

Interaction of Phosphorus Vapor with Hydrogen-Covered Evaporated Nickel Films

K. C. CAMPBELL

Department of Chemistry, University of Glasgow, Glasgow, G12 8QQ, Scotland

Received September 1, 1971

The amount of phosphorus taken up by nickel films was found to be many times greater than could be accommodated on the sites available for hydrogen chemisorption. Phosphorus uptake has been ascribed to a bulk interaction and the phase Ni₃P was identified by electron diffraction. Displacement of chemisorbed hydrogen from nickel was observed to be incomplete. The amount remaining adsorbed was dependent on the conditions of preparation of the films, but not on the film weights. The results are interpreted by a model analogous with that for the oxidation of nickel at ambient temperatures.

INTRODUCTION

The poisoning of metal catalysts by compounds of group 5 and 6 elements in unsaturated valency states is well known (1). The interaction of the poison molecules has been deduced to be by donor covalency of the lone pair of the nonmetal to the *d*-band of the metal (2). The strength of such a bond is usually sufficient for the poisoning action to be indiscriminate, although examples of beneficial poisoning are known in which the poisoning action is selective. This selectivity may be for one constituent of a mixture (3), or it may appear as a marked alteration of product distributions in parallel or consecutive reactions (4).

As an alternative to the general poisoning of adsorption sites, it was considered that an approach of selectivity based on differential poisoning of crystal faces merited study. The use as poisons of molecules whose shape caused their adsorption to be sensitive to surface site geometry would have a marked effect on structure-sensitive or *demanding* reactions (5) requiring the same surface geometry. The present work is concerned with adsorption studies relating to the poisoning of a nickel surface

bearing adsorbed hydrogen. Tetrahedral P₄ molecules were chosen as the poison species, not because of any expectation that they would remain intact on adsorption, but because their uptake was likely to be geometry-controlled at the point of entry to the surface. In this connection the hexagonal pattern of nickel atoms on the (111) plane would be expected to be a suitable arrangement, with an interatomic distance (2.49 Å) sufficiently similar to the P-P distance in the P₄ molecule (2.21 Å) (6).

EXPERIMENTAL METHODS

Films were prepared and adsorption studies made in a vacuum apparatus pumped by a mercury diffusion pump and divided into sections by greased stopcocks. The film vessel was protected by a spiral trap cooled in liquid nitrogen, and could be isolated from the rest of the apparatus by a mercury cut off.

Materials for adsorption. Impurities were removed from cylinder hydrogen by allowing it to diffuse through a heated palladium-silver alloy thimble. White phosphorus was purified by vacuum distillation into break-seal tubes which were stored in

the dark until required for use. In the radiochemical studies of displacement, ^{32}P in the form of neutron-irradiated red phosphorus was obtained from the Atomic Energy Research Establishment, Harwell, with an initial activity of $25 \mu\text{Ci}/\text{mg}$. Conversion to white phosphorus was brought about by heating it at 400°C in vacuum for several hours: the white phosphorus distilled into break-seal tubes as it was formed.

Nickel films. Nickel wire, 0.5 mm diameter, was supplied by Johnson, Matthey & Co. Ltd. Because nickel was known to be a difficult metal to degas (7), it was subjected to the following treatment. One-meter lengths were heated electrically in vacuum for 12 hr by a current of 4.0 A. The current was then gradually increased until an appreciable nickel film was formed on the walls of the vessel. After cooling, the wire was removed from the apparatus.

To produce a film for an adsorption experiment, a 120-mm loop of this pre-treated wire was connected via tungsten seals into a 20-mm diameter cylindrical Pyrex vessel, to which was attached a phosphorus break-seal tube. The vessel was maintained under vacuum for several hours at 500°C and the filament again was heated to just below evaporation temperature for the last hour of this degassing period. The film was formed by increasing the current to 6.5 A, with the vessel cooled in an ice-water bath. The spiral trap was surrounded by liquid nitrogen and the mercury cut off closed while deposition took place. The background pressure during evaporation was not determined, but a marked gettering action by the first nickel deposited would be expected under these evaporation conditions. Evaporation rates were in the range 0.35 to 0.6 mg/min, onto a geometric area of about 60 cm^2 .

