (P_H = 120 Torr; P_{HC} = 20 Torr; T = 503 K) are reported against copper content, x, in Fig. 1. Results on supported Ni–Cu alloys may be compared with those obtained on unsupported Ni–Cu powders by Sinfelt *et al.* (*7*) (after correction of temperature, partial pressures being very close in both studies). An important divergence can be observed between the two

TABLE 1

Kinetic Parameters for C_2H_6 Hydrogenolysis[a]

Sample x (copper content)	E_a (kcal/mole)	n_H	$n_{C_2H_6}$
0	39 ± 2	−2 ± 0.2	1 ± 0.1
0.03	40 ± 2	—	—
0.13	39 ± 2	−2.1 ± 0.2	1 ± 0.1
0.26	41 ± 2	—	—
0.35	40 ± 2	−1.9 ± 0.2	1 ± 0.1
0.48	40 ± 2	—	—

[a] E_a, apparent energy of activation (473–573 K; P_H = 120 Torr; P_{HC} = 20 Torr); n, orders with respect to reactants (493 K; partial pressure range: H_2, 100–600 Torr; C_2H_6, 2–25 Torr).

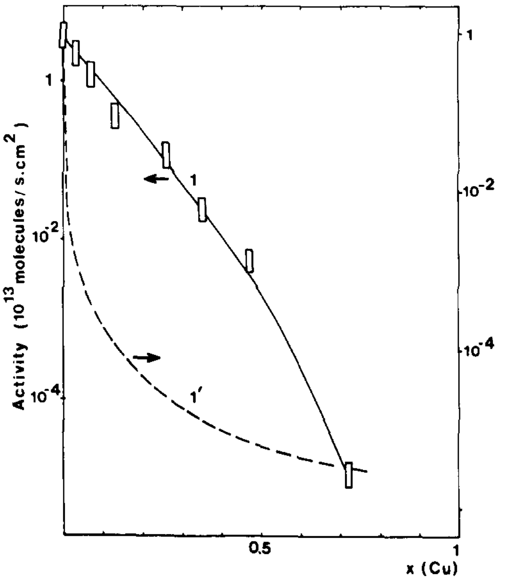


FIG. 1. Specific activities for C_2H_6 hydrogenolysis versus copper content x (503 K, P_H = 120 Torr, P_{HC} = 20 Torr). Curve 1, Ni–Cu/SiO$_2$; curve 1′, unsupported powders (*7*).

TABLE 2

Kinetic Parameters for C_3H_8 Hydrogenolysis[a]

Sample x (copper content)	E_a kcal/mole)		n_H		n_{HC}	
	(2)	(3)	(2)	(3)	(2)	(3)
0	49 ± 2	59 ± 2	−2 ± 0.2	−3 ± 0.2	1 ± 0.1	1 ± 0.1
0.13	47 ± 2	57 ± 2	−2.2 ± 0.2	−3.3 ± 0.2	1 ± 0.1	1 ± 0.1
0.21	48 ± 2	59 ± 2	−2 ± 0.2	−3 ± 0.2	1 ± 0.1	1 ± 0.1
0.35	50 ± 2	60 ± 2	−2 ± 0.2	−3 ± 0.2	1 ± 0.1	1 ± 0.1

[a] (2), Reaction (2): $C_3 \rightarrow C_2 + C_1$; (3), Reaction (3): $C_3 \rightarrow 3C_1$. E_a (483–573 K; P_H = 600 Torr; P_{HC} = 4 Torr); n (518 K; P_H, 100–600 Torr; P_{HC}, 2–25 Torr).

curves when adding a small percentage of copper to nickel.

Propane Hydrogenolysis

The kinetic parameters of Reactions (2) and (3) are listed in Table 2. Specific activities against the copper content, x, are shown in Fig. 2 (T = 540 K; P_{HC} = 4 Torr; P_H = 600 Torr). Variation of the selectivity $S = r_2/(r_2 + r_3)$ against x is reported in Fig. 3; S increases with x from 0.4 for pure nickel up to 0.8 for x near 0.4.

