Hydrogen Sorption and Exchange on Reduced–Oxide Nickel and Copper

D. A. CADENHEAD AND N. J. WAGNER*

*Department of Chemistry, State University of New York at Buffalo,
Buffalo, New York 14214*

Previously published results of hydrogen adsorption on specially prepared, reduced–oxide nickel and copper samples indicated unusually large amounts sorbed (1). By means of a series of adsorption and H_2–D_2 exchange studies on a variety of reduced oxide and heat sintered samples, these results have been shown to arise through fine pore and/or defect structure in all cases, coupled with the effects of trace impurities in the case of the copper samples. The fine pore and/or defect structure is shown to be enhanced by a special low-temperature reduction technique and is either destroyed by high-temperature heat treatment or avoided by reducing at a much higher initial temperature.

INTRODUCTION

The work described in this article was carried out in order to obtain satisfactory explanations for somewhat unusual results obtained during low-temperature hydrogen adsorption studies on nickel, copper and some copper-nickel alloys (1). Since the alloys raise certain unique questions, and since hydrogen adsorption (or the lack of it) has been well tabulated for pure samples of nickel and copper, only the latter substances will be dealt with here.

Adsorption of hydrogen on nickel was rapid at low pressures over the entire temperature range (−196 to 0°C) reaching a maximum amount adsorbed at between 10^{-3} and 5×10^{-3} Torr. These maximum values were unchanged even when the pressure was raised to 20 Torr and when plotted as an isobar, showed a maximum in the vicinity of −110°C, indicating the existence of both activated and nonactivated adsorption. The unusual behavior became apparent when the amount of hydrogen adsorbed was evaluated in terms of the number of hydrogen monolayers adsorbed

* Present Address: Department of Chemistry, Alliance College, Cambridge Springs, Pennsylvania.

based on nitrogen surface areas (−196°C), a 1:1 hydrogen to nickel atom ratio and equal representation of the 100, 110 and 111 nickel faces. When this was done, an apparent four monolayers of hydrogen were shown to be taken up at −196°C rather than the expected one monolayer. The indication of this result was that hydrogen could penetrate either fine-pore or defect structure inaccessible to nitrogen. We further deduced that the unusually large difference between the expected and obtained results was related to our use of a newly developed technique of controlled *in situ* oxide reduction in which over 99% of the entire reduction process was carried out at the lowest possible reduction temperature before raising the temperature of the sample to a predetermined maximum. We were able to partially confirm this theory by carrying out a high temperature, more drastic reduction on a similar oxide sample, after the manner of Roberts and Sykes (2), when the total amount of hydrogen adsorbed was reduced to the expected one monolayer.

Adsorption of hydrogen on copper was also observed where, in contrast to the behavior on nickel, a true maximum or

plateau value in the 10^{-3} Torr region was only observed at low temperatures, and the adsorption process was nonactivated. Once again, however, the amount of hydrogen adsorbed (almost one monolayer at $-196°C$) was the puzzling phenomenon. Others have reported hydrogen adsorption on similar materials (one-tenth monolayer at $100°C$) (3). It may well be that our special reduction technique could explain differences between our samples and other reduced–oxide materials, but it clearly failed to explain why such samples adsorb *any* hydrogen at low temperatures in contrast to the behavior reported for films (4). It was however suggested (1) that this aspect of the reduced–oxide copper materials could be explained in terms of trace impurities in the original preparative materials.

It would be easy to characterize the behavior of such samples as artifacts of reduction procedure and/or trace impurity effects. Restricting work to highly purified films (5) or filaments (6) might easily avoid such problems. However, the use of such granular materials (in both supported and unsupported forms) as practical industrial catalysts justifies a more detailed examination of the problems outlined above. The procedure we have adopted was to carry out a sequence of hydrogen and nitrogen adsorption plus H_2–D_2 exchange studies on a series of reduced–oxide samples, prepared such that both the amount and nature of the adsorbed hydrogen could be evaluated as a function of the sample treatment. In addition, similar studies were carried out on highly purified copper samples to evaluate the effects of trace impurities.