Measurement of adsorption and displacement. Adsorption studies were made at 20°C , immediately after film deposition had been completed. Quantities of hydrogen in the range 0–5 μmoles were measured using a McLeod gauge giving a precision which varied from $\pm 0.07\%$ for 5 μmoles to $\pm 1\%$ for the smallest quantities meas-

ured. Hydrogen remaining in the gas phase after adsorption was returned, by a Töpler pump, to the same McLeod gauge for measurement. It was established that no hydrogen was desorbed when the film was allowed to stand at 20°C .

In several experiments the film was evaporated in the presence of hydrogen, as in a previous study (8). The initial pressure of hydrogen was in the range 10^{-1} to 2.5×10^{-1} Torr and fell to not less than 2.5×10^{-3} Torr as it was taken up by the film, except for films B and D. For these, the evaporation was deliberately continued after all the hydrogen had been taken up. A current of 7.3 A was used to bring about evaporation in the presence of hydrogen and it was not necessary to reduce this unless the pressure fell below about 10^{-3} Torr. Mean evaporation rates in the range 0.5 to 0.8 mg/min were obtained.

To bring about hydrogen displacement, the break-seal of the tube containing the phosphorus was broken by a magnetically operated steel ball. The temperature of the phosphorus was maintained at 0°C to reduce its saturated vapor pressure to about 4×10^{-3} Torr. The hydrogen displaced when the phosphorus vapor interacted with the film was transferred to the McLeod gauge for measurement. In the radiochemical studies the arrival of radioactive phosphorus on the film was detected with a Mullard MX133 G.M. tube arranged parallel to the film vessel at a distance of 75 mm. The counter was connected to an Ekco N558 probe unit and Panax D657 scaler. Count rates were corrected for background and, in experiments of more than 4-hr duration, for decay assuming the half-life of ^{32}P to be 14.3 days.

The corrected count rates gave a relative measure of the amount of phosphorus on the film at various times and at the end of the experiment. To relate these to absolute amounts of phosphorus, the total phosphorus uptake was estimated as follows. The film was dissolved in 25 ml 10 M nitric acid. A similar solution was prepared from a weighed amount of the original radioactive red phosphorus. The activities of suitably diluted aliquots of the two

solutions were compared using a Mullard MX124/01 liquid counter with the ancillary electronic equipment described above.

Electron microscopy. Platinum-iridium alloy mounts bearing an evaporated silicon monoxide film were arranged within the horizontal film vessel, so that a sample of the film was deposited on these as well as on the walls of the vessel. They were subjected to the same adsorption and displacement treatment as the main film. The specimens obtained were examined in a Siemens Elmiskop 1A electron microscope using 80 kV electrons. In the electron-diffraction measurements, a thallium chloride diffraction pattern was used as a standard to enable lattice spacings to be computed.

RESULTS

The amount of hydrogen adsorbed per milligram of nickel was greater for films deposited in hydrogen ($0.22 \pm 0.02 \mu\text{mole}/\text{mg}$) than for those deposited in vacuum, or in amounts of hydrogen inadequate to satisfy the adsorption requirements ($0.15 \pm 0.02 \mu\text{mole}/\text{mg}$).

Displacement of adsorbed hydrogen by phosphorus from nickel films at 20°C was incomplete. The amount of hydrogen retained (Table 1) was dependent on the method of film preparation rather than the degree of surface coverage. Thus, films deposited in vacuum (C and E) retained

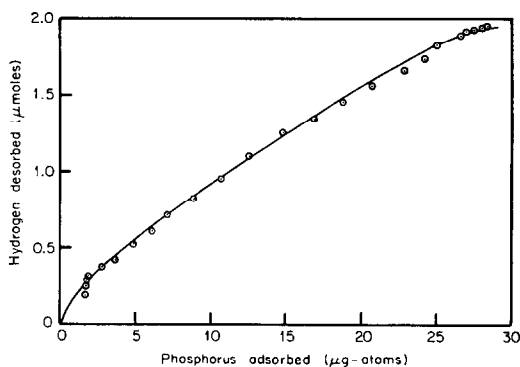


FIG. 1. Displacement of hydrogen from a nickel film by phosphorus (film A).

more of their hydrogen than those which had been deposited in excess hydrogen (A and F-J), but the two films deposited in hydrogen to incomplete coverage (B and D) were similar in their retention behavior to vacuum-deposited films.