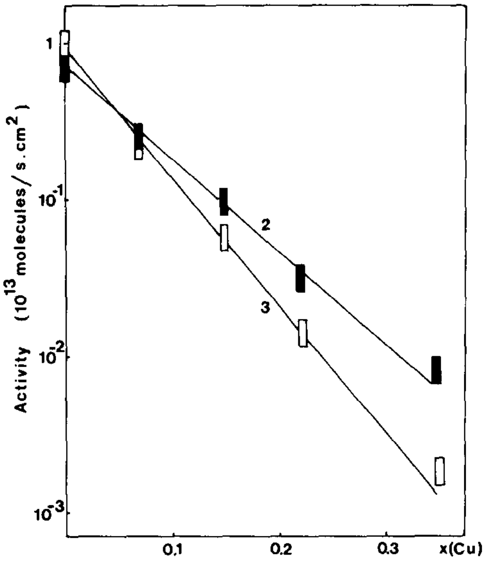


FIG. 2. Specific activities for C_3H_8 hydrogenolysis versus copper content x (540 K, P_H = 600 Torr, P_{HC} = 4 Torr). Curve 2, Reaction (2): $C_3 \rightarrow C_2 + C_1$; curve 3, Reaction (3): $C_3 \rightarrow 3C_1$.

Butane Hydrogenolysis

The rate of Reaction (4), r_4, is given directly by the rate of C_3H_8 formation. The difference between the overall rate of butane hydrogenolysis and r_4 gives ($r_5 + r_6 + r_7$). It is not possible to calculate separately r_5, r_6, and r_7 from the rates of formation of propane, ethane, and methane. It is possible, however, to estimate the extreme limits of r_7 from the rates of product formation assuming that either Reaction (5) or Reaction (6) does not occur. Kinetic parameters of Reaction (4) and Reactions [(5) + (6) + (7)] are reported in Table 3. Specific activities against x for Reactions (4), [(5) + (6) + (7)], and (7) are given in Fig. 4 (T = 503 K; P_{HC} = 5 Torr; P_H = 650 Torr).

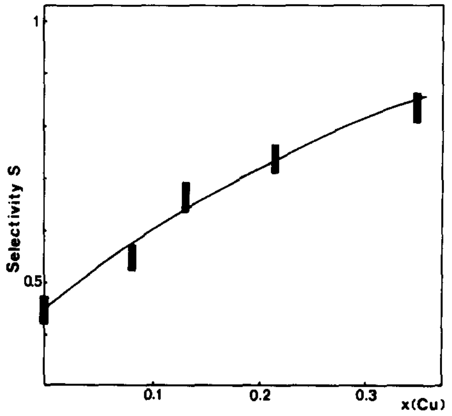


FIG. 3. Selectivity $S = r_2/(r_2 + r_3)$ in C_3H_8 hydrogenolysis versus copper content x (504 K, P_H = 600 Torr, P_{HC} = 4 Torr).

TABLE 3

Kinetic Parameters for C_4H_{10} Hydrogenolysis[a]

Sample x (copper content)	E_a (kcal/mole)		n_H		n_{HC}	
	(4)	(5) + (6) + (7)	(4)	(5) + (6) + (7)	(4)	(5) + (6) + (7)
0	44 ± 2	61 ± 2	−2 ± 0.2	−2.9 ± 0.2	1 ± 0.1	1 ± 0.1
0.12	47 ± 2	65 ± 2	−2.2 ± 0.2	−3.1 ± 0.2	1 ± 0.1	1 ± 0.1
0.21	47 ± 2	65 ± 2	−2 ± 0.2	−2.7 ± 0.2	1 ± 0.1	1 ± 0.1
0.35	45 ± 2	65 ± 2	−2 ± 0.2	−3.0 ± 0.2	1 ± 0.1	1 ± 0.1

[a] (4), Reaction (4): $C_4 \rightarrow C_3 + C_1$; (5) + (6) + (7), Reactions (5) + (6) + (7): $(C_4 \rightarrow 2C_2) + (C_4 \rightarrow C_2 + 2C_1) + (C_4 \rightarrow 4C_1)$. E_a (453–543 K; P_H = 650 Torr; P_{HC} = 5 Torr); n (503 K; P_H, 100–600 Torr; P_{HC}, 2–25 Torr).

