

THE EFFECT OF CRYSTAL PARAMETER ON HYDROGENATION AND DEHYDROGENATION

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Through measurement of the surface of oriented and unoriented evaporated porous nickel films by the B.E.T. method, using neon, krypton, methane and butane, and by measuring the number of crystallographic sites through the adsorption of hydrogen at liquid nitrogen temperature, direct proof has been obtained that (110) oriented nickel films do also expose (110) planes to the gas phase.

A study of the hydrogenation of benzene over oriented and unoriented nickel and iron films showed no difference in rate in contrast to the previously reported 5-fold rate for the hydrogenation of ethylene over (110) oriented nickel films in comparison to unoriented films. It is concluded that the observed slow hydrogenation, which kinetic considerations show, proceeds through the adsorbed state of benzene, is not influenced by the crystal geometry of the substrate.

In contrast, the dehydrogenation of cyclohexane over unoriented platinum, was found to be 10 times faster than over partially (110) oriented platinum films, indicating that the geometrical factor is of great importance in this reaction, the kinetics of which is in agreement with the assumption that cyclohexane loses 6 hydrogen atoms simultaneously when colliding with the catalyst surface.

Following the hypothesis of Balandin, this reaction should be facilitated by (111) faces, which should be more abundant in unoriented than in (110) oriented films.

I. Experimental Proof for Surface Exposure of (110) Planes in Gas-induced Orientation of Nickel Films.—In an earlier publication Beeck, Smith and Wheeler¹ have shown that by controlling the pressure of an inert gas during evaporation of metals such as nickel, iron and others, unoriented and oriented porous metal films could be produced at will. Completely oriented nickel films were obtained with an inert gas pressure of about 1 mm., the (110) plane, the least dense of the planes, lying parallel to the backing and the two remaining planes showing random distribution. Films evaporated in high vacuum were found to be unoriented. The oriented nickel films were found to have twice the surface for hydrogen adsorption per gram of metal and were about ten times as active as catalysts for the ethylene hydrogenation than the unoriented films. The oriented films therefore had five times the intrinsic activity of unoriented films. Oriented and unoriented films were found to have approximately the same thickness for the same weight, that is the same density. This demands that the oriented films have smaller pores (or a pore size distribution favouring smaller pores) since the internal surface for hydrogen adsorption per gram of metal is twice that of unoriented films.

¹ Beeck, Smith and Wheeler, *Proc. Roy. Soc. A*, 1940, **177**, 62.

Several arguments were presented ¹ (which will not be repeated here) why the crystallites of gas evaporated nickel films showing (110) orientation parallel to the backing should also actually expose (110) planes to the gas phase. No direct experimental proof was offered at that time, although all indirect proof, especially the catalytic experiments, pointed to the correctness of this deduction, particularly the fact that films evaporated in an inert gas pressure of 10 mm. were unoriented but had the intrinsic activity of oriented films. This was explained by the assumption that under conditions of high gas pressure small crystallites of nickel would form in the gas phase with (110) planes exposed and that these crystallites would then be deposited randomly to form the unoriented film of not only the intrinsic catalytic activity of oriented films but also of an especially large specific surface.

It is the purpose of Part I of this paper to bring a direct proof that gas-induced orientation of evaporated nickel films produces (110) planes as the metal-gas interface.

Experimental

It is generally accepted that when hydrogen is chemisorbed on a clean metal surface, such as a nickel surface, that each hydrogen atom occupies one crystallographic site. This has been shown by electron diffraction,^{2, 3} but is also borne out by adsorption experiments ¹ and by the fact that the heat of adsorption is high, 30 kcal. per mole for the sparsely covered nickel surface and 15 kcal. for the completely covered surface.⁵ Thus measurement of the number of hydrogen atoms adsorbed affords a means of measuring the number of crystallographic sites irrespective of size. Beeck, Ritchie and Wheeler ⁴ (see also ⁵) have shown recently that such measurements have to be done cautiously, having in mind that hydrogen is also absorbed into the interior of the metal structure. Initial adsorption at liquid nitrogen temperature of -196°C and 0.1 mm. pressure represents a true measure of the number of sites available for adsorption, although, as has been shown,³ the total sorption at room temperature as measured shortly after admission of the gas is in close agreement with the value for adsorption at -196°C .