By means of the radiochemical tracer technique it was possible to follow the course of the displacement. Fig. 1 shows the relationship between phosphorus uptake and hydrogen displacement for film A, upon which hydrogen had been adsorbed to saturation. There was an almost-linear relationship over the main course of the displacement, with a gradient which indicated the uptake of many atoms of phosphorus for each hydrogen molecule

TABLE 1
HYDROGEN ADSORPTION ON NICKEL FILMS AT 20°C AND ITS DISPLACEMENT BY PHOSPHORUS VAPOR

Film	Wt (mg)	Evaporation conditions	Hydrogen coverage (%)	Hydrogen uptake (μmoles)	Hydrogen displaced (μmoles)	Retention (%)	Displacement ratio P:H atoms	Atomic % phosphorus
A	10.5	Hydrogen	100	2.57	1.96	23.7	7.7	13.8
B	22.6	Hydrogen	80	3.30	1.21	50.5 ^a	6.3	6.5
C	11.8	Vacuum	100	1.75	0.73	58.3	11.4	5.3
D	44.6	Hydrogen	68	4.86	0.66	58.7 ^a	Hydrogen displaced by inactive phosphorus	
E	7.7	Vacuum	100	0.99	0.41	58.6		
F	7.0	Hydrogen	100	1.54	1.17	24.0		
G	4.7	Hydrogen	100	0.90	0.74	17.8		
H	15.7	Hydrogen	100	3.49	3.01	13.8		
J	16.3	Hydrogen	100	3.89	3.47	10.8		
K	9.0	(see discussion)	100	2.43	2.19	9.9		

^a Expressed as a percentage of the estimated adsorptive capacity.

displaced. A greater hydrogen displacement by a given amount of phosphorus was observed in the early stages of the displacement. The measured slope corresponded to 0.7 hydrogen molecules displaced/phosphorus atom, but it is doubtful if much significance can be claimed for this figure because of the large statistical counting error to which it is subject. The displacement took 167 min.

Corresponding results for a film incompletely covered with hydrogen (film B) are shown in Fig. 2. These differ from the results for saturated films in the respect that a delay period was observed during which phosphorus uptake produced no hydrogen displacement. When displacement commenced, its stoichiometry was similar to that of the saturated film. Phosphorus arrived on the films at a constant rate with respect to time and when displacement of hydrogen began it also was strictly linear with time; hence the coverage could be estimated from the delay period to be 80%. Displacement of hydrogen ceased 254 min after phosphorus was first admitted to the film. Phosphorus uptake on both of these films appeared to be completed when no further hydrogen was displaced, but this was investigated more fully with film C which was exposed to phosphorus vapor for a period of 8 hr. The manner in which the decay-corrected count rate

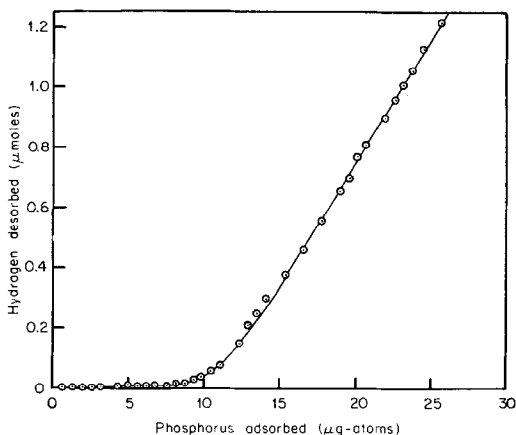


Fig. 2. Displacement of hydrogen by phosphorus from a partially hydrogen-covered nickel film (film B).

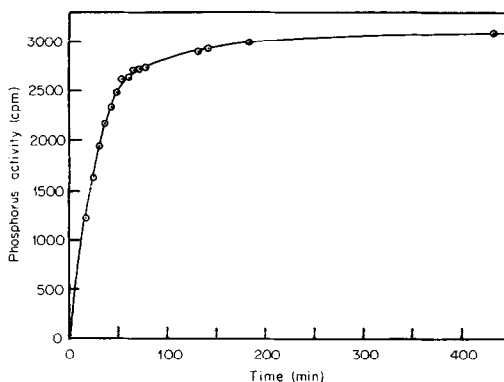


Fig. 3. Phosphorus uptake on a nickel film as a function of time of exposure to the vapor. Hydrogen displacement ceased after 52 min (film C).

varied with time is shown in Fig. 3, which reveals that phosphorus uptake continued after hydrogen displacement had ceased, but at a markedly reduced rate. On this vacuum-deposited film the displacement of hydrogen was completed much more rapidly than on films A and B.