DISCUSSION

Complete hydrogenolysis of hydrocarbons into methane can occur either directly, via

$$C_n \rightarrow n\ C_1,$$

i.e., Reactions (3) for C_3H_8 and (7) for C_4H_{10}, or through a second path via successive secondary reactions:

$$C_n \rightarrow C_{n-1} + C_1 \rightarrow \cdots \rightarrow C_2 + n - 2\ C_1 \rightarrow n\ C_1$$

with possible hydrogenolysis of the hydrocarbon residues:

$$C_{n-1} \rightarrow n - 1\ C_1$$
$$\vdots$$
$$C_2 \rightarrow 2\ C_1.$$

Comparison of the specific rates of hydrogenolysis of C_n and C_{n-1}, . . . , C_2 under the same conditions (T = 507 K; P_{HC} = 2 Torr; P_H = 600 Torr) enable us to decide whether secondary reactions are negligible.

$C_2 \rightarrow 2\ C_1$

$r \sim 0.002 \times 10^{12}$ molecules/s · cm^2,

$C_3 \rightarrow 3\ C_1$

$r \sim 0.03 \times 10^{12}$ molecules/s · cm^2,

$C_4 \rightarrow 4\ C_1$

$r \sim 0.1 \times 10^{12}$ molecules/s · cm^2.

That is, the rate of hydrogenolysis increases with the number of carbon atoms n (at least in the C_2–C_4 range). Moreover, during hydrogenolysis of hydrocarbon C_n, owing to the low conversions used in this study, concentration of species C_{n-1}, C_{n-2}, . . . are small in comparison with the concentration of C_n. This enables us to regard the second path as improbable (and to consider only Reactions (2) and (3) for propane hydrogenolysis and (4) to (7) for butane hydrogenolysis).

Before discussing the effects of alloying, the following question arises. It has been shown that after reduction by hydrogen,

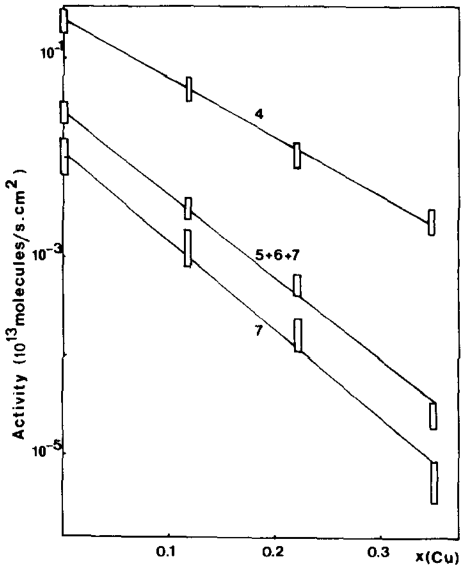


FIG. 4. Specific activities for C_4H_{10} hydrogenolysis versus copper content x (503 K, P_H = 650 Torr, P_{HC} = 5 Torr). Curve 4, Reaction (4): $C_4 \rightarrow C_3 + C_1$; curve 5 + 6 + 7: Reactions (5) + (6) + (7): $(C_4 \rightarrow 2C_2) + (C_4 \rightarrow C_2 + 2C_1) + (C_4 \rightarrow 4C_1)$; curve 7, Reaction (7): $C_4 \rightarrow 4C_1$.

the catalysts have a surface composition near the bulk one: is the surface composition changed during reaction? No direct studies were performed under these conditions, but if we assume that some changes of surface composition do occur during reaction (for instance, surface enrichment in nickel due to an "extractive" chemisorption of reactants or enrichment in copper due to a long exposure at a temperature near that used for equilibration of films), then these surface modifications will probably induce changes in the activity with time. In our case, however, no significant variations of activity nor aging phenomena were observed under our experimental conditions. Hence, the hypothesis of surface modification during reaction can probably be ruled out.

Another question is the possible influence of carbon deposition. These carbon deposits can indeed differ between pure nickel and its alloys and the observed variation in activity when alloying could be partly attributed to these changes in carbon deposition. Plunkett and Clarke (*16*) have observed in a study of ethane hydrogenolysis at 320–500°C such carbon deposition but the observed phenomena were rather limited and copper independent (at least in our composition range). In this study we observe neither an aging phenomenon which could be attributed to carbon poisoning nor a loss of activity when describing cycles of temperature or hydrocarbon partial pressure: as these carbon deposits are probably temperature and hydrocarbon pressure dependent, this reversibility indicates that if there is deposition its effect on the activity is probably limited.