The total surface, irrespective of the number of crystallographic sites, can be measured by the Brunauer, Emmett, Teller (B.E.T.) method.⁶ However, this method will give correct results only when no chemisorption of the gas employed takes place. The author and his co-workers have found ⁵ that nitrogen which is generally used in the B.E.T. method cannot be used with clean nickel, iron and many other metal surfaces because nitrogen is adsorbed on nickel at -196°C with a heat of adsorption of 10 kcal. for the sparsely covered surface decreasing to 5 kcal. for the completely covered surface.^{3, 5} The nitrogen molecule occupies two crystallographic sites and is probably only partially dissociated. This chemisorption, which cannot be detected by the usual B.E.T. procedure using nitrogen at liquid nitrogen temperature, causes the surface to appear too large by a factor of 1.55 in the case of nickel. Accordingly, gases have to be used whose adsorption is of known van der Waals' type at the temperature of measurement. Neon, krypton and butane were used in this investigation at such temperatures as to make the number of molecules in the gas phase of nearly the same order of magnitude as the number adsorbed on the small surface studied. This is necessary in order to obtain the desired high accuracy and can be achieved by using suitably small saturation pressures. The use of krypton at -196°C for the measurement of small surfaces comparable with those of the metal film has been previously described by Beebe.⁷ By measuring the number of sites relative to the total surface in cm^2 for oriented and unoriented nickel films, the average size of the site for each type of film can be established.

² Rupp, *Z. Elektrochem.*, 1929, **35**, 586.

³ Germer, *Z. Physik*, 1929, **54**, 408.

⁴ Beeck, Ritchie and Wheeler, *J. Colloid Sci.*, 1948, **3**, 505.

⁵ Beeck in *Advances in Catalysis*, Vol. II (Academic Press, New York, 1950).

Beeck, Cole and Wheeler, this Discussion.

⁶ Brunauer, Emmett and Teller, *J. Amer. Chem. Soc.*, 1938, **60**, 309.

⁷ Beebe, Beckwith and Honig, *ibid.*, 1945, **67**, 1554.

It will be seen that for unoriented films the surfaces measured by the B.E.T. method using molecules of different sizes agree well within the limits of experimental error. The oriented films, however, with their larger surfaces and smaller pores gave surfaces markedly dependent of the size of molecule used, making it necessary to extrapolate to the size of the hydrogen molecule since the chemisorption of hydrogen is used for comparison. For this purpose the area of the hydrogen molecule was taken as 1 \AA^2 . This figure may be somewhat arbitrary because adsorbed hydrogen atoms have been shown^{3,5} to migrate from site to site and the pore size necessary for this fast migration (as distinguished from the slow diffusion into the crystal lattice) would be difficult to evaluate. It will be seen, however, that whatever the choice of this figure, within the possible limits, it has little bearing on the quantitative conclusions to be drawn.

The surface measurements with neon were carried out at 16°K in a Collins helium cryostat. A full description of the experimental details will be published later.

The cross-sectional areas of methane, krypton and neon were calculated by means of the formula $A = 1.52 \times 10^{-16} (M/\rho)^{2/3}$, where ρ is the liquid density and M the molecular weight. The area of $n\text{-C}_4\text{H}_{10}$ was calculated by the method of Livingston⁸ assuming that the molecule lies flat on the surface as a cylinder with the diameter of 4.75 \AA (the distance of nearest approach between two hydrocarbons) and with a length of 1.29 \AA per carbon atom.