Electron microscopic examination of film

TABLE 2
INTERPLANAR SPACINGS OBTAINED FROM
ELECTRON DIFFRACTION BY A
PHOSPHORUS-TREATED
NICKEL FILM

Observed spacing (Å)	Ni ₂ P spacings (Å)	hkl
5.13	5.07 ^a	100
3.43	3.37 ^a	001
2.82	2.81 ^a	101
2.53	2.54 ^a	200
2.20	2.21	111
2.04	2.03	201
1.93	1.92	120
1.69	1.69	300, 002
1.67	1.67	121
1.41	1.41	310
1.29	1.30	311
1.27	1.27	212
1.19	1.19	302
1.09	1.10	231
	1.08	132

^a These spacings were calculated from the hexagonal unit cell dimensions (9). The remainder are from reference (10).

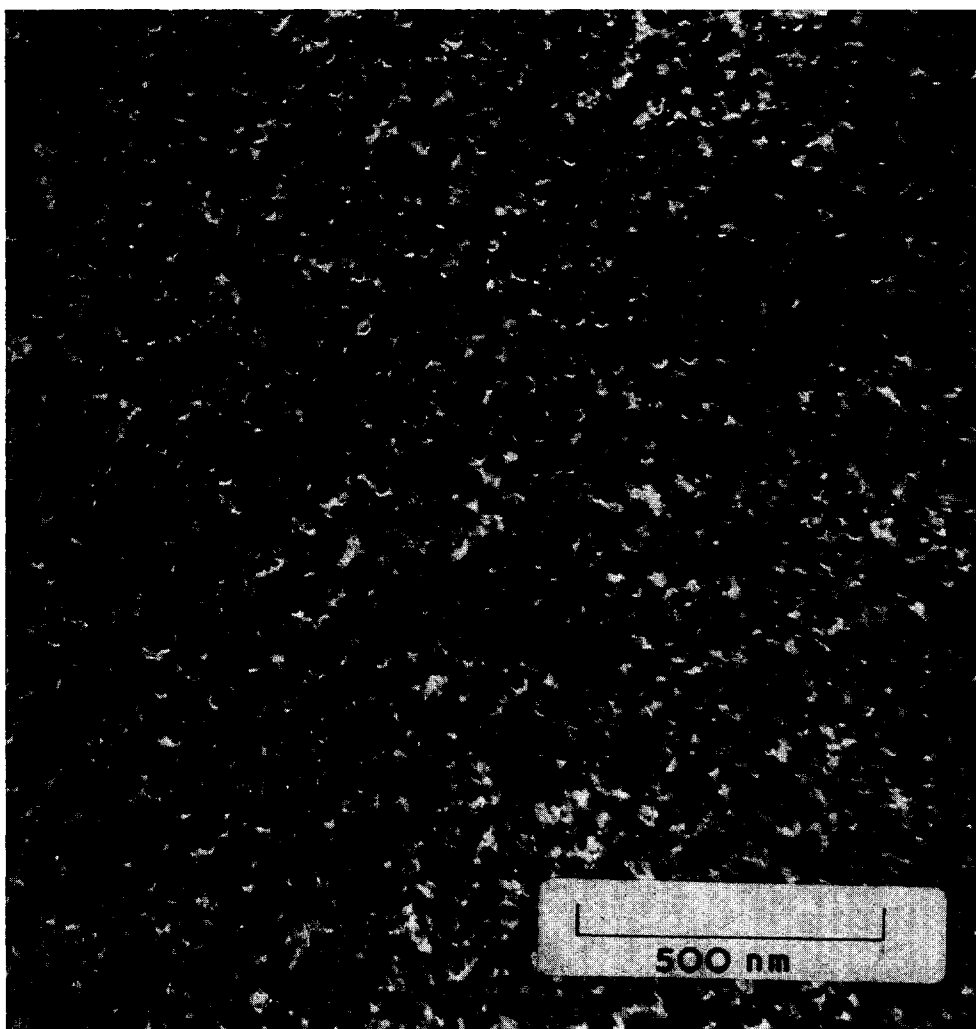


FIG. 4. Electron micrograph of a nickel film from which adsorbed hydrogen had been displaced by phosphorus.

samples removed at the completion of hydrogen displacement gave micrographs of which Fig. 4 is typical. Electron diffraction produced a series of rings which indicated random orientation of crystallites and spacings appropriate to metallic nickel. Only films which had received a prolonged exposure to phosphorus vapor showed different spacings. One such film was observed to crystallize under the influence of the electron beam, as shown in Fig. 5. Grain boundaries between the crystallites can be seen clearly, and the effect of this larger crystallinity was shown in the diffraction

pattern. The diffraction pattern showed the same spacings as a specimen prepared by ultrasonic dispersion of part of the main film taken from the walls of the vessel. These spacings can be assigned to the compound Ni_2P as shown in Table 2.