EXPERIMENTAL

Apparatus

Adsorption and exchange studies were carried out utilizing an all glass high-vacuum gravimetric adsorption system incorporating a Cahn R.G. microbalance. Further details of this system may be obtained by consulting Ref. (1). Particular care was taken to avoid the usual difficul-

ties associated with vacuum microbalance use through electrostatic, thermomolecular, or buoyancy effects. A precise description of the procedures used has also been published elsewhere (7).

Kinetic studies of H_2–D_2 exchange were conducted in the cell shown in Fig. 1. The cell was constructed of Pyrex glass and had a volume of approximately 125 cm³. Oxide samples were introduced through the hydrogen outlet line and reduced *in situ*. After reduction, the cell was evacuated and the sample cooled to some preselected temperature by immersion in a suitable liquid. After temperature equilibration was achieved, an 80 Torr pressure H_2–D_2 mixture (~1:1) was admitted to the cell. The lower stopcock of the doser was closed, and the doser was evacuated through the 10/30 joint after which the upper stopcock was closed. The cell and dewar were then attached to a Consolidated–Nier Isotope Ratio Mass Spectrometer (Model 21-291), and connecting lines to the doser were evacuated. Samples of gas from the cell were periodically collected in the 1 cm³ doser and admitted to the mass spectrometer for analysis. Such small samples allowed the pressure in the cell to remain relatively constant. Using this technique, the formation of HD as a function of time and temperature was measured for the nickel samples. Even with
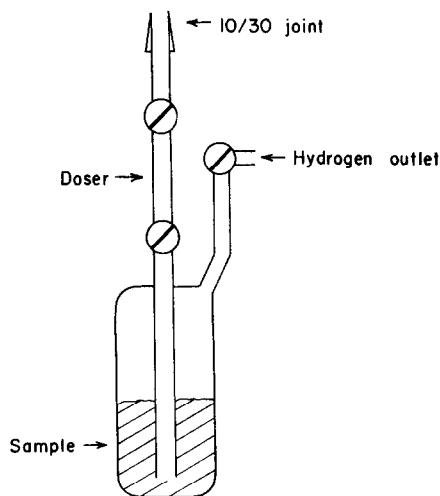

FIG. 1. Detail of H_2–D_2 exchange cell.

the small dead space of the cell however, attainment of equilibrium was relatively slow over copper samples. Thus the percentage of HD in the gas phase at 80 Torr and 0°C was only 0.2% after 2.5 hr, 2.5% after 26 hr and 29.1% after 72 hr. A considerable improvement in attainment of equilibrium mixtures for these copper samples was achieved by allowing equilibration at 80 Torr and the selected temperature for only 1 hr, then evacuating the cell to 10^{-2} Torr, and subsequently expanding this residue into a chamber at 10^{-5} Torr for analysis. All values were corrected for the amount of HD produced by the mass spectrometer filament (0.1 to 0.3%).

Adsorbates

99.95% pure *hydrogen* was further purified by passing it through a heated palladium diffusion cell (E. Bishop and Co., Model A–1–X). This hydrogen was stored and used for both sample reduction and adsorption studies. Hydrogen flow rates of up to 900 cm^3/min were possible with this arrangement. *Deuterium* used in exchange studies had a nominal purity of better than 99.5% pure and was used as supplied. *Nitrogen*, nominal purity, 99.95%, was further purified by passage through glass-bead traps cooled to liquid nitrogen temperatures.

Adsorbents

Copper and nickel samples were prepared from A.C.S. Grade $Cu(NO_3)_2 \cdot 3\ H_2O$ and $Ni(NO_3)_2 \cdot 6\ H_2O$, respectively, with A.C.S. Grade NH_4HCO_3 to form the basic carbonates, roasted at 400°C to form the oxides and finally reduced *in situ* in accordance with the procedure of Best and Russell (*8*). Detailed procedures for the oxide formation have been published elsewhere (*1, 9*). Detailed procedures for oxide reduction are given below.