The procedure of producing the evaporated metal films has already been described in detail.¹

Results

The experimental results are presented in Table I and in Fig. 2. Fig. 1 shows the B.E.T. plots for Expt. 7, 8 and 9, where the hydrogen adsorption at -196°C and the B.E.T. surface measurements with neon, krypton and butane were done on the same oriented film. The hydrogen adsorption was carried out first after experimental proof was obtained that adsorbed hydrogen had no measurable effect on the B.E.T. surface measurements. Expt. 5 and 6 were

TABLE I

No.	Film Type	Ads. Temp. $^\circ\text{C}$	Gas	Unilayer Molecules Per 100 mg. Ni $\times 10^{-18}$	Area per Molecules \AA^2	Surface Area m^2/g .	H ₂ Ads. per 100 mg. Ni Molecules $\times 10^{-18}$	Area per H Atom Site \AA^2
1	Unoriented	-196	Kr	6.15	14.6	9.00	7.28	6.18
2	Unoriented	-196	Kr	5.85	14.6	8.55	6.9	6.18
3	Unoriented	-196	CH ₄	5.40	15.68	8.46	6.9	6.14
4	Unoriented	-78	$n\text{-C}_4\text{H}_{10}$	3.48	24.5	8.53	6.9	6.18
5	Oriented	-196	Kr	11.70	14.6	17.09	13.33	6.42
6	Oriented	-257	Ne	15.00	9.95	14.92	10.35	7.25
7	Oriented	-196	Kr	12.08	14.6	17.64	13.85	6.37
8	Oriented	-78	$n\text{-C}_4\text{H}_{10}$	5.29	24.5	12.95	13.85	4.68
9	Oriented	-257	Ne	20.00	9.95	19.90	13.85	7.18
10	Dep. Temp. -183°C Unoriented	-196	Kr	3.68	14.6	5.37	6.9	3.9

made with two different oriented films, the hydrogen adsorption at -196°C preceding the B.E.T. measurements. Numbers 2, 3 and 4 are averages of measurements on several different unoriented films. In these experiments the hydrogen adsorption at 23°C was used, while Expt. 1 was preceded by a hydrogen adsorption measurement at -196°C . The average value for the area per H atom site for the unoriented films is 6.17 \AA^2 and is independent of the size of molecule used for the B.E.T. measurement.

⁸ Livingston, *J. Amer. Chem. Soc.*, 1944, **66**, 569.

Extrapolation to 1 \AA^2 for the oriented film is obviously best done by a curve through the points from Expt. 7, 8 and 9, where the same film was used. This happens to be a straight line and extrapolation leads to the value 8.65 \AA^2 for the (110) oriented films.

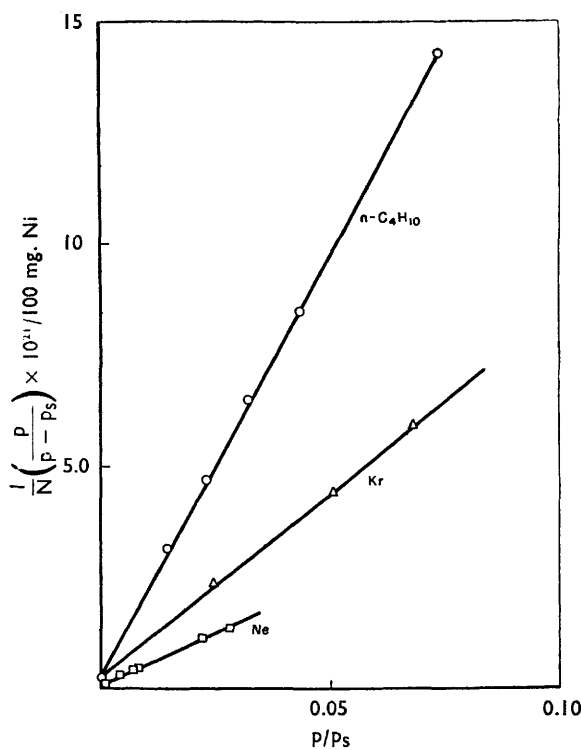


FIG. 1.

