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Decomposition of Formic Acid on Copper, Nickel, and Copper–Nickel Alloys

I. Preparation and Characterization of Catalysts

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Copper–nickel powders were prepared and shown to be monophasic, homogeneous alloys. Their surface composition was determined by strong hydrogen chemisorption with an assumed surface stoichiometry of 1 : 1 hydrogen to Ni. The surface analysis agrees with previous experimental and theoretical estimates. Nickel particles supported on silica were prepared. The metal dispersion was calculated from the uptake of strongly adsorbed hydrogen with a 1 : 1 stoichiometry of hydrogen to Ni surface atoms. The extent of Ni reduction, determined from dioxygen uptake measurements, was in excess of 80%. The titration of Cu surface atoms with oxygen from nitrous oxide on powders and alumina-supported Cu agrees with results of BET N_2 physisorption and X-ray line-broadening, respectively, when a surface stoichiometry of 2 : 1 Cu to O is assumed.

INTRODUCTION

The determination of the dispersion and surface composition of metal and alloy catalysts is required for the measurement of turnover rates and for the study of the effects of alloying, side reactions, and physical transport processes on the rate of catalytic reactions. Selective chemisorption is used to measure dispersion (*1*), or less frequently the surface composition of alloys (*2–5*). In contrast with surface-sensitive techniques requiring ultrahigh vacuum, such as Auger and photoelectron spectroscopy (*6–9*), selective chemisorption yields surface composition data under conditions more closely resembling those of many catalytic reactions. In this study, the use of H_2, CO, and O_2 chemisorption in the selective titration of Ni and Cu atoms is studied.

EXPERIMENTAL

Catalyst Preparation

Copper–nickel oxide powders were prepared by coprecipitation of metal carbonates (*10*). A 2 *M* solution of mixed nitrates ($Ni(NO_3)_2$–$6H_2O$, Baker; $Cu(NO_3)_2$–$3H_2O$, Mallinckrodt) was added slowly to a 1 *M* solution of NH_4HCO_3 (Mallinckrodt) at room temperature. The resulting slurry was stirred for 1 h, settled overnight, and filtered, and the solids were washed with 1–2 liters deionized, double-distilled water. The mixed carbonates were dried in vacuum at 363K for 24 h. Pure copper (Cu) and nickel (Ni) powders were prepared by an identical procedure.

Carbonate powders were crushed, calcined in air at 673K for 2 h, and recrushed to about 100 mesh. The resulting oxide powder (~10 g) was placed in a Pyrex reactor and reduced with flowing Pd-diffused H_2 in the apparatus described elsewhere (*11*). The reactor temperature was raised from room temperature to 533K over 0.5 h in flowing He (Liquid Carbonic) at a bulk contact frequency of 0.5 h^{-1}. The bulk (or site) contact frequency, $\nu_M{}^b$ (or $\nu_M{}^s$), is defined as the number of molecules of a species M entering the reactor per bulk (or surface) metal atom in the reactor. The dihydrogen concentration (Liquid Carbonic, Pd-diffused) was increased gradually to pure H_2 ($\nu^b = 2.0\ h^{-1}$) over 4 h. The temper-

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ature was then increased to 623K and reduction in pure H_2 was carried out for 16–20 h. The samples were passivated by cooling to room temperature in flowing He, gradually increasing the concentration of O_2 (0–15%) in the He stream over 2 h. They were exposed to air and stored. Their bulk composition was measured by atomic absorption.

Pure copper, Cu(A), and nickel, Ni(A), powders were also prepared by calcination of the respective metal nitrate (Baker) in air at 793K for 12 h, and subsequent reduction as described above. Copper powders, Cu(B), were prepared by reduction of CuO (Matheson, Coleman and Bell) at 573 K in flowing H_2 (23% H_2/He, $\nu_{H_2}{}^{b} = 0.3\ h^{-1}$) for 24 h. They were passivated by cooling to room temperature in He and exposing in air. Nickel powders, Ni(B), were prepared by calcination of $NiCO_3$ in flowing O_2 ($\nu_{O_2}{}^{b} = 12\ h^{-1}$) at 670K for 2 h, reduction in flowing H_2 (23% H_2/He, $\nu_{H_2}{}^{b} = 2.4\ h^{-1}$), passivation by cooling in He to room temperature, and exposure to air.