High purity copper samples were prepared by electrodeposition (*10*) from A.C.S. Grade $Cu(NO_3)_2 \cdot 3\ H_2O$ and triple (quartz) distilled conductivity water. A 1 g sample was dissolved in 20 cm^3, A.C.S. reagent grade H_2SO_4 and heated to drive off the nitrate. The solution was then di-

luted with water and the copper was deposited slowly on a platinum cathode. The reaction was stopped before the deposition of copper was complete, and the copper deposit was washed with conductivity water. Approximately one-half of the copper deposit was then stripped from the electrode using 40% HNO_3 (A.C.S. Reagent Grade). This solution was then heated and condensed to approximately 10 cm^3. The sample in solution was then transferred to the vacuum microbalance sample holder and taken to dryness. It was subsequently oxidized at 340°C in an oxygen atmosphere for 6 hr then reduced at the same temperature for 64 hr, using a hydrogen flow rate of 450 cm^3/min.

Sample Analysis

Qualitative analysis of normal samples, utilizing an emission spectrograph indicated primary impurities in nickel and copper to be copper and nickel, respectively, though the copper sample also contained traces of iron. Quantitative analysis was carried out using electrodeposition techniques (*10*) to give total impurities by depositing copper in an acid media and nickel in a basic media. Minimum detectable impurity weights were limited by the balance used. Typical samples (1 g) were analyzed with Mettler HGT (minimum detectable weight change 0.1 mg). Purified copper samples, however, were analyzed using a Cahn R.H. microbalance (sensitivity $\pm\ 2\ \mu g$). The improved balance sensitivity coupled with an increase in original sample size from one to 9 g permitted the detection of much lower impurity levels.

Analysis of copper for nickel requires electrodeposition be carried out in basic media. Under such conditions both nickel and iron are deposited on the electrode as their reduction potentials in basic media are similar (*11*). Thus the final weight deposited due to impurities should include both iron and nickel. The composition of the $Cu(NO_3)_2 \cdot 3\ H_2O$ used to prepare copper samples indicates that the maximum impurity level of iron and nickel should be about equal and that the combined total should be about 140 ppm. This figure is in

good agreement with the electrodeposition results obtained on typical copper samples.

Final impurity levels in typical nickel and copper samples were 0.039 ± 0.010% and 0.016 ± 0.003%, respectively, while for purified copper samples a corresponding value was 0.0006 ± 0.0005%.

Preparative Techniques

1. Low temperature controlled reduction. As has already been indicated, the reduction procedure which produced the unusual effects reported, consists of a low-temperature controlled reduction procedure, aimed at producing as balanced a reduction process as possible (*1*). This was achieved by programming a slow temperature increase (10°/hr) for a furnace surrounding the sample hangdown tube of the vacuum microbalance system while flowing a stream of hydrogen over the sample itself. Reduction initiation was detected (in terms of a weight change) by the sensitive microbalance. At this time, the furnace temperature was held constant until virtually all (>99.9%) of the reduction had occurred, this part of the process taking approximately 10 hr. The furnace temperature was subsequently raised to 350°C for 12 hr, with an increased hydrogen flow to complete the reduction process. The adequacy of this procedure was checked for several samples by exposing them to hydrogen at temperatures up to 650°C with subsequent system evacuation, without further sample weight loss (i.e., less than 0.5 μg for a 500 mg sample).

2. High temperature initial reduction (fast reduction). An alternative reduction to the controlled process desorbed above was also used to reduce oxide samples based on that described by Roberts and Sykes (*2*). Essentially the metal oxides were heated in a vacuum to (say) 450°C. Hydrogen was then admitted to the system, and the weight loss followed as a function of time. Oscillation in the microbalance arising through the drastic pressure change on admitting the hydrogen, usually prevented weight readings for times less than 8 min from the initiation of reduction. Nevertheless, this first reading usually in-

dicated that, as far as weight loss was concerned, the reduction of the sample was better than 99% complete, although Roberts and Sykes indicate that much longer time periods were required for "complete" reduction of nickel oxide. To be consistent with this latter requirement, samples were held at 450°C for 96 hr with hydrogen flowing over the sample at 450 cm³/min. Typical weight loss values for a nickel sample with this procedure are shown in Table 1.