Discussion

The X-ray values for the short and long distances in the face-centred cubic nickel lattice are 2.48 \AA and 3.51 \AA , respectively. The (110) site area is therefore $2.48 \times 3.51 = 8.70 \text{ \AA}^2$ in unexpectedly good agreement with the experimental value of 8.65 \AA^2 . The area of the (100) site is $2.48^2 = 6.15 \text{ \AA}^2$, again in excellent agreement with the experimental value of 6.17 \AA^2 . Since planes involving higher indices would undoubtedly adsorb more than 1 H atom per site, it may be safely concluded that (110) oriented films exhibit only (110) planes to the gas phase. In the case of the unoriented films the agreement with the (100) site area may be more fortuitous since the average size of the three major planes including the (111) plane is $\bar{A} = 5.84 \text{ \AA}^2$ very close to the (100) value. If, therefore, only a small number of planes along the cube edges were (110) planes and another small number at the corners were (111) planes, one would expect an overall value close to that of the (100) plane. It was also shown¹ that relatively heavy high vacuum films (film weights of several hundred mg. were used in these experiments) showed a tendency to slight (110) orientation with increasing thickness, if deposited at 23°C . Since such films showed also a slightly increased activity per unit weight, it must be concluded that heavy high vacuum films expose a certain unknown fraction of (110) planes also for this reason. One film (Expt. 10)

was deposited at -183°C and the size for the site derived from this measurement is 3.9 \AA^2 indicating that (111) planes with an area of 2.66 \AA^2 are fairly abundant. The straight line relationship between the surface of the oriented films and the size of the molecules employed for its measurement shows perfect randomness of pore size.

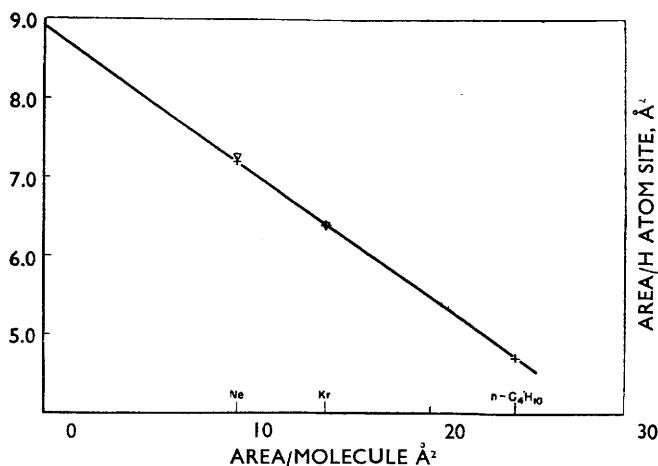


FIG. 2.

The dependence of surface on pore size makes it also necessary to adjust the ratio of the intrinsic activities of the two film types. It was earlier reported¹ that the intrinsic activity of oriented nickel films for the hydrogenation of ethylene was about five times greater than for unoriented film. If it is assumed that the surface available for ethylene hydrogenation in oriented films is the same as that measured by methane adsorption (which would be the lower limit), the new factor becomes $5 \times 1.4 = 7$, as can readily be deduced from Fig. 2, since the earlier comparison was based on hydrogen adsorption only. Oriented evaporated nickel films are, therefore, at least about seven times more active than unoriented films.

II. Hydrogenation of Benzene and Dehydrogenation of Cyclohexane.—After having demonstrated that (110) planes are exposed in oriented evaporated nickel films and are at least five, but possibly seven times more active (see Part I) as catalyst for the hydrogenation of ethylene than the planes exposed by unoriented films (which may either be (100) planes only or contain some (110) and (111) planes also) it was tempting to test such films for the hydrogenation of benzene or the dehydrogenation of cyclohexane for the latter of which Balandin⁹ has proposed his "multiple adsorption" hypothesis. According to this hypothesis dehydrogenation of cyclohexane takes place on the octahedral face, i.e. (111) planes, of a face-centred cubic metal lattice. He further specified that the lattice constant must lie between those of nickel and palladium. Since at the temperature necessary for dehydrogenation (about 300°C) nickel and iron films sinter to the extent that they lose nearly completely their internal surface⁴ only the hydrogenation of benzene at 23°C and at about 60°C was studied over these two metals. Dehydrogenation of cyclohexane was carried out over tungsten, nickel and platinum films. No systematic study was attempted in these experiments.

⁹ Balandin, *Z. physik. Chem. B*, 1929, **2**, 289; *ibid.*, 1929, **3**, 167.

