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Study of Well-Defined Silica-Supported Nickel–Copper Catalysts

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Ni–Cu/silica catalysts were prepared by reduction of the cosupported hydroxides with H_2 at relatively high temperatures (900 to 1350°K). Magnetic study (saturation magnetization at 4°K, Curie points) showed that a homogeneous alloy was formed; the metallic particle size depended on the temperature of reduction and varied between 6 and 13 nm. The surface composition studied by volumetric hydrogen titration and the magnetic effects of hydrogen and oxygen chemisorption were found to be very similar to the bulk concentration, in contrast with the surface enrichment in copper generally observed on Ni–Cu catalysts.

INTRODUCTION

Catalytic properties of alloys have been widely studied for theoretical reasons, particularly to correlate catalytic activities with the electronic structures of metals (*1*); alloying provides a way of progressively changing the electronic properties of a metal. Another field of interest of alloys is more practical, in that metal-based alloy catalysts might be used as a substitute for noble metals such as Pt or Pd. Among the numerous studies dealing with correlations between catalytic activities and electronic structures of metals, alloys of nickel with copper have received particular attention, probably for two leading reasons: (i) this system forms a continuous series of solid solutions at elevated temperatures; (ii) copper is much less active than nickel in many catalytic reactions, and consequently it seems possible to try to correlate the variation of activity of the alloy with the changes of the electronic structure of the nickel. Such correlations, however, were made difficult by the segregation of the more volatile constituent (copper) to the surface of the alloy. Such surface enrichment, which can be explained by theoretical calculation (*2*, *3*), was observed in the case of Ni–Cu alloys on unsupported powders (*4*, *5*), films (*6*, *7*), and single crystals (*8*, *9*) by means of chemisorption (*4*, *10*), catalytic activity (*5*, *11*, *12*), work function (*6*, *7*), and AES (*8*, *9*) investigations. Nevertheless, in the case of highly dispersed alloy particles, some authors (*13*, *14*) have considered the possibility of formation of single phase microcrystals with unsegregated surfaces; the problem was also discussed by Burton *et al.* (*15*).

Most of the experimental studies in the field of chemisorption and catalysis on Ni–Cu alloys were performed on poorly divided materials (unsupported powders, single crystals) or on films; another way to obtain rather well-dispersed catalysts is to prepare supported alloys (*16–18*). In this paper we report some results of the study of formation and chemisorption properties of silica-supported Ni–Cu catalysts.

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TABLE 1

Composition, Reduction Temperature, Particle Sizes, and Particle Size Heterogeneity of NiCu/SiO$_2$ Samples

Sample	Weight, % $\frac{\text{Ni + Cu}}{\text{Ni + Cu + SiO}_2}$	Weight, % $\frac{\text{Cu}}{\text{Ni + Cu}}$	Reduction temperature T_R (°K)	D_1 (nm)	D_2 (nm)	D_S (nm)	Δ
1	11.6	0	920	6.2	4.8	5.5	0.25
2	16.0	0	920	7.0	5.5	6.3	0.24
3	16.0	0	1270	15.9	11.1	13.5	0.36
4	23.0	0	920	7.6	5.8	6.7	0.27
5	23.0	0	1270	18.8	11.3	15.0	0.50
6	15.5	1.5	940	6.4	5.2	5.8	0.21
7	15.9	5.9	940	6.4	5.0	5.7	0.25
8	20.1	8.0	940	6.7	5.6	6.2	0.18
9	19.2	14.6	940	6.7	5.4	6.1	0.21
10	14.3	26.0	940	6.1	5.0	5.6	0.20
11	24.0	36.6	940	7.1	6.6	6.9	0.07
12	13.0	35.0	940	6.4	5.2	5.8	0.21
13	13.0	48.2	1270	17.0	9.5	13.3	0.56
14	12.6	57.8	1270	18.0	9.0	13.5	0.66
15	10.5	71.7	1270	—	—	—	—
16	10.8	93.0	1270	—	—	—	—
17	10.8	100.0	1270	—	—	—	—