Silica-supported Ni and Cu were prepared by impregnation of the support (Cabosil HS-5, Cabot Corp.) to incipient wetness with a solution of the respective metal nitrate (Baker) and subsequent drying in vacuum at 373K for 4 h. The supported Ni nitrate (10 g) was decomposed in flowing H_2 ($\nu_{H_2}{}^{b} = 10\text{–}20\ s^{-1}$) by heating from room temperature to 523K over 1 h. After 2 h, the temperature was increased to 723K, and the samples were reduced at this temperature and contact frequency for 24 h. They were passivated by cooling in He and exposing to air. Alumina-supported Ni was prepared by an identical procedure. Silica-supported Cu nitrate was reduced in flowing H_2 (23% H_2/He, $\nu_{H_2}{}^{b} = 3.0\ h^{-1}$) for 24 h, and similarly passivated. These samples were denoted M(*X*)/Y, where M is the metal (Cu, Ni), *X* is its loading in weight percentage, and Y is the support (SiO_2, Al_2O_3).

Alumina-supported Cu was prepared by precipitation of $Cu(OH)_2$ in the presence of γ-Al_2O_3 (Dispal M, Continental Oil Co.) (*12*). Basic Cu sulfate ($CuSO_4 \cdot 3Cu(OH)_2$) was precipitated by the reaction of $CuSO_4$ (1.5 liters, 0.35 *M*, Mallinckrodt) with a stoichiometric amount of NH_4OH (5 *M*, Baker) at 348K for 2 h. The precipitate was washed with 2 liters of water to remove sulfate ions. Sodium hydroxide (Baker) was added to the precipitate slurry in order to form $Cu(OH)_2$. The solids were filtered, washed, dissolved in 10 *M* NH_4OH, and added to Al_2O_3. Precipitation of $Cu(OH)_2$ onto the support was carried out by vacuum evaporation of ammonia while stirring at room temperature. Copper powders, Cu(C), were prepared by a similar procedure followed by vacuum evaporation in the absence of Al_2O_3. The solids were filtered, washed with 5 liters of water, and dried in air at 333K. $Cu(OH)_2$ was dehydrated in flowing He ($\nu_{He}{}^{b} = 20\text{–}1000\ h^{-1}$) at 383K. The samples (10 g) were reduced at 474K in H_2 ($\nu_{H_2}{}^{b} = 10\text{–}5000\ h^{-1}$) for 24 h and passivated by cooling in He and exposing to air.

Characterization

Gas uptake. Chemisorption measurements were carried out in a volumetric system with a Texas Instruments precision pressure gauge; the apparatus is described in detail elsewhere (*13*). Before these experiments, prereduced and passivated catalysts (1–5 m^2 metal surface area) were rereduced in flowing H_2 ($\nu_{H_2}{}^{s} = 10^2\text{–}10^4\ h^{-1}$) at 723K for 2 h, except for supported Cu and Cu(C), which were reduced at 493K for 2 h. All samples were then evacuated to 10^{-3}–10^{-2} Pa for 0.25 h at 723K, except for supported Cu samples, which were cooled in H_2 to 360–370K and then evacuated for 0.25 h.

The total surface area of the catalysts was determined by N_2 physisorption at its normal boiling point, using 0.162 nm^2 for the area of a N_2 molecule.

The total H_2 uptake was measured at 298 ± 5K and 2–30 kPa. The samples were then evacuated (10^{-4}–10^{-3} Pa) for 600 s at this temperature and a new isotherm was measured (backsorption). The difference between the total and backsorption uptake, extrapolated to zero pressure, was denoted as strongly held hydrogen (*3*). The CO uptake at 195K and 2–30 kPa was measured by an identical procedure (*14*).

Copper surface atoms were titrated by oxygen chemisorbed during the decomposition of nitrous oxide (N_2O) at 358–368K and 27–29 kPa (*15*). The oxygen surface density was calculated from measurements of the residual N_2 pressure after unreacted N_2O was condensed for 2 h in a Pyrex coil cooled by liquid nitrogen. N_2O was purified by repeated freeze–thaw cycles, vacuum distillation, and outgassing, as described elsewhere (*14*).

