# Determination of the Surface Composition of Copper-Nickel Alloy Powders: A Comparison between Hydrogen Chemisorption and the Reaction of N<sub>2</sub>O Decomposition

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The surface composition of copper-nickel alloy powders was measured by chemisorption. Three different techniques were used for comparison, namely, strong hydrogen chemisorption, temperature-programmed desorption of hydrogen, and decomposition of  $N_2O$ . The agreement between the compositions determined by these three techniques was excellent. A segregation of copper atoms to the powder surfaces was confirmed. The chemisorption strength of hydrogen atoms on nickel is weakened by alloying with copper. © 1985 Academic Press, Inc.

#### INTRODUCTION

Powders of bimetallic allovs have been studied for several decades (1-4) in an attempt to modify the catalytic properties of pure metals, such as reactivity and selectivity, and to develop new catalysts. Quantitative determinations of the composition of alloy surfaces are fundamental to these interesting studies. The methods generally used include Auger electron spectroscopy, work function measurement, and selective chemisorption. Auger spectroscopy detects not simply the composition of the outermost surface layer, but the average composition of a few layers. Work function measurements have the drawback of giving only qualitative information. Selective chemisorption remains the most dependable method for the quantitative determination of surface composition.

Many textbooks on catalysis select the work of Sinfelt *et al.* (5) to illustrate the power of the chemisorption technique. In this pioneering work the BET method was used to measure the total surface area of copper-nickel alloy particles. Knowing that copper does not chemisorb hydrogen strongly, the number of surface nickel atoms on the alloys was then determined from the extent of strong hydrogen chemisorption (SHC). The variation of the fraction of nickel atoms at the surface  $(F_{Ni})$ with that in the bulk of the alloys  $(X_{Ni})$  was thus quantitatively determined. In the bulk composition range between  $X_{\rm Ni} = 0.90$  and 0.30,  $F_{\rm Ni}$  was found to be about 0.20. A segregation of copper atoms to the surface of the alloys was suggested. Such a segregation can be predicted by the regular solution theory (3, 6) and also observed by Auger spectroscopy studies. However, there is a discrepancy between the experimental results and the theoretical prediction of the degree of segregation. It is of interest to check whether  $F_{Ni}$  calculated by BET and SHC can be confirmed by other chemisorption techniques.

Generally speaking, chemisorption techniques are not very successful in determining the quantity of surface copper atoms. H<sub>2</sub> chemisorbs too weakly on Cu, while under normal conditions O<sub>2</sub> tends to oxidize the Cu sublayers. Up to now, the following reaction represents the best method for Cu(s)<sup>1</sup> measurement (7–12):

 $X_{\rm m}$ Cu(s) + N<sub>2</sub>O  $\rightarrow$  Cu(s)<sub>X<sub>m</sub></sub>O + N<sub>2</sub>, (1)

 $^{1}$  Cu(s) denotes a copper atom on the surface of a powder.

where  $X_{\rm m}$  is the stoichiometry of chemisorption at monolayer coverage.  $X_{\rm m}$  values have been measured in this way by many researchers and have been found to be temperature dependent. At room temperature a value of  $X_{\rm m} = 3.3 \pm 0.3$  was recently reported from this laboratory (11).

The corresponding reaction between N<sub>2</sub>O and nickel

$$X'_{\rm m} \operatorname{Ni}(s) + \operatorname{N}_2 \operatorname{O} \rightarrow \operatorname{Ni}(s)_{X'_{\rm m}} \operatorname{O} + \operatorname{N}_2$$
 (2)

has also been studied.  $X'_{\rm m}$  was found in this laboratory to be 0.63 at room temperature. Assuming that the  $X_{\rm m}$  values are not influenced by alloying, the N<sub>2</sub>O reaction is potentially a feasible system for the study of the surface composition of Cu–Ni alloys. This reaction may be used to check the composition measured by BET and SHC. Hopefully, the method will be applied in the future in combination with SHC to characterize supported Cu–Ni alloy catalysts.

## **EXPERIMENTAL**

Catalyst preparation. Cu–Ni alloy powders with  $X_{Ni} = 0, 0.1, 0.3, 0.5, 0.7, 0.9$ , and 1.0 have been prepared by the procedures of Best and Russell (13). Copper and nickel ions were coprecipitated from a solution of mixed nitrates with ammonium bicarbonate. These precipitates were subsequently aged at room temperature, washed with deionized water, and dried in an oven at 110°C. Alloy powders were obtained by calcination at 400°C followed by reduction in a stream of ultrapure hydrogen. The degree of reduction was determined by the following TPR studies.