EXPERIMENTAL

Catalyst preparation. Samples were prepared by adding SiO$_2$ (Aerosil 200 m^2 g^{-1}) to solutions of hexammine nickel and copper nitrates. After filtration, complexes adsorbed on the surface were destroyed by evaporating ammonia, and Ni(OH)$_2$ and Cu(OH)$_2$ were precipitated. The atomic ratio Cu/(Ni + Cu) in the solution was varied to cover the 0 to 100% range of copper; in some cases various Ni + Cu concentrations were used in the solution, with neighboring Cu/(Ni + Cu) ratio to obtain catalysts with different metallic amount (Table 1).

The compounds thus obtained were reduced at high temperature (up to 1350°K) in a gas flow (4 liters/hr) of very pure H$_2$ (99.999%) for about 15 hr. The reduced sample was then rapidly cooled to room temperature and transferred into a measuring cell, without exposure to air. After reduction the catalyst was outgassed at 673°K for 2 hr under about 10^{-6} Torr.

Experimental techniques. Adsorption experiments were performed in a conventional volumetric apparatus. Volumes of adsorbed gas were calculated from the change in gas pressure measured with a Texas Instruments pressure gage. Desorption experiments were performed in the following way: Desorbed gas was forced back into the rough vacuum tank of the pumping system where the pressure increase was measured.

The amounts of metallic surface presented were deduced from chemisorption experiments with H$_2$. Assuming Freundlich isotherms, the adsorbed volume at saturation V_s was obtained from the intersection of log p vs log v graphs at different temperatures (195 to 423°K). After deducing the volume adsorbed on copper (which is about 1/10 of the quantity adsorbed on a nickel sample of same metallic area), and assuming that H$_2$ chemisorption on copper is not influenced by the presence of nickel, the volume of hydrogen V_{sNi}

adsorbed on nickel per gram of the metallic phase is obtained. One can then calculate a metallic surface of nickel per gram of the metallic phase $S_{\mathrm{H_2Ni}}$ (in m^2/g), assuming dissociative chemisorption of H_2 on nickel (*17*) and exposure of (100) and (111) planes at the surface of the metallic particle by:

$$S_{\mathrm{H_2Ni}}\ (\mathrm{m^2/g}) = 3.11 V_{\mathrm{sNi}}\ (\mathrm{ml\ NTP/g\ Ni}).$$

The values thus obtained were compared to those calculated from H_2 adsorption in more conventional conditions (45 Torr pressure of hydrogen at 298°K).

Carbon monoxide chemisorption was also used to determine the metallic surface area. CO was adsorbed at 298°K and 5 Torr (the pressure of CO was limited to prevent $Ni(CO)_4$ formation). A metallic surface of Ni per gram of metallic phase, S_{CONi}, was then calculated taking into account the quantity of CO adsorbed on copper (determined from CO adsorption on a Cu/SiO$_2$ sample) and the change of stoichiometry of CO adsorption on niclel when alloying with copper, as determined by magnetic methods and infrared spectroscopy (*19*):

$$S_{\mathrm{CONi}}\ (\mathrm{m^2/g}) = 1.55 nV\ (\mathrm{ml\ NTP/g\ Ni})$$

n is the number of Ni atoms bonded to one molecule of adsorbed CO and decreases from 1.8 for pure nickel to 1.2 for sample 12 (*19*) and V is the volume of CO adsorbed on nickel for 1 g of the metallic phase.

Magnetic measurements were performed, using the Weiss extraction method, mainly in an electromagnet (magnetic field H up to 21 kOe; the temperature of the sample could vary between 800 and 290°K or be fixed at 77 or 4.2°K). Some experiments were performed in a superconductive coil (70 kOe) at 4.2°K or in a liquid nitrogen-cooled coil (8 kOe) at a temperature between 4.2 and 350°K.