The extent of reduction of supported Ni was calculated from O_2 uptake at 673K and 20–30 kPa. The ratio of absorbed oxygen to bulk Ni atoms yields the reduced Ni fraction, provided the stoichiometry of the bulk oxide phase corresponds to NiO.

X-Ray Diffraction

X-Ray diffraction measurements were carried out using Cu$K\alpha$ radiation. The lattice constant of CuNi powders was measured from the angle of the (111) and (200) reflections. The diffraction angle was calibrated from measurements on pure Cu powders with large crystallite size (3.4 μm).

The crystallite size of supported Cu particles was calculated from the width of the (111) and (200) diffraction peaks, using the Scherrer equation (*16, 17*), and following a procedure described in detail elsewhere (*14, 16, 17*).

Bulk Composition Measurements

Cu, Ni, and Na bulk concentrations were determined by atomic absorption spectrophotometry. C and S concentrations were determined by titration and thermal conductivity measurements of the products of O_2 treatment of the samples at high temperature.

RESULTS

Copper, Nickel, and Copper–Nickel Powders

Lattice constants. The lattice constants of prereduced and passivated CuNi powders are shown in Table 1. The maximum deviation from Végard's law (*18*) is 0.5 pm and occurred near equimolar alloy compositions. Only one (111) and one (200) diffraction peak are observed on all alloys;

TABLE 1

Characterization of CuNi Powders

Cu bulk atomic fraction[a]	Total surface area[b] (m^2 g^{-1})	Strongly held hydrogen surface density (10^{15} cm^{-2})	Weakly held hydrogen surface density (10^{15} cm^{-2})	Surface Cu atomic fraction	Lattice constant[c] (pm)
0	1.15	1.45	0.36	0	352.4
0.005	1.0	0.67	0.26	0.55	352.1
0.05	0.45	0.60	0.28	0.61	352.5
0.10	0.95	0.41	0.58	0.73	353.3
0.25	1.55	0.34	0.37	0.77	354.2
0.50	1.30	0.34	0.39	0.78	356.5
0.70	1.20	0.28	0.37	0.81	358.4
0.90	0.80	0.14	0.21	0.91	360.2
0.95	0.75	0.05	0.06	0.97	361.0
1.0	0.85	0.00	0.02	1.0	361.4

[a] Atomic absorption.

[b] From BET dinitrogen physisorption, assuming 0.162 nm^2 per adsorbed N_2 molecule.

[c] Average of lattice constants calculated from (111) and (200) diffraction angles.

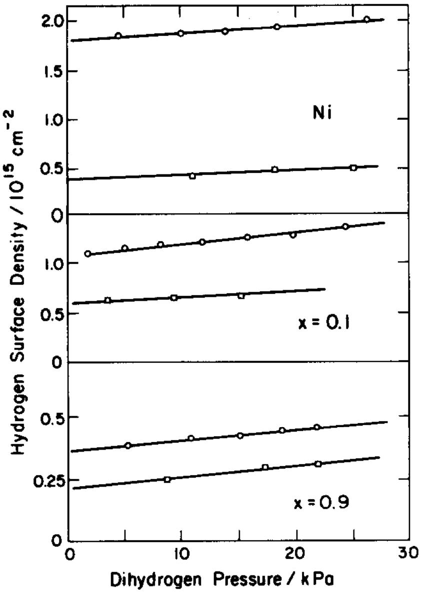

FIG. 1. Dihydrogen uptake isotherms. CuNi powders, 298 ± 5K, x = bulk Cu atomic fraction. ○, Adsorption; □, backsorption.

therefore, the CuNi powders are monophasic, homogeneous alloys.

Hydrogen chemisorption. Dihydrogen uptake isotherms at room temperature on some CuNi powders are shown in Fig. 1. Total and backsorption uptakes increase slightly with pressure. The amount of strongly held hydrogen, however, remains constant. Backsorption uptakes are independent of evacuation time (0.08–0.4 h).