DISCUSSION

The results of the radiotracer experiments reveal that the amount of phosphorus required for the displacement is many times greater than would be needed to saturate the adsorption sites. Thus it is clear that the interaction of the phosphorus is not limited

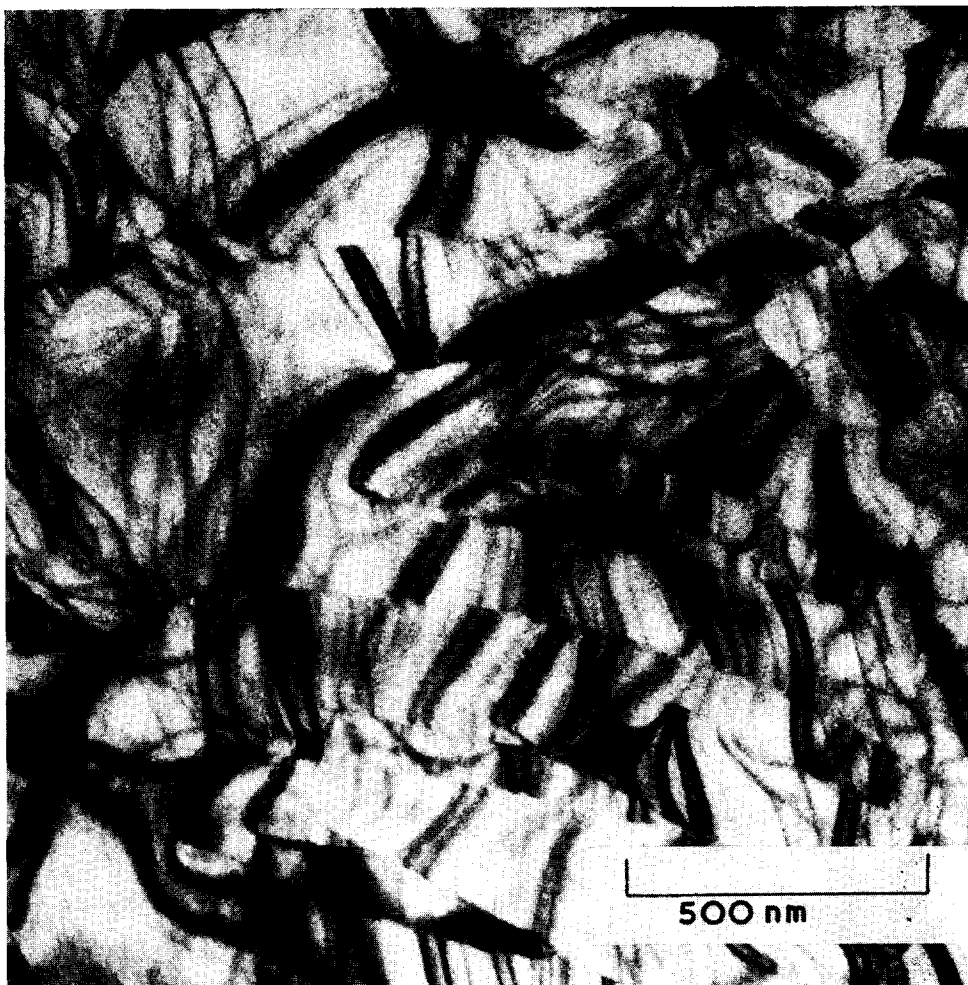


Fig. 5. Electron micrograph of a nickel film after prolonged exposure to phosphorus vapor, and recrystallization.

to the surface, but that there must be incorporation into the bulk to the extent of between 10 and 20 atomic layers of nickel. The initially greater release of hydrogen, relative to the phosphorus uptake, shown in Fig. 1 possibly indicates that the first action of the phosphorus is one of surface displacement. Evidently, from this adsorbed state easy access to several layers of bulk nickel is possible. It is interesting to note that surface adsorption and displacement is not completed before this occurs, but that the incorporation proceeds while the surface displacement is being extended. Furthermore, Fig. 3 shows that the part of the phosphorus uptake which oc-

curs readily is almost complete when hydrogen displacement ceases. Further incorporation of phosphorus is much more difficult.