Magnetic measurements give information both on the morphology of reduced catalysts (degree of reduction, metal particle size) and on the nature of adsorbed species (*20*). Saturation magnetization (M_s) was calculated by plotting the magnetization M against $1/H$ and extrapolating to $1/H = 0$. Curie points were measured with a technique similar to that used for bulk compounds (*21*): Graphs of M against H at various temperatures are used to draw curves H against T at constant magnetization which are then linearly extrapolated to zero field; this constant magnetization is equal to the spontaneous magnetization M_{sp} at the temperature derived from this extrapolation. To estimate the Curie point, M_{sp}^2 is plotted against T and the relation is extrapolated to $M_{\mathrm{sp}}^2 = 0$.

Superparamagnetic behavior was checked by plotting $M(T)/M_s(T)$ against $\log H/T$. Average diameters can then be calculated using approximate forms at low and high fields of the Langevin function:

$$D_1 = \left(\frac{\sigma}{H}\frac{18kT}{\Pi\rho\sigma_s^2}\right)^{\frac{1}{3}} \quad \text{(low fields)}$$

$$D_2 = \left(\frac{6kT\rho\Pi H}{\sigma_s - \sigma}\right)^{\frac{1}{3}} \quad \text{(high fields)}$$

where σ is the specific magnetization of the alloy at the absolute temperature T (in our case 77°K), σ_s is the specific magnetization at saturation, k is the Boltzmann constant, and ρ is the specific weight of the alloy. Surface diameters D_S and particle size heterogeneity Δ were calculated by (*22*):

$$D_S = \frac{D_1 + D_2}{2}; \quad \Delta = \frac{D_1 - D_2}{D_S}.$$

Variations of saturation magnetization ΔM_s occurring during gas adsorption were expressed in Bohr magnetons (BM) per adsorbed molecule and may be related to macroscopic parameters by the relation:

$$\alpha = 4\frac{\Delta M_s}{q}$$

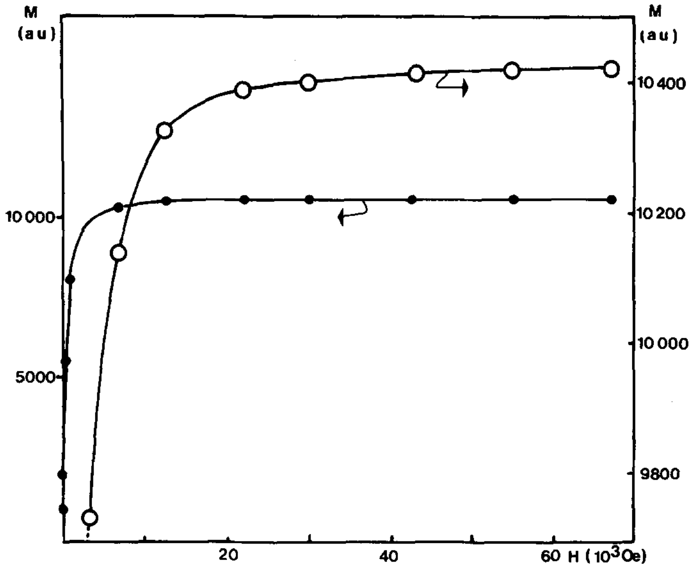


FIG. 1. Magnetization M (arbitrary units) of sample 8 at 4°K against applied magnetic field H.

where ΔM_s is in emu cgs and q, the quantity of adsorbed gas, is expressed in ml NTP. Magnetic bond numbers, n, were calculated assuming that nickel atoms in interaction with adsorbed molecules cease to participate in the collective ferromagnetism (*17*, *20*). The number of metallic atoms which are demagnetized by the adsorption of one molecule is the ratio of α to the magnetic moment of the nickel atom in the alloy μ_{Ni} (in BM) at the temperature of the magnetic experiment:

$$n = \frac{\alpha}{\mu_{Ni}}.$$

RESULTS

Figure 1 shows the magnetization of sample 10 as a function of applied field at 4°K, after reduction at 940°K. Saturation magnetization determined from these $M(H)$ curves was calculated for each