The total and strongly adsorbed hydrogen surface densities were calculated from extrapolation of the respective uptake isotherms to zero pressure (Table 1). They agree with previous data on similarly prepared CuNi alloy powders (*3*) (Fig. 2) and on CuNi films (*5*).

The surface density of strongly adsorbed hydrogen on Ni powder corresponds to a value of 0.9 for the ratio of hydrogen to Ni surface atoms, if the surface of the powder contains equal concentrations of (100), (110), and (111) planes (1.55×10^{15} cm^{-2}). On Cu powder, the hydrogen surface density is less than 10^{13} cm^{-2}. The fraction of the hydrogen which is reversibly adsorbed on CuNi powders at room temperature increases with Cu content, but the surface density of weakly adsorbed species remains fairly constant up to 0.7 Cu bulk atomic fraction. In contrast, the density of strongly adsorbed hydrogen decreases faster than linearly with increasing bulk Cu content.

Bulk composition. The bulk composition of CuNi powders, measured by atomic absorption, is reported in Table 1. No Na or S (<50 ppm) were detected in any of the samples analyzed; the carbon content of the prereduced and passivated samples was 50–200 ppm.

Nickel Catalysts

Hydrogen and carbon monoxide chemisorption. Nickel dispersion was calculated from the uptake of strongly held hydrogen. A hydrogen to Ni surface atom ratio of unity was assumed. The agreement between Ni surface areas calculated by this method and by BET N_2 physisorption on powders supports this stoichiometry (Table 2).

The rate of H_2 uptake on Ni is initially

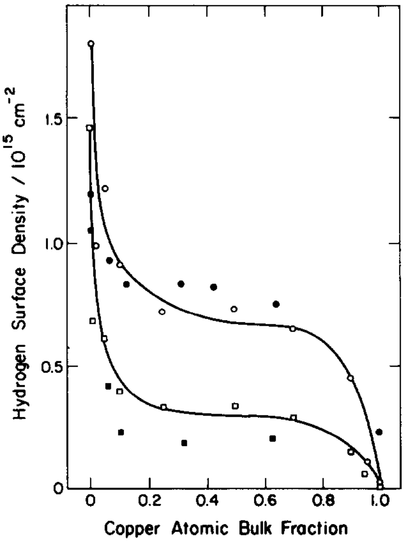

FIG. 2. Dihydrogen uptake on CuNi powders (298 ± 5K). Total uptake, circles; strong uptake, squares. ○, □, This study, 2–30 kPa H_2, extrapolated to zero pressure. ●, ■, Sinfelt *et al.* (*3*), 13.3 kPa H_2.

rapid; more than 90% of the uptake occurred in 200–600 s at room temperature. Thereafter, slow uptake of weakly held hydrogen was observed. It has been proposed that this occurs by activated dissociative chemisorption of H_2 on a "saturated" Ni surface (*19, 20*).

Dihydrogen and carbon monoxide uptake isotherms on Ni/SiO_2 are shown in Fig. 3. Neither the total nor the backsorption H_2 uptake changes with pressure. The uptake rate is negligible after 0.5 h. In contrast, the CO uptake rate is measurable even after 2 h. The "saturation" uptake is defined as that measured when the rate of change of the uptake, defined as the ratio of CO to bulk Ni atoms, was 10^{-6} s^{-1}. The "saturation" uptake increases with CO pressure. The ratio of CO to H strongly held species increases with decreasing loading and increasing dispersion.

Dioxygen uptake. The ratio of absorbed oxygen to bulk Ni atoms on supported samples is between 0.86 and 1.14, similar to its value on reduced Ni powder (1.05). These values agree with those reported by other authors (*21*); they obtained ratios of 1.06–1.08 on Ni/Al_2O_3, calculated on the basis of