With a partially hydrogen-covered nickel film (Fig. 2), the delay period and the absence of an initially greater rate of displacement is ascribed to readsorption on vacant sites of hydrogen displaced in the early stages.

It may be concluded that the phosphorus forms a separate bulk phase, and this is supported by the electron diffraction work which gives a clear indication that this is the compound Ni_2P .

Valuable comparisons can be made be-

tween the behavior of phosphorus in the present work and the oxidation of many metals at ambient temperatures. Thus, for example, the oxidation of copper at 18°C has been observed to proceed rapidly to form a surface film approximately 85 Å thick but oxidation beyond this was very slow (11). The graph of the oxidation rate resembled Fig. 3 in form. Using films of iron in the temperature range -195 to 60°C, Roberts (12) has observed the formation of six to 10 layers of Fe₂O₃ even at -195°C. The kinetics of growth of similar oxide layers has recently been studied (13). On nickel films rapid adsorption of oxygen has been observed, followed by a slow uptake resulting in the formation of a nickel oxide film 10-100 Å thick (14). Klemperer and Stone (15) observed multi-layer coverages for oxygen adsorption but with an additional feature, namely the regeneration of the capacity of the surface to adsorb oxygen at 18°C after it had been heated to 200°C. This was interpreted as the incorporation of adsorbed oxygen into the bulk, to leave a surface free for further adsorption. The same regeneration phenomenon has been observed with a nickel powder (16), and has been noted at temperatures as low as -78°C (17).

Regeneration has been studied further by Anderson and Klemperer (18) in relation to the work function of the surface. They postulate that chemisorption of oxygen on the film produces regions of different surface structure having different work functions. In the regions of high work function, rearrangement of the oxygen atoms to give a two-dimensional NiO structure which initiates the growth of bulk oxide, is thought to occur. This would be expected to happen most readily on crystal planes of suitable spacing, and electron microscope studies have indeed shown preferential growth of oxide on the (100) face of nickel (19). Recrystallization of nickel oxide on preferred faces of nickel has also been observed (20). The remainder of the surface showed, after regeneration, a low work function, lower than that for clean nickel. This is thought to consist of regions where nucleation of oxide growth is not

possible, but on which oxygen penetration of the surface occurs by place exchange with nickel (21) to give a positive surface dipole. Roberts and Wells (22) found that the regenerated surface was capable of adsorbing hydrogen but not carbon monoxide, which confirmed that the low work function regions were essentially oxide and not metallic nickel. This incorporation phenomenon is not confined to the interactions of oxygen with metals. Similar behavior has been found with sulfur, derived from hydrogen sulfide, on nickel (23) and iron (24).

With this interpretation of nickel oxidation in mind, it is of interest to examine reasons for hydrogen retention after the displacement of hydrogen by phosphorus. Owing to the undoubted bulk attack on the nickel by phosphorus, retention cannot be ascribed to a surface isolation mechanism as has been done for displacement by mercury (25). Nor can it be ascribed to mechanical trapping of hydrogen within the film. The volume occupied by nickel as phosphide is 1.8 times that of the same amount of metallic nickel so that the sealing of pores and fissures might be expected, causing trapping of hydrogen and prevention of further access of phosphorus. This is unlikely, however, because such a mechanism would be expected to give retentions related to the film weight; the thicker the film, the less hydrogen would be accessible for displacement by phosphorus. In contrast, the results show similar percentage retentions over a wide range of weights (7.7 to 44.6 mg) for films deposited in vacuum or partially in hydrogen.

The relationship which is observed in the experimental results is one between hydrogen retention and the method of film preparation. This may be explained by a model analogous to that proposed for the situation of nickel oxide after the regeneration process (18). If the nickel phosphide is formed by crystallization on preferred faces of the nickel, hydrogen will be displaced from sites on such faces. The retained hydrogen will be present on faces of unsuitable geometry for the crystallization of nickel phosphide to take place.