Experimental

The experimental technique was that used previously¹ except that metal valves were used instead of greased stopcocks in order to avoid solution⁹ of benzene and cyclohexane in the grease. The benzene was Merck Reagent, thiophene-free and was used without further purification, except for removal of air by repeated freezing at liquid nitrogen temperature and pumping to high vacuum. The cyclohexane was an A.P.I.-N.B.S. spectrographic standard sample of better than 99 % purity. All metal films were sintered at the reaction temperature at which they were to be used and the hydrogen adsorption at 23°C was used for a measure of the surface available for the reactions to be studied.

Results

Benzene Hydrogenation.—Both oriented and unoriented nickel films were active for the benzene hydrogenation at 58°C. The initial rates were slow, i.e. of the order of 1 mm. pressure decrease per minute for a benzene-hydrogen ratio of 1/3 at the initial total pressure of about 240 mm. The reaction was found to be independent of the benzene pressure and proportional to the 0.44th power of the hydrogen pressure at 58°C and proportional to the 0.56th power at 100°C. The rate at 19°C was six times lower than that at 58°C, corresponding to an activation energy of 8.7 kcal. for this temperature interval. The specific reaction rate per unit surface was found to be greater for the oriented films than for the unoriented film by a factor of 1.24.

Comparative experiments on nickel and iron were carried out at 23°C on unoriented films and the specific activity of nickel was found to be 2.3 times that of iron. All measurements are tabulated in Table II.

TABLE II

Run	Metal	Film Type	Reaction Temp. °C	$p_{H_2}^0$ (mm.)	$p_{C_6H_6}^0$ (mm.)	$-\frac{dp}{dt}$ per 100 mg. Corrected to $p_{H_2}^0 = 183.0$ mm. (mm./min.)	H_2 Ads./100 mg. at 23°C Molecules $\times 10^{-18}$ (Sintered at 23°C)	H_2 Ads./100 mg. at 23°C Molecules $\times 10^{-18}$ Sintered at Reaction Temp. (Calc.)	Relative Activity	Remarks
1	Ni	Oriented	58	181.0	57.5	1.48	8.42	6.31	0.234	Evaporated at 0°C
2	Ni	"	58	183.0	58.0	1.83	10.10	7.56	0.239	Evaporated at 0°C
3	Ni	Un- oriented	57	171.5	58.5	1.03	6.91	5.18	0.199	Film evaporated at -183°C
4	Ni	"	58	159.5	40.5	1.02	7.51	5.63	0.181	" "
5	Fe	"	23	318.5	67.0	0.46*	11.90	11.90	0.039	Evaporated at 0°C
6	Ni	"	21.5	342.0	63.0	0.52*	5.95	5.95	0.091	" "

* Corrected to $p_{H_2}^0 = 318.5$.

Cyclohexane Dehydrogenation.—The cyclohexane dehydrogenation was investigated over tungsten and platinum films and was attempted over palladium. Those three metals sinter much less than nickel (see Table II). In spite of this fact tungsten was found to be inactive at 324°C. Platinum and palladium were both very active, although proper evaluation in the case of palladium was impossible due to the high rate of solution of hydrogen in this metal. The measurements on platinum are set forth in Table III.

¹⁰ Beeck, this Discussion.

TABLE III

Run	Film Type	Reaction Temp. °C	p° Cyclohexane (mm.)	$-\frac{dp}{dt}$ 100 mg. Corrected to 57.0 mm. Cyclohexane	H ₂ Ads. 23° C After Sintering Molecules $\times 10^{-18}$	Relative Activity
1	Unoriented	324	57.0	14.8	0.57*	13.0
2	"	324	58.0	7.48	0.34* (1.34†)	11.0
3	"	324	29.5	10.60	0.45	11.6
4	"	324	29.0	10.41	0.46	11.5
5	"	324	32.5	6.63	0.31	12.1
6	"	324	32.0	8.06	0.37	12.2
7	"	324	32.0	7.98	0.36*	11.0
8	Partially oriented	325	57.0	1.06	0.37*	1.4
9	"	322	57.0	0.57	0.37*	0.8
10	"	324	57.0	0.85	0.37* (1.46)†	1.1

* Calculated (see text).

† H₂ adsorption before sintering.