TABLE 1

REDUCTION OF NICKEL OXIDE AT 450°C AS A FUNCTION OF TIME IN A HYDROGEN ATMOSPHERE

Time elapsed	Weight loss (mg)	Cumulative weight loss (mg)
0	0.00	0.00
8 min	106.00	106.00
24 min	2.00	108.00
4 hr	2.00	110.00
30 hr	0.70	110.70
52 hr	0.10	110.80
60 hr	0.02	110.82
96 hr	0.10	110.92

Following this procedure the system was evacuated, the temperature lowered to −196°C, and the amounts of hydrogen and nitrogen adsorption measured.

We soon became aware that this "fast" initial reduction technique could easily result in temperatures well above that of the furnace, particularly for the highly exothermic cupric oxide reduction process. Clearly the reduction process was not under control and could be observed flashing through portions of the granular oxide producing the long recognized "glowing" phenomenon (*12, 13*). It should be noted that "glowing" was never observed when the initial low temperature reduction procedure (Technique 1) was followed.

3. High-temperature sintering of metal samples. Initially a metal sample would be produced from the appropriate oxide, using the reduction procedure described on Technique 1, and placed in the gravimetric adsorption system.

After measuring hydrogen adsorption at —196°C and evaluating the sample nitrogen surface area, the sample was reevacuated, the temperature raised to 500°C for 18 hr, and the amount of hydrogen and nitrogen adsorption again measured. This process was then repeated with the sample held at 650°C for 18 hr.

RESULTS

Samples of nickel and copper prepared by the low-temperature reduction technique (Technique 1) were subjected to high temperature sintering treatments at 500 and 650°C (Technique 3). After each treatment, the amounts of hydrogen and nitrogen adsorbed at —196°C were measured. The results are given in Table 2 with the final column expressing the hydrogen adsorption in terms of the number of monolayers adsorbed.

Reduction of the oxides of nickel and copper were also carried out by Technique 2 with the extent of hydrogen and nitrogen adsorption on the resultant samples being listed in Table 3, where again the final column expresses the hydrogen adsorption in terms of the number of monolayers adsorbed.

The high-purity copper sample, prepared as previously described was evacuated *in situ* and then heat-treated at 644 ± 10°C for 20 hr. The temperature was then lowered to —196°C under vacuum and both hydrogen and nitrogen adsorption recorded

TABLE 2

DATA OBTAINED IN HIGH TEMPERATURE TREATMENTS OF NICKEL AND COPPER (TECHNIQUE 3)

Sample	Temperature of treatment (°C)	Surface area measured with nitrogen (m²/g)	Hydrogen adsorption at —196°C in (g)	Number of monolayers of hydrogen adsorbed
Nickel	350	0.623	70.0	4.3
	500	0.445	44.0	3.8
	650	0.296	11.0	1.4
Copper	350	0.397	11.0	1.0
	500	0.324	4.5	0.49
	650	0.317	3.5	0.39

TABLE 3

DATA OBTAINED IN FAST REDUCTION OF NICKEL AND COPPER (TECHNIQUE 2)

Sample	Temperature of treatment (°C)	Surface area measured with nitrogen (m²/g)	Hydrogen adsorption at —196°C in (g)	Number of monolayers of hydrogen adsorbed
Nickel	450	0.81	22.0	0.96
Copper	450	0.33	4.0	0.43
Purified Copper Sample	350 644	0.11	0.0	0.0

as before. The results are also given in Table 3.