In the case of ethane hydrogenolysis, the specific activities of supported and unsupported pure nickel catalysts are similar (Fig. 1). (As nickel surface areas are very different, viz., 100 and 1 m^2/g respectively, this could be considered as evidence for the structure insensitivity of the reaction. In fact, this is a coincidence, as already discussed elsewhere (*17*), and ethane hydrogenolysis is in fact a structure-sensitive reaction.) When adding a small percentage of copper, catalytic activities exhibited by supported and unsupported alloys became very different: for 10% copper, the specific activity of supported catalysts is about 5×10^3 higher than that of the unsupported powders. This difference is probably due to the strong enrichment in copper at the surface which appears on the unsupported alloys at low copper percent (*8*) and confirms the better homogeneity between surface and bulk compositions of our supported alloys. As a matter of fact the two curves join at about 80% copper, a composition above which the equilibrated system became homogeneous (same surface and bulk compositions).

For each reaction (C_2, C_3, C_4 hydrogenolysis), when the experimental conditions (temperature, partial pressures) are close, kinetic parameters (apparent energy of activation, orders with respect to reactants) are, within experimental error, independent of the copper content. This suggests that every reaction has the same mechanism on pure and alloyed nickel (at least in the range studied). Thus, the observed variations in the activities when adding copper to nickel are probably due to changes in the number of active sites. Now, what is the nature of the active sites?

Experimental decreases in activity with increasing copper content x are best represented by

$$A_x = A_{x=0}(1 - x)^N, \tag{8}$$

where A_x is the activity of the alloy of copper content x. Figure 5 shows results for Reactions (1), (3), and (7) (complete hydrogenolysis). Results for benzene hydrogenation (*18*) are also reported on the same graph. Values of the exponent N for each reaction are collected in Table 4. Assuming that

—surface and bulk compositions of the supported alloy are very close (*14*),

—distribution of Ni and Cu atoms at the

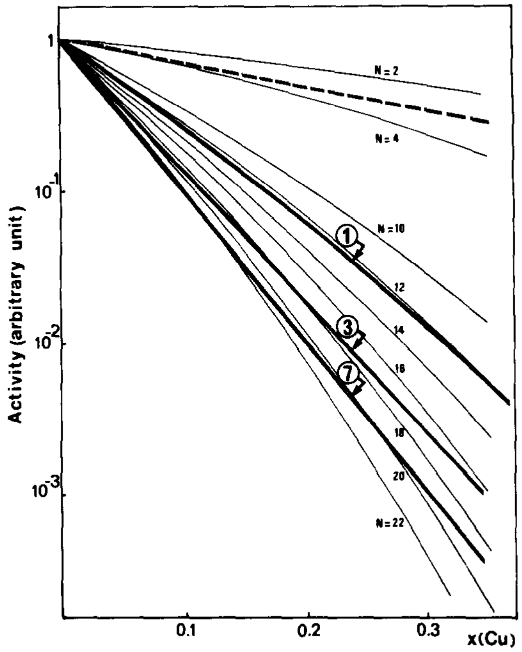


FIG. 5. Determination of parameters N for complete hydrogenolysis (Reactions (1), (3), and (7)). The dashed line corresponds to benzene hydrogenation (*18*).

surface is random (no short-range ordering of nickel and copper atoms) (*14*),

—no change in surface composition occurs during reaction, and there is no effect of carbon deposition (see discussion above),

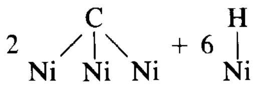
then the term $(1 - x)^N$ represents the probability of finding, in the alloy of copper content x, at least N neighboring Ni atoms at the surface of the metallic particle. Equation (8) suggests that the activity of each reaction decreases as the probability of finding ensembles of at least N adjacent nickel atoms. Those ensembles would be the active sites for the different reactions.