Temperature-programmed reduction (TPR). TPR experiments were performed to find the minimum temperature that may be used to reduce NiO-CuO mixtures completely. A conventional system with a thermal conductivity detector (TCD) was employed. A stream of 10% H<sub>2</sub> in Ar with a flow rate of 50 ml min<sup>-1</sup> was passed through a reactor in which 200 mg of mixed oxides was reduced. The reduction reaction was controlled by a programmable Eurotherm temperature controller. The temperature was increased from room temperature to 550°C at a rate of 5 K min<sup>-1</sup> and was then brought back automatically to room temperature. The TCD enabled the consumption of hydrogen by the oxides to be determined as a function of reactor temperature. A detailed diagram of the TPR apparatus may be found elsewhere (14).

Temperature-programmed desorption (TPD). After reduction, the surface of the alloys is covered by chemisorbed hydrogen. In order to measure the surface composition by hydrogen chemisorption and the N<sub>2</sub>O reaction, this hydrogen has to be desorbed. TPD is a good method for examining desorption phenomena and finding the minimum temperature for complete desorption. TPD was performed with the same setup as was used for TPR. Reduced alloys were cooled in a bath at 194 K. Pure argon (flow rate 50 ml min<sup>-1</sup>) was used as the carrier gas to replace the 10%  $H_2$  in Ar. The cold bath was then removed. Weakly chemisorbed hydrogen was desorbed when the reactor was warmed to room temperature. After the baseline of the TCD became stable, a temperature program with 5 K min<sup>-1</sup> increase was then applied to determine the desorption profile of the strongly chemisorbed hydrogen.

Adsorption. Physisorption and hydrogen chemisorption were measured in a volumetric apparatus that could be evacuated to 1  $\times$  10<sup>-5</sup> Torr. A precision gauge from Texas Instruments was installed for pressure monitoring. N<sub>2</sub> was used for BET surfacearea measurements. The cross-sectional area of  $N_2$  was assumed to be 16.2 Å<sup>2</sup>. Hydrogen (purified with a Matheson hydrogen purifier) was chemisorbed at room temperature to obtain the so-called "total uptake." Part of the adsorbed gas could be desorbed under a vacuum of  $10^{-4}$  Torr in 10 min at room temperature. The amount of the desorbed hydrogen, defined by Sinfelt et al. (5) as "weak chemisorption," may be measured by readsorption.

 $N_2O$  reaction. The reaction was per-





FIG. 1. TPR of NiO (---), 90% NiO (---), 70% NiO (----), and CuO (----).

formed in the same volumetric apparatus as was used for the adsorption studies. A pump was added to this apparatus in order to recycle  $N_2O$  at 760 Torr through the reduced and predesorbed alloy powders.  $N_2O$ was purified by distillation. The yield of  $N_2$ was monitored every 30 min by measuring the pressure indicated on the precision gauge after freezing out the unreacted  $N_2O$ in a liquid-nitrogen trap. Details of this setup are published elsewhere (11).

# **RESULTS AND DISCUSSION**

Figure 1 illustrates the TPR results of CuO, NiO, and their mixed oxides. In accordance with an earlier report (14), CuO and NiO are found to reduce around 200 and 350°C, respectively. Except for a minor peak around 350°C, mixed oxides are reduced mainly around 250°C. A shift of the reduction temperature of NiO in the mixed oxides from 350 to 250°C is therefore indi-

cated. This shift may be caused by spillover of hydrogen from the reduced copper atoms to the unreduced NiO during the reduction. The minimum temperature for a complete reduction to metal can be determined from Fig. 1. NiO and mixed oxides should be reduced at 400°C while CuO may be reduced at 300°C. These reduction conditions were accepted in this study.

The desorption behavior of hydrogen also varies with the alloy composition. TPD results for various Ni-Cu alloys are shown in Fig. 2, where the unsmoothed curves for the desorption of hydrogen versus the reactor temperature are shown. Since weakly chemisorbed hydrogen is not stable at room temperature (20°C), the peak area of each curve represents the amount of strongly chemisorbed hydrogen only. Pure nickel powder shows the largest peak area. Cop-



FIG. 2. TPD of strongly adsorbed hydrogen from various Cu-Ni alloys.