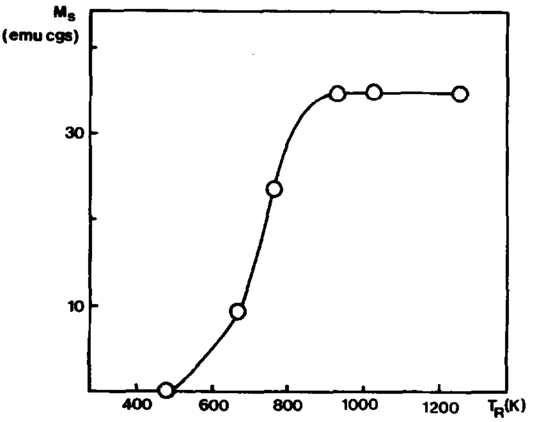


FIG. 2. Saturation magnetization M_s (emu cgs per gram of nickel) against temperature of reduction of sample 12.

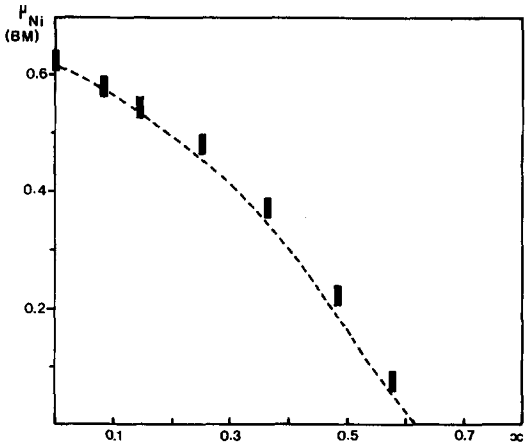
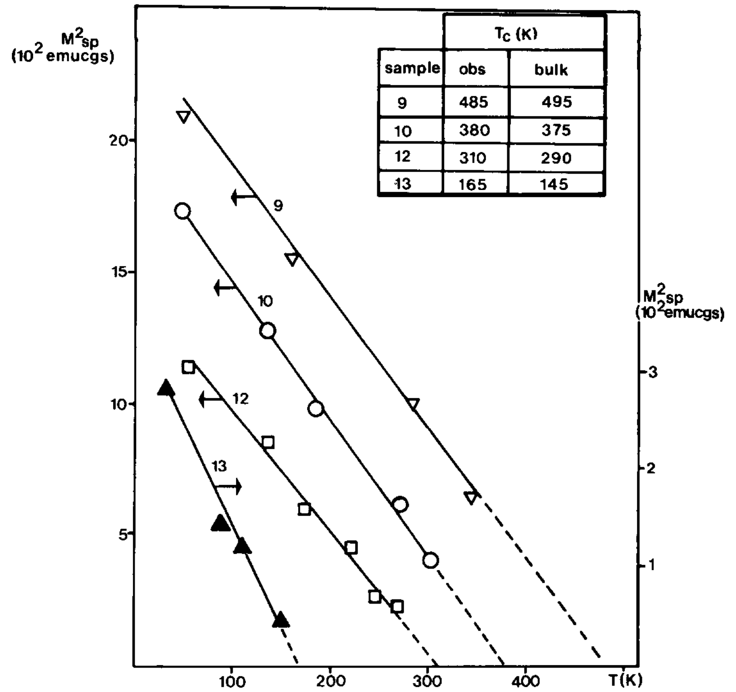


FIG. 3. Magnetic atomic moment of nickel (in Bohr magnetons) as a function of copper content x. The dashed line corresponds to bulk alloys (*23*).



	T_c (K)	
sample	obs	bulk
9	485	495
10	380	375
12	310	290
13	165	145

FIG. 4. Graphs of M_{sp}^2 (M_{sp}: spontaneous magnetization in emu cgs per gram of nickel) against temperature T. Extrapolations at $M_{sp}^2 = 0$ give Curie points T_c.

sample after reduction at increasing temperatures up to constant values (Fig. 2). These values (expressed in Bohr magnetons per nickel atom in the alloy) are plotted against copper content in Fig. 3 and may be compared with values of bulk alloys (*23*). For samples with less than 40% of Cu in the metallic phase, a reduction temperature (T_R) of 940°K was used; samples with higher copper content were reduced at 1270°K (constant value of M_s was not obtained at lower temperature); for nonferromagnetic catalyst (samples 15, 16, 17), the same value of T_R (1270°K) was used. Figure 4 shows typical graphs of M_{sp}^2 against temperature for different samples, and extrapolations giving Curie points. Some X-ray experiments were performed: After reduction at 940°K, a large band is observed; after reduction at 1270°K, a rather narrow band appears, showing that neither pure nickel nor pure copper is present in the alloys.