As shown in Fig. 3, where the logarithm of cyclohexane pressure is plotted against time, the initial reaction rate over platinum is first order with respect to the partial pressure of cyclohexane which allows for easy normalizing of the measured rates. From the temperature coefficient of the rates at 326° C and

356° C an activation energy of 9.3 kcal. was calculated. In Expt. 2 and 10 adsorption of hydrogen was measured at 23° C before sintering, and in agreement with previous findings there is little difference in the adsorption of oriented and unoriented films. In Expt. 3 to 10, hydrogen adsorption at 23° C after sintering was measured showing that one-third of the surface is still available after sintering at 325° C. In Expt. 1, 2, 7, 8, 9 and 10 hydrogen adsorption was not measured after sintering, and the values were calculated for 1, 2 and 7 from a plot of the figures in column 5 against those in column 6 for Expt. 3 to 6. The values for the oriented films 8, 9 and 10 were assumed to be the same and adjusted through the adsorption measurements of the unsintered films 2 and 10. From the ratio of the averages in column 8 it is seen that the unoriented films are more active by a factor $11.9/1.1 = \sim 11$ than the oriented films. This figure is likely to be much greater since electron diffraction studies showed the "oriented" films to be partially oriented only.

All that can be said with regard to palladium films is that a high-vacuum film which was not strictly unoriented but showed mixed orientation under electron diffraction study was for the same film weight 2.5 times more active than a (110) oriented film deposited in 1 mm. of nitrogen.

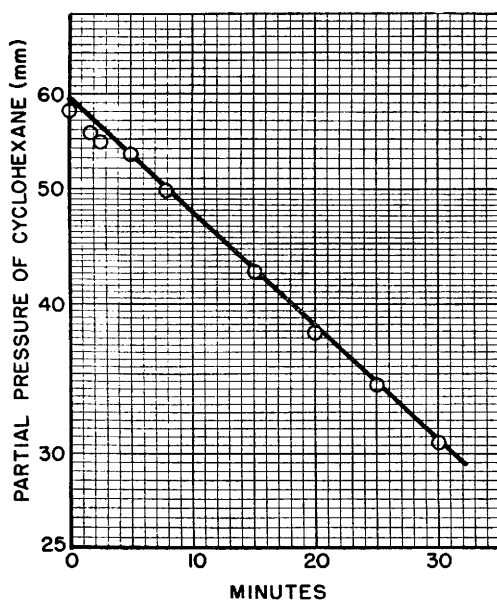


FIG. 3.

Discussion

Because of the zero-order reaction rate with regard to benzene it must be concluded that the benzene hydrogenation proceeds through the adsorbed state of benzene and is therefore possibly not subject to influence by the size of the crystallographic sites but is simply a function of total surface available which, as has been shown in Part I, is 1.4 times larger for oriented than for unoriented films for the same hydrogen adsorption. This should make the rate on oriented films 1.4 times faster. A smaller factor would be expected since benzene may not be able to enter the smallest pores. Within the experimental limits the rates may be regarded as equal. If the same argument were applied to the comparison of unoriented iron and nickel films, iron should be 2.7 times more active than nickel if one assumes that the large (100) face is exposed. Actually the activity for the same hydrogen adsorption is half as large. Further discussion of this point will be postponed until after Part III.

The tenfold activity of unoriented films even over only partially oriented films suggests that Balandin's hypothesis may be operating if the assumption is made that unoriented films expose, in part at least, (111) planes. In the later stage of this reaction the adsorption of benzene poisons the reaction, reducing the initial rate of a second run on the same film by a factor 20.

It is likely that the inactivity of tungsten films (the surface of which after sintering at 325° C is still about 1/2 of that at 23° C) is due to poisoning by a reaction product with the surface. Experimental proof of a highly unsaturated residue was obtained by admitting small amounts of cyclohexane to both platinum and nickel films at 250° C. In both cases 4 hydrogen molecules appeared in the gas phase for each cyclohexane molecule admitted. Even at room temperature cyclohexane is strongly adsorbed on tungsten and nickel with evidence that dissociation to benzene and hydrogen takes place. This strongly suggests that poisoning by residues is responsible for the inactivity of tungsten.

For further discussion of the results presented in Parts I and II of this paper in connection with other aspects of metal film catalysis see (10).

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