TABLE 1

TPD Peak Areas for H<sub>2</sub> on Cu, Ni, and Cu-Ni Alloys

X <sub>Ni</sub>	BET surface area (m <sup>2</sup> g <sup>-1</sup> )	A <sub>t</sub> (m <sup>2</sup> )	Ps	$P_{\rm S}/A_{\rm t}$	F <sub>Ni</sub>
0.00	1 16	8 04	0	0	0
0.10	0.95	4.75	0.02	$3.43 \times 10^{-3}$	0.08
0.30	1.41	7.07	0.06	8.36 × 10 <sup>-3</sup>	0.18
0.50	1.52	7.60	0.06	7.76 × 10 <sup>-3</sup>	0.17
0.70	1.94	9.70	0.10	$1.06 \times 10^{-2}$	0.23
0.90	2.24	11.20	0.15	$1.30 \times 10^{-2}$	0.29
1.00	1.90	9.50	0.41	$4.27 \times 10^{-2}$	1.00

*Note*.  $X_{\text{Ni}}$ , fraction of nickel atoms in bulk;  $A_t$ , total surface area = (BET surface area) × (sample weight);  $P_{\text{S}}$ , peak area of strong adsorption;  $F_{\text{Ni}}$ , fraction of nickel on the surface =  $(P_{\text{S}}/A_t)$  of alloy/ $(P_{\text{S}}/A_t)$  of nickel.

per powder, on the contrary, does not show any strongly chemisorbed hydrogen (SCH). The peak areas for the alloys falls between these two extremes.

Assuming that surface copper atoms on the alloys do not engage in strong hydrogen chemisorption and that each surface nickel atom on the alloys adsorbs the same amount of SCH as the atoms on the surface of pure nickel, the peak areas in Fig. 2 may be used to calculate  $F_{Ni}$  of the alloys. Table 1 illustrates the procedure and the results of such calculations.  $F_{Ni}$  is shown to decrease dramatically from 1.0 to 0.3 as  $X_{Ni}$  changes from 1.0 to 0.9. A segregation of Cu to the surface of Cu–Ni alloys is thus indicated, in close agreement with results of previous work (15).

Figure 2 shows that the strength of the chemisorption is also dependent on the alloy composition. For alloys with  $X_{\text{Ni}} \leq 0.7$ , chemisorbed hydrogen desorbs completely at a temperature lower than 250°C. The desorption of hydrogen from pure nickel, however, continues to 450°C. Evidently hydrogen is chemisorbed more strongly on the surface nickel atoms of pure nickel than on those of the alloys. An electronic effect on

surface nickel atoms due to alloying with copper is therefore apparent. This result is different from that of Au-Pt alloys for which only a geometric effect due to alloying was found from the TPD of adsorbed hydrogen (16). It is of interest to note here that the alloy with  $X_{Ni} = 0.9$  is somewhat exceptional. Although most hydrogen is desorbed at temperatures lower than 250°C, an appreciable amount remains adsorbed at this temperature and is desorbed from this sample in the temperature range between 250 and 450°C. These hydrogens may be desorbed from a small amount of pure nickel crystallites in the  $X_{Ni} = 0.9$  alloy.

The variation of  $F_{Ni}$  with the  $X_{Ni}$  of Cu-Ni alloys has been determined volumetrically by Sinfelt *et al.* (5) through the strong chemisorption of hydrogen. The same method has been repeated in the present study, and some results are illustrated in Fig. 3. Both the total uptake and the back (or weak) uptake of H<sub>2</sub> by each alloy are seen to increase with the hydrogen pressure



FIG. 3. Hydrogen adsorption on Cu, Ni, and Cu–Ni alloy ( $X_{Ni} = 0.70$ ).  $\bigcirc$ , Total H<sub>2</sub> adsorption;  $\Box$ , H<sub>2</sub> "back" adsorption.