Ratios $M(T)/M_s(T)$ for sample 12 are plotted against log H/T in Fig. 5. Superposition of curves obtained at different temperatures shows superparamagnetic behavior; this was observed for all ferromagnetic samples. Calculated average magnetic diameters are indicated in Table 1 and seem to be, for given reduction temperature and metallic content, independent of the alloy composition. Average diameters, roughly estimated from X-ray line broadening, are about 7 nm for catalysts reduced at 940°K and about 15 nm when the reduction is performed at 1270°K.

Figure 6 shows results of H_2 adsorption on sample 14, with log v against log p graphs and subsequent extrapolation giving the total coverage. In Fig. 7 are represented the ratios of the surface of nickel of 1 g of the metallic phase to the specific surface of the metallic phase (S_{Ni}/S_A), the specific surface of the metallic phase being determined from the magnetic diameters. Different ratios are plotted for each sample

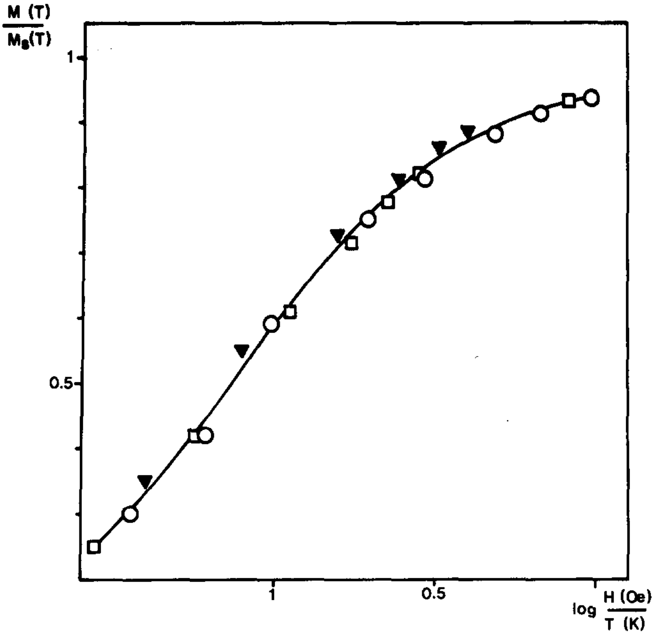


FIG. 5. Ratios $M(T)/M_s(T)$ = (magnetization at temperature T/saturation magnetization at T) versus log H/T for sample 12. ○, 77°K; ▼, 200°K; □, 285°K.

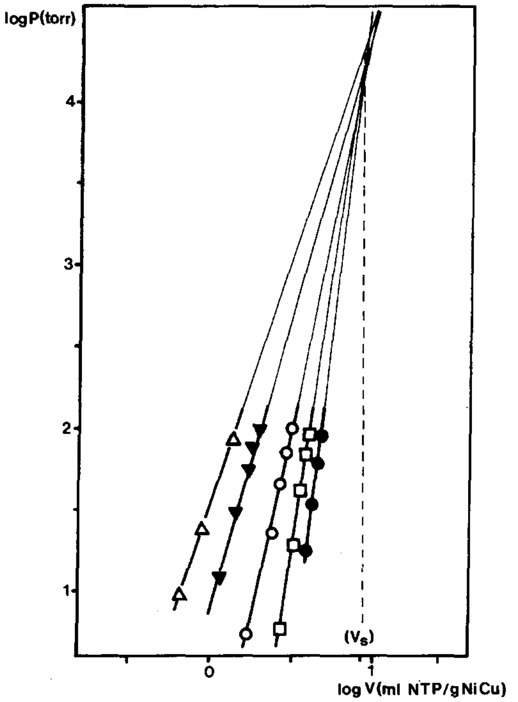


FIG. 6. Graphs of log p versus log v for H_2 adsorption on sample 14, and extrapolation giving the total coverage. Adsorption at: ●, 195°K; □, 296°K; ○, 357°K; ▼, 426°K; △, 627°K.