Hydrogen–deuterium exchange studies were carried out on the various samples to provide information on the nature of the adsorbed species. Studies carried out initially (1) in the microbalance chamber proved inconclusive, due to the large dead-space, and necessitated the use of the cell shown in Fig. 1. Such experiments were carried out over a wide temperature range —196 to 0°C for samples of nickel, copper, and purified copper.

Nickel showed exchange over a wide temperature range, the rate becoming too fast for accurate measurement above 0°C. Using the expansion technique at 10^{-5} Torr, copper showed a significant ability to promote exchange at 0°C, though this ability diminished rapidly as the temperature was lowered. Typically, the percentage of HD fell from 48.7% at 0°C to 23.3% at —78°C to 1.7% at —196°C. This should be compared with 29.1% HD at 80 Torr and 0°C after 72 hr in the gas phase over a copper sample. Purified copper, even after 75 hr at 80 Torr and 0°C showed no ability to promote exchange but could be made to do so in the temperature range 250–300°C.

The activation energies for exchange on these samples were determined by assuming the process to be first order and following the treatment of Mikovsky, Boudart, and Taylor (14). The Arrhenius plot for a regular copper sample over the temperature range 20 to 35°C is shown in Fig. 2. The resultant activation energy was
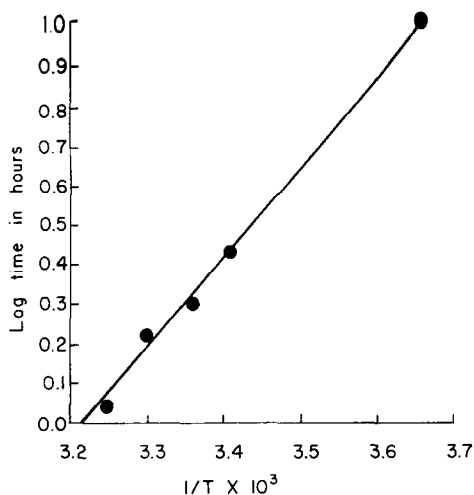
FIG. 2. Plot of log (time of reaction) vs $1/T$ for constant H_2–D_2 conversion on a typical copper sample over the temperature range 0–35°C.

10 ± 2 kcal/mole. For nickel over the range -17.5 to $0°C$, the corresponding value was 2 ± 2 kcal/mole, while for the purified copper (248 to 270°C) it was 17 ± 2 kcal/mole.

DISCUSSION

(a) Nickel Samples

The measured sorption of hydrogen on typical nickel samples amounted to about 4 monolayers at $-196°C$, rising to a maximum (6 monolayers) at $-110°C$, and subsequently decreasing back to about 4 monolayers once again at $0°C$. On lowering the temperature to $-196°C$, the amount adsorbed increased steadily and resulted in an increase in the amount of hydrogen originally adsorbed at $-196°C$. Removal of this additional hydrogen was only achieved through outgassing for several hours at elevated temperatures (1). Adsorption clearly involved both an activated and a nonactivated process. Furthermore, the considerable attention paid to reduction procedures makes residual surface oxygen a highly unlikely cause of the activated adsorption.

Ponec and Knor (15) observed a similar variation in hydrogen coverage on nickel films over the same temperature range and attributed it to multiple binding sites.

Starting at $-196°C$, they observed an increase in hydrogen adsorption as the temperature of their film was raised. This increase in hydrogen adsorption was attributed to diffusion of hydrogen from accessible surface sites to less accessible sites where it was adsorbed. The accessible surface sites were thus freed for further adsorption, accounting for the initial increase in hydrogen adsorption as the temperature was increased. At higher temperatures $(-100°C)$, the more accessible surface sites with their smaller heats of adsorption again desorbed hydrogen accounting for the decrease in adsorption at high temperatures. Thus, Ponec and Knor were able to explain the temperature dependence of hydrogen adsorption on the basis of diffusion into less accessible sites and adsorption from low energy sites.