TABLE 2

Hydrogen Chemisorption on Cu, Ni, and Cu-Ni Alloys

F <sub>Ni</sub>	$H_2$ chemisorption (×10 <sup>18</sup> ) atoms m <sup>-2</sup>		BET surface area (m <sup>2</sup> g <sup>-1</sup> )	X <sub>Ni</sub>	
	Strong	Total			
0.02	0.23	2.75	1.69	0.00	
0.05	0.68	1.71	0.95	0.10	
0.14	1.70	4.95	1.41	0.30	
0.08	0.98	1.62	1.48	0.50	
0.22	2.65	5.64	1.94	0.70	
0.43	5.27	7.15	2.24	0.90	
1.00	12.20	13.00	2.62	1.00	

*Note*.  $X_{Ni}$ , fraction of nickel in bulk alloy;  $F_{Ni}$ , fraction of Ni calculated from strong chemisorption of H<sub>2</sub>.

at room temperature. The values obtained by extrapolating these uptakes to zero pressure are denoted in this study as the chemisorption. The difference between the total chemisorption and the weak chemisorption of each alloy is defined by Sinfelt *et al.* as the strong chemisorption. The experimental data of H<sub>2</sub> chemisorption are correlated in Table 2 with the BET surface areas to estimate the surface composition. The variations of  $F_{Ni}$  with the  $X_{Ni}$  are presented in the last column of this table.

Reaction with N<sub>2</sub>O is the third method used in this study for the determination of the surface composition of Cu-Ni alloys. The reaction stoichiometry for Cu and Ni is given by Eqs. (1) and (2) stated earlier. Figure 4 illustrates the  $N_2$  production per unit surface area as a function of reaction time for various alloy compositions. The extent of each reaction is seen to increase with reaction time. The rate of the N<sub>2</sub>O decomposition is initially fast and becomes much slower after the formation of a monolayer of oxygen atoms. The yield of  $N_2$  per unit surface area at limiting coverage  $(Y_{N_2})$  may be estimated by extrapolating the  $N_2$  yield in the low-rate region to zero reaction time. Table 3 shows that the  $Y_{N_2}$  values are also composition dependent.



Reaction Time (hr)

FIG. 4.  $N_2$  production as a function of time in the decomposition of  $N_2O$  on Cu–Ni alloy powders at 700 Torr  $N_2O$  and room temperature.

 $Y_{N_2}$  values are generally converted into  $\theta$ , the average number of oxygen atoms bound per surface metal atom at limiting coverage, using the equation

$$\theta = Y_{\rm N_2}/n_{\rm s}, \qquad (3)$$

## TABLE 3

The Reaction of N<sub>2</sub>O with Cu, Ni, and Cu-Ni Alloys at Room Temperature

X <sub>Ni</sub>	BET surface area (m <sup>2</sup> g <sup>-1</sup> )	$Y_{N_2}$ (×10 <sup>18</sup> molecules m <sup>-2</sup> )	F <sub>Ni</sub>	θ
0.00	1.90	5.10	0.00	0.30
0.10	1.46	6.20	0.05	0.37
0.30	1.26	8.15	0.14	0.49
0.50	1.10	7.73	0.12	0.46
0.70	1.86	9.67	0.21	0.58
0.90	1.40	10.04	0.23	0.60
1.00	1.80	25.10	1.00	1.63

Note.  $F_{Ni}$ , calculated from Eq. (6);  $\theta$ , calculated from Eq. (4).

Authors	Temperature range (°C)	N <sub>2</sub> O pressure (Torr)	t a	Reference
Dell et al.	20	0.4	$0.27 \pm 0.03$	(7)
Osinga et al.	20 to 120	600	$0.28 \pm 0.02$	(8)
Dvořák and Pašek	20 to 60		$0.28 \pm 0.02$	(9)
Scholten and Konvalinka	0 to 120	200	0.2 to 0.5	(10)
Chen and Yeh	20 to 80	760	$0.33 \pm 0.03$	(11)
Evans et al.	20 to 110		0.33 to 0.50	(12)
Present study	20	760	0.30	

TABLE 4

Review of Determined N<sub>2</sub>/Cu(s) Values at Limiting Coverage as Reported in the Literature

<sup>a</sup> By assuming  $n_s(Cu) = 1.70 \times 10^{19}$  atoms m<sup>-2</sup>.

where  $n_s$  denotes the number of surface atoms per unit area of powder.  $\theta$  values for pure copper powder ( $\theta_{Cu}$ ) have been reported many times in the literature, and values are compiled in Table 4. By accepting  $n_s(Cu) = 1.70 \times 10^{19}$  atoms m<sup>-2</sup>,  $\theta_{Cu} = 0.30$ seems to be a reasonable value at room temperature.