according to the method of titration of surface nickel which is used, namely, chemisorption at complete coverage,

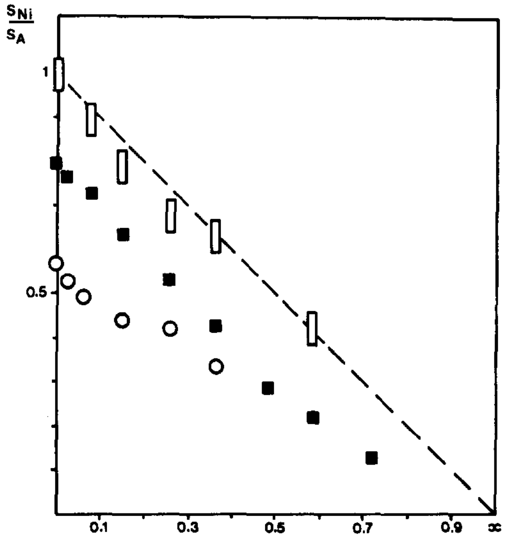


FIG. 7. Ratios S_{Ni}/S_A = surface of nickel per gram of the metallic phase/specific surface of the metallic phase against the copper content x. S_{Ni} from: □, H_2 adsorption at saturation; ■, H_2 adsorption at 45 Torr; ○, CO adsorption.

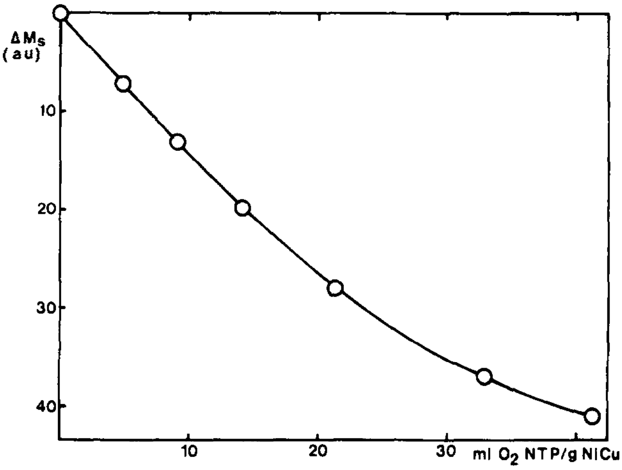


FIG. 8. Variation of saturation magnetization ΔM_s of sample 9 (arbitrary units) against the adsorbed volume of O_2.

volume of hydrogen chemisorbed at 45 Torr, chemisorption of CO at 5 Torr.

Figure 8 shows the variation of saturation magnetization of sample 9, measured at 4°K, against the quantity of oxygen adsorbed at 195°K. During this experiment, only small quantities of O_2 were successively introduced to avoid overheating of the sample. At low coverage, a constant value of the slope, α, is observed; these values of α observed at low coverages, are shown against the copper content of the metallic phase in Fig. 9.

DISCUSSION

Formation of the Catalyst

If the temperature of reduction is high enough, no variation of saturation magnetization is observed when increasing this temperature (Fig. 2); this result suggests that the metallic phase is completely reduced and, in view of the strong dependence of magnetization on the composition of Ni–Cu compounds, that no further development of the composition of the metallic phase takes place. Specific saturation magnetization of completely reduced samples (Fig. 3) is in rather good agreement with corresponding values of bulk alloys, showing that supported alloys are obtained. Curie points of these supported alloys (Fig. 4) very close to those of bulk compounds (*24*) also indicate the alloy formation. Moreover, the rather good linear extrapolations obtained from M_{sp}^2 versus T graphs indicate a good homogeneity of these alloys; therefore, (i) the average composition of each metallic particle is close to the overall composition, (ii) in the metallic particle there is no phase segregation, which should produce two alloys containing about 80 and 2% of Cu (*6*), the nonferromagnetic copper-rich phase surrounding the nickel-rich one (furthermore, should this "cherry model" occur, the specific magnetization should be higher than the observed one).