Kavtaradze (16) chose to explain similar data on the basis of strongly and weakly bonded portions of the adsorbed layer being composed, respectively, of atomic and molecular forms of chemisorbed hydrogen. The amounts of the two forms of hydrogen existing on the nickel surface would be strongly dependent upon the temperature.

Simon et al. (17, 18) have proposed a similar scheme for adsorption on nickel ribbons at 27°C with equilibrium existing between the weakly bound state of the hydrogen molecule and the strongly bound hydrogen atom. Simon (19) has further proposed that temperature effects upon the equilibrium between adsorbed atomic and molecular hydrogen together with surface diffusion into less accessible sites might well explain the hydrogen adsorption maxima at $-100°C$.

Thus it seems that most explanations of the temperature dependence of hydrogen adsorption are based upon diffusion into less accessible sites, or equilibrium between various forms of hydrogen, or a combination of both. In our own case, we observed the sorption of 4 monolayers at $-196°C$ indicating the ability of hydrogen atoms and/or molecules to penetrate to regions inaccessible to nitrogen molecules. At $-196°C$, three-fourths of the total amount sorbed fell into this classification. More-

over, the relatively rapid times of equili-
bration for sorption on our samples (<30
min) indicates that the extra amount is not
dissolved in the bulk nickel. The ability of
nickel at —196°C to exchange hydrogen, in
agreement with the results of others (20),
shows that at this temperature the hydro-
gen is at least in part dissociatively ad-
sorbed. While the isobar slope is still nega-
tive at —196°C, this temperature lies close
to a minimum (see Fig. 6, Ref. (1)) and
suggests that a significant fraction of the
amount sorbed is a result of an activated
process. The additional two monolayers
sorbed between —196° and —110°C are
clearly a result of an activated sorption
process.

Others (3, 21) have reported sorption in
excess of a monolayer on reduced-oxide
nickel, but no such observations have been
made at low temperatures. We believe that
the magnitude of the effects we observed
relates to the unique controlled low-tem-
perature reduction technique employed.
Confirmation of this is partially provided
by the initial high-temperature reduction
(Technique 2) results where the final sam-
ple adsorbed 0.96 monolayers of hydrogen
(Table 3). Further confirmation is pro-
vided by the reduction of the amount sorbed
at —196°C for normal samples from 4 to
1.3 monolayers by high temperature sinter-
ing (Technique 3). Such sintering of a
previously reduced sample would tend to
destroy existing fine pore and/or defect
structure, while an initial high temperature
reduction would prevent the formation of
such structure in the first place. It would
appear that when reduction is initiated
and primarily carried out at lower temper-
atures, nucleation of the metallic nickel
lattice occurs at an increased number of
sites resulting in a relatively large number
of crystallites and correspondingly high
fine pore/defect structure. As the initial
reduction temperature is raised, sample
temperatures may frequently exceed those
of the furnace. In such cases, the metal lat-
tice formation takes place rapidly from a
smaller number of sites resulting in a rela-
tive absence of fine pore or high defect
structure.

Apart from the amounts of hydrogen
sorbed, our nickel samples showed com-
parable behavior to those preferred by al-
ternative techniques including evaporated
films and filaments, suggesting that the
trace copper impurities have little or no
effect on either hydrogen adsorption or ex-
change. Eley and Norton (22) have mea-
sured H_2–D_2 exchange on nickel wires over
the temperature range —73 to 27°C and
found an activation energy of 2.36 kcal/
mole in good agreement with our observa-
tion. Zhavoronkova, et al. (20) measured
H_2–D_2 exchange on nickel films over an
even wider temperature range (—196–
100°C) and found that from —196 to
—130°C, the activation energy was close
to zero, while from —130 to —30°C, it
jumped to 3.2 kcal/mole. This difference in
activation energy was ascribed to a change
in mechanism at —130°C. At higher tem-
peratures (—20–100°C), they found an ir-
reversible drop in activity attributed to
poisoning of the surface with more firmly
bonded hydrogen resulting in an increase
in activation energy to 7.5 kcal/mole. The
onset of a second type of activated adsorp-
tion observed in our work (1) around 0°C
might well be explained in this manner
while the low temperature (—196–110°C)
activated adsorption occurs in the region
of the proposed mechanism change. More
recently, Gasser et al. (23) have reported
hydrogen exchange on a nickel filament as
becoming observable at —130°C but under-
going a rapid rise in rates of equilibration
above —40°C.