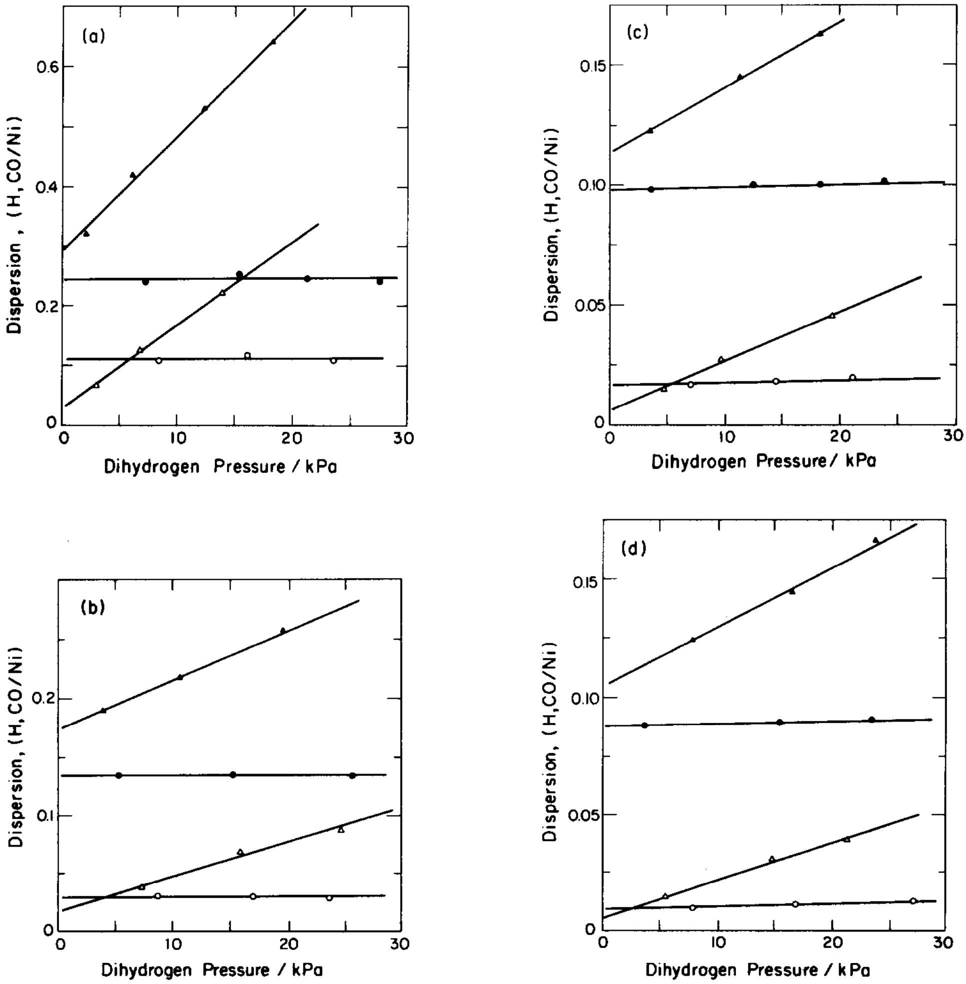

FIG. 3. Dihydrogen uptake isotherms, Ni/SiO_2. (a) $Ni(2.2)/SiO_2$, (b) $Ni(8.5)/SiO_2$, (c) $Ni(11.3)/SiO_2$, (d) $Ni(22.0)/SiO_2$. Total, solid symbols; backsorption, open symbols. Dihydrogen, ●, ○, 298 ± 5K; carbon monoxide, ▲, △, dry ice/acetone.

reduced nickel atoms, as measured by CO extraction.

Copper Catalysts

Chemisorption measurements. The metal surface area of supported and unsupported Cu was measured from the oxygen uptake during N_2O decomposition (Table 3). The uptake is initially fast but reaches a constant value after 5–10 h. A value of 0.5 for the ratio of O to Cu surface atoms, previously reported (*15*), was used to calculate Cu dispersion. The dispersion of Cu powders (Cu, Cu(A), Cu(B)), calculated from these measurements, agrees with the values obtained from N_2 physisorption data. N_2O decomposition and the concurrent oxygen adsorption do not occur on CuO or γ-Al_2O_3 at 363K.

Exposure of Cu/Al_2O_3 to H_2 at room temperature and 5–20 kPa results in a surface density of strongly held hydrogen (10^{14} cm^{-2}) corresponding to 0.06 monolayer. Exposure of the same sample ($Cu(19.2)/Al_2O_3$) to O_2 (40 kPa) at room temperature results in the uptake of the equivalent of 2–3 oxygen monolayers. Therefore, neither H_2 nor O_2 are selective titrants for surface Cu atoms.