The difference in behavior of the vacuum

(C,E) and the hydrogen deposited films (A,F,G,H and J) is ascribed to differences in the relative proportions of various planes exposed to the gas phase. The structure of evaporated metal films is known to be influenced by the presence of gas during their deposition (26, 27). Evidence of preferred orientation has been deduced from electron or X-ray diffraction, but it is necessary to recognize that this orientation may not be the predominant one at the gas/solid interface. For example, photoelectric work function measurements show that nickel films grown epitaxially on rock salt, with (110) bulk orientation, do not present this plane predominantly at the surface (28). Sachtler, Dorgelo and Van der Knaap (27) conclude from examination of electron micrographs that the plane of orientation is probably not represented on the surface to any significant extent. Nevertheless, deposition in a gas or contaminant which interacts chemically with the film can have a marked effect both in determining the crystal planes present at the surface (27, 29) and on the rate of sintering of the film (7). This is thought to result from the effect of the adatoms in restricting the diffusion of metal atoms over the surface (30).

Two possibilities are now considered for the manner in which the retained hydrogen was held by the film after this had been exposed to phosphorus vapor. If the phosphorus does not interact with those nickel crystal planes which are of unsuitable geometry for nickel phosphide growth, the hydrogen will remain adsorbed as on a clean nickel surface. On the other hand, if a structure is formed analogous with the low work function regions when oxygen interacts with nickel, it may be that such a surface would be particularly retentive towards hydrogen. It has been found in a previous study (31) that a nickel film partially covered with oxygen, then allowed to chemisorb hydrogen, showed a marked increase in the proportion of this hydrogen which could not be displaced by mercury. After hydrogen displacement by phosphorus was completed on film C, the film was exposed to mercury vapor for 16 hr. Al-

though displacement of hydrogen would be expected if the remaining hydrogen were simply chemisorbed on nickel (25) no further release was observed, so that the second of the situations discussed above is more likely for the hydrogen which could not be displaced by phosphorus.

Sada, Takahashi and Morikawa (32) have studied a catalyst prepared by reduction of an aqueous suspension of nickel hydroxide with hypophosphite ion. This method of preparation was claimed to produce an amorphous solid solution of nickel and a compound of formula $Ni_{1.8}P$. A sample of nickel catalyst has been made by this method. Electron microscopic examination confirmed its amorphous nature, but on being heated in the microscope a diffraction pattern was obtained which showed most of the spacings of Ni_2P . The catalyst thus seems to resemble in its constituents the phosphorus-treated nickel films of the present study. The interesting feature of this catalyst was its ability to reduce benzaldehyde to benzyl alcohol (33), rather than to produce toluene which is the main product when a conventional reduced nickel catalyst is employed. The analogy between this and the interpretation of the present work suggests that the catalyst owes its selectivity to the blocking of specific crystal faces by nickel phosphide, or by modification of the surface environment of the hydrogen which remains.

The resemblance between the retention behavior of fully covered vacuum-deposited films (films C and E) and partially hydrogen-covered films (films B and D) is more difficult to explain. The partially covered films were formed by evaporating nickel in an amount of hydrogen insufficient to satisfy the adsorption requirements of the whole film. As a consequence of this the nickel which was deposited in the later stages was evaporated in vacuum. Thus, the retention results are consistent with the overall characteristics of the film being determined by the topography of the nickel which arrives last. Support for this view comes from two studies of film growth. First, Anderson, Baker and Sanders (34) conclude that nickel films are one crystal

thick, so that during their formation continuing growth takes place by adding to existing crystals rather than by the creation of new ones. Secondly, Sachtler, Dorgelo and Van der Knaap (27) have developed a model for film growth in which the crystal planes presented to the gas phase in the completed film are determined by the different relative rates of growth of crystal faces. On this basis, if the relative rates were changed during the course of the evaporation because of the change in conditions, the completed film would be expected to present a surface appropriate to the conditions prevailing in the final stages of the deposition. To test this idea, film K was made by evaporating nickel in vacuum until an appreciable film had formed. Hydrogen was then admitted and the deposition was continued. Subsequent phosphorus-displacement of the hydrogen resulted in a low retention (9.9%) typical of a hydrogen-deposited film.

ACKNOWLEDGMENTS

The author gratefully acknowledges the assistance of Dr. T. Baird in examining specimens in the electron microscope, and of Dr. K. W. Muir in the calculation of the first four spacings listed in Table 2.