(b) Copper Samples

While the adsorption of atomic hydrogen
at low temperature has been observed on
copper films, that of molecular hydrogen
has not been observed to any appreciable
extent (4, 15, 24, 25). Moreover, Taylor
et al. (14) have shown that temperatures of
300°C or greater are required to obtain sig-
nificant exchange on copper foils. The en-
hanced activity at high temperatures is
believed to occur because of surface bond
formation with vacant d orbitals in the
metal, the vacant d orbitals being created
through a d–s electron promotion. In con-

trast, it would seem that typical copper samples used in this investigation were somehow adsorbing molecular hydrogen at low temperatures.

Shield and Russell (26) did observe the heats of adsorption of molecular hydrogen on granular copper at room temperatures and proposed that trace impurities in the copper were responsible for the adsorption. In our case, it seemed reasonable to try to separate the effects of surface structure and impurity content for the copper samples. The results of the fast reduction procedure (Technique 2) listed in Table 3 show only 0.43 monolayers still adsorbed on the sample at $-196°C$. By comparison Takeuchi et al. (3) found 0.1 monolayers at 100°C on reduced oxide copper samples prepared by a fast reduction technique at 200°C.

The alternative procedure of sintering a previously reduced sample (Technique 3) was also adopted. Examination of Table 2 shows that exposure to temperatures between 500 and 600°C results in a significant reduction in the amount of hydrogen taken up (from 1.0 to 0.49 monolayers). Clearly, as is the case with nickel, fine pore/defect structure can exaggerate the hydrogen/nitrogen adsorption ratio.

The nature of the hydrogen adsorption is indicated by the ability of such samples to exchange hydrogen. Allowing the sample to exchange with the gas phase at 80 Torr and 0°C failed to achieve an equilibrium mixture in 72 hr, though exchange clearly had taken place. The technique evolved of evacuating the exchange cell to 10^{-2} Torr and subsequently expanding residual plus adsorbed gas into a lower pressure chamber was designed to bypass a limiting desorption step. The results clearly indicate that equilibration at the copper surface has been achieved in less than 1 hr at 0°C, though at lower temperatures this was not the case. The picture presented bears considerable resemblance to that described by Pritchard for the adsorption of *atomic* hydrogen on pure copper films (4, 25). He reports that such atoms are immobile at $-196°C$, mobile but not desorbed at $-78°C$, while at 0°C such atoms are both

mobile and capable of exchange with the gas phase. Provided our copper samples could achieve the dissociative adsorption of the molecular hydrogen, their behavior is consistent with a slightly enhanced hydrogen atom-metal surface interaction. The activation energy on a typical copper sample of 10 ± 2 kcal/mole at about 25°C would appear to be a measure of the energy required for hydrogen atom surface migration.

The ability of these copper samples to dissociatively adsorb hydrogen can only be explained in terms of transition metal impurities. That this is the case is clearly indicated by the failure of the purified copper samples (approximately 6 ppm impurities) to either adsorb or exchange hydrogen under similar conditions. The activation energy of exchange at much higher temperatures (17 ± 2 kcal/mole at 250°C) is probably determined by the initial adsorption process on a "clean" copper surface. The value is comparable with that obtained by Taylor, et al. on copper foils (23.1 kcal/mole at 330°C). Precisely how impurities enable typical copper samples to absorb approximately 0.4 monolayers hydrogen at $-196°C$ or to promote exchange is a matter of conjecture. It may be that the *surface* impurity content is much higher than that in the bulk. Regrettably, facilities for checking this possibility were not available. The suggestion of Campbell and Emmett (27) that dissociative hydrogen adsorption could take place on a combined copper atom-nickel atom site is particularly interesting in this regard. Finally the possibility of tailor-making copper catalysts by "doping" with transition-metal impurities in the low concentration range would appear to be a very real one.