X-Ray diffraction. Copper particle sizes calculated from oxygen uptake data were compared with those obtained from line-broadening of the (111) and (200) Cu diffraction peaks. Detailed data and calculation procedures are shown elsewhere (*14*). The particle diameters calculated from the geometric average of the crystallite length in the (111) and (200) directions are shown in Table 3, and are compared with oxygen uptake data in Fig. 4. Absolute values of particle size from line-broadening data are inaccurate because of uncertainty in the shape of the particles (*16, 17*). Also, line-broadening measurements yield a volume-averaged particle size, while chemisorption measurements yield surface-averaged diameters; for reasonably shaped particle diameter distributions, the latter is always smaller. Therefore, the disagreement in particle diameters between the two techniques is not surprising. Relative diameters calculated from the two techniques are, however, very similar (Fig. 4).

DISCUSSION

The surface density of hydrogen adatoms on Ni powder (1.4×10^{15} cm^{-2}) agrees with values reported from adsorption measure-

TABLE 2

Characterization of Ni Catalysts

Sample	Dispersion[a] (H)	Dispersion[b] (CO)	Total surface area[c] (m^2 g^{-1})	Ni surface area[d] (m^{-2} g^{-1})	Oxygen uptake[e]
Ni	0.0017	—	1.20	1.15	1.05
Ni(A)	0.0009	—	0.45	0.55	—
Ni(B)	0.0007	—	0.55	0.60	—
$Ni(2.2)/SiO_2$	0.13	0.26	270	85	0.87
$Ni(8.5)/SiO_2$	0.104	0.15	—	69	1.14
$Ni(11.3)/SiO_2$	0.083	0.11	—	55	1.00
$Ni(22)/SiO_2$	0.078	0.10	—	52	0.94
$Ni(O)/SiO_2$	No adsorption	—	250	—	—

[a] Ratio of strongly held hydrogen to bulk Ni atoms.

[b] Ratio of strongly held CO to bulk Ni atoms.

[c] From N_2 physisorption measurements, 0.162 nm^2/N_2 molecule.

[d] From H_2 uptake, assuming 0.0645 nm^2/H atom.

[e] Ratio of O to bulk Ni atoms.

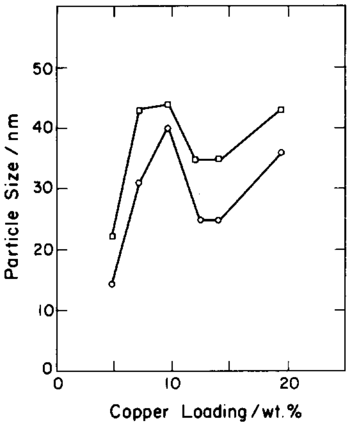

FIG. 4. Copper crystallite size. Comparison of results from X-ray line-broadening and nitrous oxide decomposition. □, X-Ray line-broadening; ○, oxygen uptake during N_2O decomposition.

ments at high H_2 exposure (>10 Pa-s) on other Ni catalysts (1.2–2.0 × 10^{15} cm^{-2}) (*3*, *22–29*) near room temperature. At lower exposures (<10^{-2} Pa-s), characteristic of ultrahigh-vacuum studies, the surface density is lower (0.3–0.8 × 10^{15} cm^{-2}) (*30–36*), and only chemisorption processes with high sticking probability and low activation energy occur at measurable rate. "Saturation" coverage is then determined by the density of adspecies at which the sticking coefficient becomes smaller than about 0.01; this often occurs at 0.25–0.5 monolayers, following the formation of ordered structures. At exposures typical of selective chemisorption measurements (10^6–10^9 Pa-s), chemisorption with sticking probability as low as 10^{-10} occurs readily at room temperature.