A reliable  $\theta$  value for pure nickel powder  $(\theta_{Ni})$  has not yet been found in the literature. Figure 5 presents the N<sub>2</sub> yield as a function of time from the reaction between N<sub>2</sub>O and nickel powder at selected temperatures. The  $Y_{N_2}$  values obtained increase with the reaction temperature. At room temperature,  $\theta_{Ni} = 1.63 \pm 0.10$  is found,



Reaction time (hr)

FIG. 5.  $N_2$  production as a function of time in the decomposition of  $N_2O$  on nickel powder at 700 Torr  $N_2O$  at various temperatures.

assuming  $n_s(Ni) = 1.54 \times 10^{19}$  atoms m<sup>-2</sup> (1). A ratio of 1.6 oxygen atoms to 1 surface Ni atom for reaction (2) is interesting. The radius of the oxygen ion (1.40 Å) is larger than the radius of the nickel atom (1.15 Å). It is impossible for more than one oxygen atom to adsorb on one surface nickel atom. Dell et al. have studied the interactions of  $O_2$  and of  $N_2O$  with Ni (17). They found that the adsorption limit of oxygen chemisorption on nickel powder increased with temperature. At 90 K this limit had a value of 1.66, and was greater than 2.0 at room temperature. An incorporation of adsorbed oxygen atoms to form subsurface oxide was suggested by them.

On the basis that  $\theta_{Cu}$  and  $\theta_{Ni}$  values do not change on alloying, the  $\theta$  value of any Cu-Ni alloy may be represented as

$$\theta = (1 - F_{\rm Ni})\theta_{\rm Cu} + F_{\rm Ni}\theta_{\rm Ni}.$$
 (4)

According to Eq. (3),  $\theta$  is the yield of  $N_2$  per surface metal atom on the alloy at limiting coverage, and hence

$$\theta = Y_{N_2}/[(1 - F_{N_i})n_s(Cu) + F_{N_i}n_s(N_i)].$$
 (5)

 $F_{\rm Ni}$ , the fraction of nickel on the alloy surface, may be obtained by combining Eqs. (4) and (5) to give

$$F_{\rm Ni}^2 - 10.4F_{\rm Ni} + (4.70 \times 10^{-19}Y_{\rm N_2} - 2.40) = 0,$$
 (6)

by accepting the above-mentioned  $n_s$  and  $\theta$  values for pure copper and nickel powders



FIG. 6. Summary of experimental  $F_{Ni}$  values as a function of  $X_{Ni}$  (solid line). Dashed line assumes  $F_{Ni} = X_{Ni}$ .  $\Box$ , Data from TPD;  $\bigcirc$ , data from SHC;  $\diamondsuit$ , data from N<sub>2</sub>O reaction;  $\bigcirc$ , data from Sinfelt *et al.* (5).

and expressing  $Y_{N_2}$  in units of molecules per square meter. Equation (6) has two roots. Only  $F_{N_i}$  values between 1 and 0 are acceptable.  $F_{N_i}$  values obtained from Eq. (6) for different  $X_{N_i}$  values are listed in Table 3.

Figure 6 summarizes experimental values of  $F_{Ni}$  as a function of  $X_{Ni}$ . A reasonable agreement among the data from the three described methods and the SHC data of Sinfelt *et al.* (5) is apparent. The solid line in the figure, which represents the measured surface composition of the alloy powders, is seen to run substantially lower than the dashed line which would be valid if the surface composition. Hence, segregation of copper atoms to the alloy surface during reduction (5, 16) is confirmed.

The agreement between the  $F_{Ni}$  data in Fig. 6 supports the assumption that the chemisorption stoichiometries of SHC and of N<sub>2</sub>O decomposition on pure copper and nickel powders are not drastically changed by alloying. However, the validity of the chemisorption stoichiometry does not warrant the conclusion that the chemical properties of the surface atoms remain the same. The TPD results in Fig. 2 clearly suggest that the binding strength between chemisorbed hydrogen atoms and surface nickel atoms decreases with decreasing  $F_{\rm Ni}$ .

The agreement demonstrated in Fig. 6 also supports the suggestion of Sinfelt *et al.* (5) that the strong hydrogen chemisorption should be used, instead of the total hydrogen chemisorption, to estimate the quantity of surface nickel atoms in Cu-Ni alloys.

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