TABLE 4

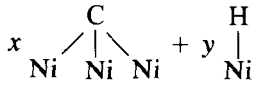
Values of Parameters N, n (Theoretical and Experimental), and X for C_2H_6, C_3H_8, and C_4H_{10} Hydrogenolysis

Reaction	N	n		X
		Theory	Expt	
(1) $C_2 \rightarrow 2C_1$	12 ± 2	12	13	15 ± 2
(2) $C_3 \rightarrow C_2 + C_1$	12 ± 2	—	—	17 ± 2
(3) $C_3 \rightarrow 3C_1$	17 ± 2	17	18	24 ± 2
(4) $C_4 \rightarrow C_3 + C_1$	12 + 2	—	—	—
(5) $C_4 \rightarrow 2C_2$	18 ± 2	—	—	—
(6) $C_4 \rightarrow C_2 + 2C_1$				
(7) $C_4 \rightarrow 4C_1$				
(7) $C_4 \rightarrow 4C_1$	20 ± 4	22	19	—

This hypothesis is strengthened on the one hand by the magnetic study of hydrocarbon chemisorption (*19, 20*) and on the other by kinetic studies of C_2H_6 and C_3H_8 hydrogenolysis on pure nickel (*21, 22*): the magnetic study of C_2H_6 chemisorption and reactivity of adsorbed species toward H_2 enabled us to propose as a possible intermediary in ethane hydrogenolysis the following adsorbed species:



corresponding to a "magnetic bond number" (*23*), $n = 12$: this means that 12 nickel atoms of the surface are bonded to this completely dehydrogenated and cracked adsorbed molecule. If we generalize this species as the intermediate species in complete hydrogenolysis of hydrocarbons, for a hydrocarbon C_xH_y we will have:



The magnetic study of propane and butane chemisorption gives for these cracked species magnetic bond numbers n of 17 and 19, respectively (*19*) (theoretical values 17 and 22).

Kinetic studies of hydrogenolysis of C_2H_6 and C_3H_8 over Ni/SiO_2 catalysts (*21, 22*), in which hydrogen adsorbed on Ni is considered as playing the same diluting role as copper in Ni–Cu catalysts, have shown that reactions take place on ensembles of X adjacent nickel atoms free from adsorbed hydrogen.

Values of n and X are reported in Table 4 and may be compared with the corresponding values of N. The rather good agreement between these parameters strengthens our assumptions, i.e., the diluting effect of copper creates ensembles of adjacent nickel atoms, the active sites, and the probability of finding these ensembles governs the activity.

Table 4 shows that for Reactions (1), (2), and (4) where a single rupture of C–C bond occurs, values of N are very close, suggesting similar ensembles for these three reactions. According to this hypothesis, in the case of Reactions (2) and (4), residual C_2 or C_3 species are adsorbed on the same number of atoms as the C_1 residue of Reaction (1) and consequently are probably partially dehydrogenated and bonded to the surface by only one carbon.

Another point is the change in selectivity with increasing copper content in the alloy. As indicated in Fig. 3, the reaction which needs the smallest ensemble N is favored in comparison with the others. Thus, when increasing the copper content the demethylation reactions of propane and butane are favored.

Comparison of N for hydrogenolysis and hydrogenation of benzene shows that the latter reaction is less influenced by alloying. This is in qualitative agreement with the results of Sinfelt *et al.* (*7*) on ethane hydrogenolysis and cyclohexane dehydrogenation, the reverse reaction of benzene hydrogenation, on unsupported powders: Sinfelt *et al.* observed a strong decrease in C_2H_6 hydrogenolysis when alloying, and a small increase in cyclohexane dehydrogenation for a few percent of copper in the alloy. This increase, which seems at first sight to be in contradiction with the small decrease in the case of benzene hydrogenation, can be attributed to the strong inhibition, when adding a few percent of copper, of the hydrogenolyzing character of these segregated Ni–Cu powders, hydrogenolysis of C_6H_{12} being probably a side reaction of C_6H_{12} dehydrogenation at the temperature of the experiment (590 K).

CONCLUSION

The same, or very nearly the same, surface and bulk compositions of silica-supported Ni–Cu alloys enable us to observe a quantitative correlation between the changes in activity or selectivity in hydrogenolysis and the effects of dilution of active nickel atoms in inert copper, giving rise to Ni atom ensembles constituting the active site of the reaction. Thus, purely geometric effects of dilution fully account for the observed catalytic variations on these systems. This interpretation appears to be in good agreement with the electronic structure of Ni–Cu alloy (*24*), where, in contrast with the previous idea of the rigid *d*-band model, each metallic element of the alloy keeps a separate and not very altered *d*-band and retains probably most of the electronic properties of the pure metal.

Assuming that our reasoning on the dilution effects of an active metal by an inactive one is well founded, studies of catalytic activities versus surface composition of such alloys will lead to interesting information on the number of metallic atoms involved in the active site and, hence, on the nature of the active species in catalytic reactions.

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