The ratio of strongly adsorbed hydrogen to Ni surface atoms is near unity in all pure Ni powders. On CuNi powders, the use of this value in the titration of surface Ni atoms requires that:

(i) ensemble or ligand effects (*37*) do not result in identical binding energy on Ni and Cu ensembles;

(ii) kinetic limitations do not prevent the titration of isolated Ni surface atoms; their titration may occur by direct dissociation of H_2 on isolated Ni atoms, or by migration of H adatoms, dissociated on larger Ni ensembles, onto them.

Temperature-programmed desorption data (*23*, *32*, *38*, *39*) show that alloying has little effect on the binding energy of H atoms adsorbed on Ni ensembles. The position of the H surface atom may vary with alloying. On pure Ni, it may reside on fourfold or threefold hollow sites; it may sequentially move to bridged and on-top sites with increasing surface Cu concentration, in order to maximize interactions with Ni atoms, as the number of Ni atoms surrounding the hollow site decreases. Theoretical treatments suggest that the difference in binding energy among these configurations is small (~10%) (*40*, *41*). Therefore, the difference in binding energy between Cu and Ni ensembles is largely unchanged by alloying.

The sticking coefficient for dissociative H_2 chemisorption under ultrahigh-vacuum conditions is proportional to the fourth power of the surface Ni fraction on CuNi alloys (*32*, *38*, *39*), suggesting that four adjacent Ni atoms are required for chemisorption with sticking probability greater than about 0.01. Processes with sticking probability as small as 10^{-10} are readily measurable at much higher exposure. Under these conditions, smaller Ni ensembles will, albeit with finite activation energy, dissociate H_2. Indeed, activated adsorption is observed often in normal pressure chemisorption and catalysis (*43*), and even mononuclear coordination complexes are known to dissociate H_2 (*44*). Along with the observed mobility of H_2 adatoms on Ni (*42*), this suggests that even isolated Ni surface atoms are titrated by impinging H_2 in chemisorptive titration experiments.

In this study, the surface composition of CuNi powders is calculated assuming a value of unity for the ratio of H to Ni surface atoms, irrespective of alloy composition. The results are shown in Table 1. The measured composition agrees with previous theoretical (*45–50*) and experimental

TABLE 3

Characterization of Cu Catalysts

Sample	Dispersion[a]	Cu surface area[b] ($m^2 g^{-1}$)	Total surface area[c] ($m^2 g^{-1}$)	Diameter[d] (nm)	Diameter[e] (nm)
Cu(0.33)/Al_2O_3	0.054	33.0	—	20.5	—
Cu(1.0)/Al_2O_3	0.074	45.5	—	15.0	—
Cu(1.7)/Al_2O_3	0.148	90.5	—	7.5	—
Cu(2.4)/Al_2O_3	0.218	133.0	—	5.0	—
Cu(3.1)/Al_2O_3	0.084	51.5	—	13.0	—
Cu(4.8)/Al_2O_3	0.082	50.0	—	13.5	23
Cu(7.2)/Al_2O_3	0.035	21.5	—	31.0	43.5
Cu(9.6)/Al_2O_3	0.028	17.0	—	39.5	44
Cu(12.0)/Al_2O_3	0.043	26.5	—	25.3	34
Cu(14.4)/Al_2O_3	0.045	26.5	—	25.3	34
Cu(19.2)/Al_2O_3	0.031	18.5	—	36.0	43
Cu(0)/Al_2O_3	—	—	195	—	—
Cu(35)/SiO_2	0.040	24.0	—	28.0	40
Cu	0.0011	0.7	0.8	950	—
Cu(A)	0.00033	0.20	0.25	3400	—
Cu(B)	0.00098	0.60	0.70	1100	—
Cu(C)	0.003	1.8	4.0	380	—

[a] Ratio of surface to total Cu atoms, calculated from oxygen uptake.

[b] Calculated from dispersion assuming 1.5×10^{15} Cu cm^{-2}.

[c] From N_2 physisorption, assuming 0.162 nm^2/N_2 molecule.

[d] From oxygen uptake data, assuming hemispherical particles.