X-Ray diffraction results also suggest that the alloy is homogeneous: The observed line broadening seems due to the particle size (diameters calculated by magnetic methods are not far from the X-ray ones). The position of the line is likewise near the expected one.

All these experiments suggest that a supported and homogeneous alloy is formed when the temperature of reduction is high enough. Nevertheless, the rather poor dispersion of these alloys (about 20% for catalysts reduced at 940°K) do not allow definitive conclusion on the surface composition of the metallic particles. This problem is examined in the next section.

Study of the Surface Composition

Following a suggestion of Sachtler (*25*), we try to titrate the surface nickel of the metallic particle by chemisorption of hydrogen and carbon monoxide. In the case of a surface composition identical to the bulk one, the ratio $S_{\mathrm{Ni}}/S_{\mathrm{A}}$ should decrease linearly from 1 (pure nickel) to 0 (pure copper) as represented by the dashed line of Fig. 7. Experimental points calculated from chemisorbed volumes of hydrogen at 45 Torr pressure at room temperature are clearly below the theoretical curve but fall rather well in line with the experimental point of pure nickel and the point of 100% of copper, suggesting more a lack of saturation in the adsorbed volume of hydrogen than a change in the surface composition with respect to the bulk one. As a matter of fact, when the ratio $S_{\mathrm{Ni}}/S_{\mathrm{A}}$ is calculated using a saturation volume obtained by extrapolation from log v versus log p graphs, the points are in rather good agreement with the theoretical curve. In the case of carbon monoxide the ratio $S_{\mathrm{Ni}}/S_{\mathrm{A}}$ is close to 0.6 for pure nickel. This value is smaller than 1, probably due to the moderate pressure of measurement or to coverage limited by the nature of adsorbed species; nevertheless, when adding copper to nickel experimental points are rather well aligned with the representative points of pure nickel and pure copper, taking into consideration the change in the bond number of CO when alloying copper with nickel; this result is also in good agreement with a surface composition not far from the bulk one.

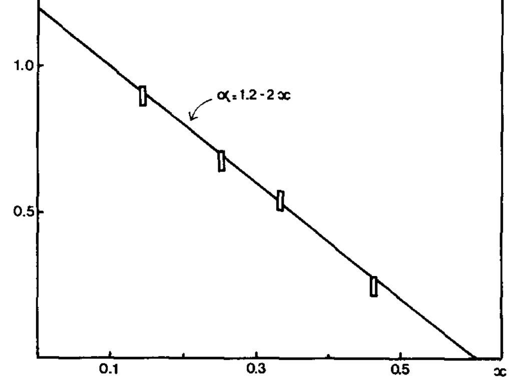


FIG. 9. Parameter α for oxygen adsorption as a function of copper content x.

Another way to obtain information on the surface composition of Ni–Cu catalysts is to make a magnetic study of the adsorption of gases. Hydrogen chemisorption (*17*) on Ni–Cu/SiO$_2$ samples gives a decrease in the saturation magnetization, α_{H_2}, such that N:

$$\alpha_{\mathrm{H}_2} \simeq 2\mu_{\mathrm{Ni}}. \qquad (1)$$

μ_{Ni}, which is determined from the saturation magnetization at 4°K of the outgassed sample, is representative of the magnetization of the whole metallic particle and agrees with magnetic atomic moment of the homogeneous alloy. α_{H_2}, in the hypothesis of magnetic decoupling (*20*), is representative of the magnetic moment of the surface atom, which depends strongly upon the composition of the Ni–Cu system.