REFERENCES

1. CADENHEAD, D. A., AND WAGNER, N. J., J. Phys. Chem. 72, 2775 (1968).

2. ROBERTS, M. W., AND SYKES, K. W., *Trans. Faraday Soc.* **54**, 548 (1958).

3. TAKEUCHI, T., TAKABATAKE, T., SAKAGUCHI, M., AND MYOSHI, I., *Bull. Soc. Chem. Jap.* **35**, 1390 (1962).

4. PRITCHARD, J., *Trans. Faraday Soc.* **59**, 437 (1963).

5. DELCHAR, T. A., AND TOMPKINS, F. C., *Trans. Faraday Soc.* **64**, 1915 (1968).

6. GASSER, R. P. H., ROBERTS, K., AND STEVENS, A. J., *Trans. Faraday Soc.* **65**, 3105 (1969).

7. CADENHEAD, D. A., AND WAGNER, N. J., *Vac. Microbalance Tech.* **8**, (1970).

8. BEST, J. R., AND RUSSELL, W. W., *J. Amer. Chem. Soc.* **76**, 838 (1954).

9. WAGNER, N. J., Ph.D. Thesis, State University of New York at Buffalo, May 1970.

10. PIERCE, W. C., HAENISCH, E. L., AND SAWYER, D. T., "Quantitative Analysis," p. 447. John Wiley and Sons, Inc., New York, 1960.

11. LATIMER, W. M., "Oxidation Potentials," Prentice Hall, New York, 2nd Edition, 1952.

12. WRIGHT, C. R. A., LUFF, A. P., AND RENNIE, E. H., *J. Chem. Soc.* 475 (1879).

13. HALL, W. K., AND SCHOLTUS, N. A., *Trans. Faraday Soc.* **59**, 969 (1963).

14. MIKOVSKY, R. J., BOUDART, M., AND TAYLOR, H. S., *J. Amer. Chem. Soc.* **76**, 3814 (1954).

15. PONEC, V., AND KNOR, Z., *Actes. Int. Congr. Catal. 2nd P. 1960* **1**, 195 (1961).

16. KAVTARADZE, N. N., *J. Res. Inst. Catal. Hokkaido Univ.* **3**, 196 (1966).

17. LICHTMAN, D., SIMON, F. N., AND KIRST, T. R., *Surface Sci.* **9**, 325 (1968).

18. SIMON, F. N., LICHTMAN, D., AND KIRST, T. R., *Surface Sci.* **12**, 299 (1968).

19. SIMON, F. N., private communication.

20. ZHAVORONKOVA, K. N., BORESKOV, G. K., AND KAKIPELOV, V. N., *Kinetics Catal.* (USSR) **8**, 1714 (1967).

21. HALL, W. K., CHESELSKE, F. J., AND LUTINSKI, F. E., *Actes Int. Congr. Catal., 2nd P. 1960* **2**, 2199 (1961).

22. ELEY, D. D., AND NORTON, P. R., *Discuss. Faraday Soc.* **41**, 135 (1966).

23. GASSER, R. P. H., ROBERTS, K., AND STEVENS, A. J., *Surface Sci.* **20**, 123 (1970).

24. LEE, R. N., AND FARNSWORTH, H. E., *Surface Sci.* **3**, 461 (1965).

25. PRITCHARD, J., AND TOMPKINS, F. C., *Trans. Faraday Soc.* **56**, 540 (1960).

26. SHIELD, L. S., AND RUSSELL, W. W., *J. Phys. Chem.* **64**, 1592 (1960).

27. CAMPBELL, J. S., AND EMMETT, P. H., *J. Catal.* **7**, 252 (1967).