REFERENCES

1. MAXTED, E. B., in "Advances in Catalysis" (W. G. Frankenberg, V. I. Komarewsky and E. K. Rideal, eds.), Vol. 3, p. 129. Academic Press, New York, 1951.
2. DILKE, M. H., ELEY, D. D., AND MAXTED, E. B., *Nature (London)* **161**, 804 (1948).
3. CORNER, E. S., AND PEASE, R. N., *Ind. Eng. Chem., Anal. Ed.* **17**, 564 (1945).
4. AFFROSSMAN, S., AND THOMSON, S. J., *J. Chem. Soc., London* **2024** (1962).
5. BOUDART, M., ALDAG, A. W., PTAK, L. D., AND BENSON, J. E., *J. Catal.* **11**, 35 (1968).
6. MAXWELL, L. R., HENDRICKS, S. B., AND MOSLEY, V. M., *J. Chem. Phys.* **3**, 699 (1935).
7. ANDERSON, J. R., AND BAKER, B. G., *J. Phys. Chem.* **66**, 482 (1962).
8. SHERIDAN, M. H., AND CAMPBELL, K. C., *J. Catal.* **13**, 245 (1969).
9. RUNDQVIST, S., *Acta Chem. Scand.* **16**, 992 (1962).
10. NOWOTNY, H., AND HENGLEIN, E., *Z. Phys. Chem.* **40**, 281 (1938).
11. EVANS, U. R., AND MILEY, H. A., *Nature (London)* **139**, 283 (1937).
12. ROBERTS, M. W., *Trans. Faraday Soc.* **57**, 99 (1961).
13. CHANG, S., AND WADE, W. H., *J. Phys. Chem.* **74**, 2484 (1970).
14. HORGAN, A. M., AND KING, D. A., *Surface Sci.* **23**, 259 (1970).
15. KLEMPERER, D. F., AND STONE, F. S., *Proc. Roy. Soc., Ser. A* **243**, 375 (1957).
16. DELL, R. M., AND STONE, F. S., *Trans. Faraday Soc.* **50**, 501 (1954).
17. MÜLLER, J., *J. Catal.* **6**, 50 (1966).
18. ANDERSON, J. S., AND KLEMPERER, D. F., *Proc. Roy. Soc., Ser. A* **258**, 350 (1960).
19. LAWLESS, K. R., YOUNG, F. W., AND GWATHMEY, A. T., *J. Chim. Phys.* **53**, 667 (1956).
20. MARTIUS, U. M., *Can. J. Phys.* **33**, 466 (1955).
21. LANYON, M. A. H., AND TRAPNELL, B. M. W., *Proc. Roy. Soc., Ser. A* **227**, 387 (1955).
22. ROBERTS, M. W., AND WELLS, B. R., *Trans. Faraday Soc.* **62**, 1608 (1966).
23. SALEH, J. M., KEMBALL, C., AND ROBERTS, M. W., *Trans. Faraday Soc.* **57**, 1771 (1961).
24. ROBERTS, M. W., AND ROSS, J. R. H., *Trans. Faraday Soc.* **62**, 2301 (1966).
25. CAMPBELL, K. C., AND THOMSON, S. J., *Trans. Faraday Soc.* **55**, 306 (1959).
26. BEECK, O., SMITH, A. E., AND WHEELER, A., *Proc. Roy. Soc., Ser. A* **177**, 62 (1940).
27. SACTLER, W. M. H., DORGELO, G., AND VAN DER KNAAP, W., *J. Chim. Phys.* **51**, 491 (1954).
28. BAKER, B. G., JOHNSON, B. B., AND MAIRE, G. L. C., *Surface Sci.* **24**, 572 (1971).
29. BRADSHAW, A. M., AND PRITCHARD, J., *Surface Sci.* **19**, 198 (1970).
30. DOBSON, P. J., AND HOPKINS, B. J., *Thin Solid Films* **5**, 97 (1970).
31. CAMPBELL, K. C., AND THOMSON, S. J., *Trans. Faraday Soc.*, **57**, 279 (1961).
32. SADA, S., TAKAHASHI, Y., AND MORIKAWA, K., *Catalyst (Tokyo)* **8**, 2 (1966).
33. MORIKAWA, K., SHIRASAKI, T., AND OKADA, M., in "Advances in Catalysis" (W. G. Frankenberg, V. I. Komarewsky, and E. K. Rideal, eds.), Vol. 20, p. 131. Academic Press, New York, 1969.
34. ANDERSON, J. R., BAKER, B. G., AND SANDERS, J. V., *J. Catal.* **1**, 443 (1962).