Relation (1) suggests that the magnetic moment of the surface atom is within experimental error the same as the bulk one, i.e., the surface composition is the same as the bulk composition. Moreover, should enrichment in copper of the metallic surface occur, the surface alloy would be probably non- or very weakly ferromagnetic, and adsorption of hydrogen would produce no magnetic effect or a weak effect, independent of global copper concentration in the metallic phase. Experimental results allow us to rule out this state.

Oxygen chemisorption was also used to study the surface composition. In the case of pure nickel, α is close to 1.3 (*26*), suggesting the formation of NiO; experimental values of α for O$_2$ adsorption (α_{O_2})

on Ni–Cu/SiO$_2$ catalysts fit rather well with the expression:

$$\alpha_{O_2} \simeq 1.2 - 2x \simeq 2\mu \qquad (2)$$

where x is the copper content in the alloy ($0 \leqslant x \leqslant 1$), and μ the magnetic atomic moment of the alloy [$\mu \simeq 0.6 - x$ as indicated by the linear decrease of μ when increasing x; μ_{Ni}, the magnetic atomic moment of nickel in the alloy, is $(0.6 - x)/(1 - x)$]. Relation (2) suggests that for the adsorption of one molecule of oxygen, two atoms of the alloy cease to participate to the ferromagnetism, therefore relation (2) suggests the formation of $2[(1 - x)NiO + xCuO]$ for one adsorbed oxygen molecule. The ratio of the oxides formed at the surface during O$_2$ adsorption corresponds to the bulk composition, which is in accordance with unsegregated surface. It should be noticed that relation (2) is valid only at low coverages, the decrease of α observed at higher coverage (Fig. 8) being probably due to a modification in the ratio of formation of the oxides, perhaps induced by the migration at the surface of one of the metals. This illustrates a probable drastic change in the surface composition of the catalysts on exposure to the atmosphere.

The magnetic study of CO chemisorption (*19*) also suggests homogeneity between surface and bulk; the reasoning is the same as for H$_2$ chemisorption, but is complicated by the change in the bond number n of CO when increasing Cu content, as seen from ir spectroscopy and magnetic methods.

Assuming that no compensation effects between copper surface enrichment and some inhomogeneity in composition from particle to particle occur, all the experimental results suggest identical or very nearly equal composition between surface and bulk. It is difficult to give an explanation of this phenomenon, which is in contrast with results obtained on Ni–Cu films, single crystals, and unsupported powders. Some hypotheses could be suggested: (i) The effect of the support, hardly probable in this particular case, (ii) the effect of particle size, but theoretical calculations suggest unsegregated surfaces only in the case of highly dispersed alloy particles, which is not exactly our case, (iii) the effect of preparation–reduction by hydrogen at relatively high temperatures, followed by a very rapid cooling under hydrogen was used; this phenomenon of hardening in a gas phase liable to be bonded to nickel could perhaps stabilize the surface of the metallic particle, (iv) the effect of elevated temperature, which is known to decrease the surface segregation phenomenon, and (v) predominance of a particular crystal face (*27*) though the point does not seem entirely clear (*8*).

Another problem relates to clustering phenomena, expressing the trend of one of the metals of the alloy to be bonded preferentially to itself with respect to the statistical distribution; this phenomenon was described, as far as we know, only in the bulk of macroscopic Ni–Cu alloys at equilibrium (*28*) and seems to be rather weak in these systems. In the case of the surface of our supported catalysts the effect of hardening after reduction can maintain the random distribution which probably exists at high temperature.

CONCLUSION

Homogeneous Ni–Cu alloys supported on silica were obtained; volumetric titration by H$_2$ and magnetic studies of H$_2$, O$_2$, and CO suggest a surface composition very near to the bulk one, in contrast with results generally obtained on other Ni–Cu catalysts. Taking into account this unexplained result, it will be possible to correlate quantitatively the results of catalytic activities with the electronic state of alloyed nickel or with geometric effects of dilution based on a statistical distribution of ensembles of nickel atoms. Some preliminary results (*29*) of hydrogenolysis of C_2H_6 on Ni–Cu/SiO_2 catalysts agree well with the second kind of effects, and are quantitatively interpreted in terms of geometric dilution only.

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