[e] From X-ray line-broadening data (average of (111) and (200) reflections).

estimates (*7, 8, 46–48, 51, 52*). The latter are compared with the results of this study in Fig. 5. The agreement is excellent and demonstrates that selective chemisorption, as proposed by Van der Plank and Sachtler (*5*) and Sinfelt *et al.* (*3*), may be used to measure the surface composition of CuNi alloys. Moreover, it shows that H_2 chemisorption at room temperature does not induce segregation of Ni to the surface of the alloys, as thermodynamically predicted (*45, 53*), presumably because of low bulk diffusion rates.

The lattice constants of CuNi powders, prepared by calcination and H_2 reduction of coprecipitated carbonates at 673K, are identical to those of bulk alloys, prepared from the molten metals and annealed above 1273K (*54, 55*), and for powders prepared by reduction of mixed oxides at 623K (*3, 56, 57*). The powders are monophasic. Indeed, phase segregation is predicted only below 500K (*14, 58, 59*). Therefore, the

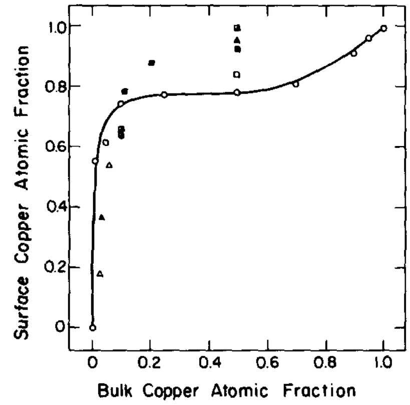

FIG. 5. Surface composition of CuNi alloys. Comparison of selective hydrogen chemisorption with other surface-sensitive techniques. ○, This study, strongly adsorbed hydrogen, Ni : H = 1 : 1, 623K reduction, powders. □, Brongersma and Buck (*51*), polycrystalline bulk samples, 1000K anneal, LEIS. ■, Brongersma *et al.* (*52*), polycrystalline bulk samples, 923K anneal, LEIS, composition measured at 723K. Helms and Yu (*7*), single crystals, 873K anneal, AES; ◑, (110); ◩, (100). ▲, Helms (*8*), polycrystalline bulk samples, 873K anneal, AES. Ng *et al.* (*46–48*), polycrystalline tips, 923K, AP-FIM; △, (111); ▲, (100).

"cherry" model of biphasic alloy crystallites (*58, 59*) does not explain the constant surface composition of these alloy powders at intermediate bulk composition (Fig. 5). This behavior is theoretically predicted (*45–50*) and experimentally observed (*8, 52*) on monophasic CuNi alloys.

The large CO uptake on Ni/SiO_2 (Table 2) may result from the formation of subcarbonyl species ($Ni(CO)_x$, $x < 4$) at the surface. Infrared bands corresponding to these species have been observed (*60–62*); their intensity decreased with increasing particle size, disappearing for Ni particles greater than 10 nm (*60*). This suggests that low-coordination surface atoms are required for their formation. The increased ratio of strongly adsorbed CO to H reported here may result from the concomitant increase in metal dispersion. However, particle size effects of this magnitude are unlikely in the dispersion range of these samples (0.08–0.13). Although thermodynamically favored, the rate of formation of $Ni(CO)_4$ is very slow at 195K. Extrapolation of the reported rates (*63, 64*) to 195K and 20 kPa CO yields 10^{-12}–10^{-7} s^{-1} for the probability that a Ni surface atom is removed by this reaction. Therefore, $Ni(CO)_4$ formation should not be observed.

The failure to account for unreduced Ni may lead to ambiguous calculations of dispersion and particle diameter, in the range in which these may affect turnover rates and selectivity most markedly. Oxygen uptake measurements on Ni/SiO_2 show that more than 80% of the Ni atoms are in the metallic state after reduction at 723K. The ratio of O to reduced Ni atoms in dispersed samples may change with dispersion because of differences in the effective Ni valency between bulk and surface atoms. Therefore, the application of this technique to highly dispersed Ni catalysts ($D > 0.3$) is difficult. In this study, the ratio of O to Ni atoms in Ni powders ($D = 0.0017$) is 1.05, very similar to that measured on supported Ni ($D = 0.08$–0.13). Because of the low dispersion of these samples, the apparent bulk stoichiometry (O : Ni = 1.05 : 1) is used to calculate the fraction of unreduced Ni.

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