

and energy of activation has usually been derived either on the assumption of a rate of activation fast enough to maintain the full Maxwell-Boltzmann quota of activated molecules, or on the assumption that the activational process consists in the absorption of radiation. In this article a derivation has been presented making *no specific assumptions either as to the rate or mechanism of activation*, which shows that Equation 1 will be at least approximately valid under a wide variety of conditions.

2. Derivations have also been presented for the familiar equation

$$-dC/dt = k CC' = k' T^{1/2} e^{-(E + E')/RT} CC' \quad (2)$$

connecting the rate of second-order bimolecular reactions with temperature and energy of activation, both on the assumption that the reacting molecules have received their energies of activation preceding the collision which leads to reaction, and on the assumption that the processes of activation and reaction are merged in one collision having sufficient available kinetic energy.

3. These results re-emphasize the necessity of discovering mechanisms of activation which will supply fast enough the large energies of activation calculated from Equations 1 and 2.

4. Since the quantity E occurring in Equation 1 is the excess per mole in the energy of the molecules that react over the *average* energy of the unactivated molecules, it cannot be assumed that this average energy is available as part of the energy of activation.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

AN APPLICATION OF X-RAY CRYSTALLOMETRY TO THE STRUCTURE OF NICKEL CATALYSTS

BY GEORGE L. CLARK, W. C. ASBURY AND R. M. WICK

RECEIVED JULY 2, 1925

PUBLISHED NOVEMBER 5, 1925

The purpose of this investigation was to examine hydrogenation and dehydrogenation of nickel catalysts, prepared in different ways and with different activities,¹ by means of the X-ray powder-diffraction method to obtain information upon three questions: (1) whether there is a fundamental difference in the space lattice; (2) whether there is a fundamental variation in the particle size; (3) whether X-ray analysis will indicate the condition of the surface of nickel catalysts.

¹ Excellent comparative studies of activity as it depends upon the method of preparation of the catalyst have been made recently by (a) Armstrong and Hilditch, *J. Soc. Chem. Ind.*, **42**, 217 (1923); (b) **44**, 701 (1925); (c) Thomas, *ibid.*, **42**, 21T (1923); (d) Adkins and Lazier, *THIS JOURNAL*, **46**, 2291 (1924). This last paper states that nickel catalysts which show different hydrogenation and dehydrogenation activities are even *more widely* dissimilar in their abilities to break carbon chains.

Incidentally, powder photographs were also taken of nickel monoxide and sesquioxide, which were later reduced to the metallic catalysts, of two forms of nickel dioxide and of nickelo-nickelic oxide, Ni_3O_4 .

Experimental Part

Catalysts of known activities were prepared by following exactly the methods outlined by Armstrong and Hilditch^{1a} and by Adkins and Lazier.^{1d}

Nickel Oxides.—The black nickel sesquioxide, Ni_2O_3 , whose composition was closely checked from initial and final weights, was prepared by heating previously ignited and decomposed pure nickel nitrate hexahydrate in an electric furnace for ten hours at 450° .

A portion of this oxide was subjected to heat treatment at 650° for five hours, followed by cooling in an atmosphere of nitrogen; the light green monoxide was the resultant product.

Reduction to Metallic Catalysts.—These two oxides were the starting points for the production of various nickel catalysts by reduction with carbon, hydrogen, methyl alcohol and ethyl acetate, exactly under the conditions defined in the papers on comparative activities.¹

With sugar charcoal both oxides at $550\text{--}600^\circ$ gave a bluish metallic nickel in $1\frac{1}{4}$ hours.

With hydrogen at 460° after 39 hours, reduction was complete to within 0.1%, a grayish, metallic powder being the final product.

Methyl alcohol at 420° for $2\text{--}2\frac{1}{2}$ hours gave complete reduction to a grayish, metallic powder.

Reduction with hot vapors of ethyl acetate at 420° was completed in $1\frac{1}{2}$ hours. A small amount of carbon produced by the decomposition of the acetate proved to be amorphous in the X-ray photograph subsequently taken.

Other Nickel Catalysts.—A very fine, gray metallic powder was produced by reduction in solution according to the equation,² $\text{Ni}(\text{NO}_3)_2 + 2\text{NaH}_2\text{PO}_2 = \text{Ni} + 2\text{H}_3\text{PO}_4 + 2\text{NaNO}_3 + 3\text{H}_2$.

In order to compare the catalysts thus prepared with a mechanically pulverized or "abraded" product, pure nickel was ground in a tool-steel mortar until the particle size had reached 200-mesh.

Higher Oxides.—It has been stated that nickel sesquioxide, Ni_2O_3 , has the structure represented by $\text{NiO}\cdot\text{NiO}_2$. In order to test this hypothesis, as a matter of interest, nickel dioxide, NiO_2 , was prepared. This evidently exists in two forms, one the black,

true dioxide with the structure $\text{Ni} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{O} \end{array} -x\text{H}_2\text{O}$, and the other a green peroxide with the

structure $\text{Ni} \begin{array}{l} \diagup \text{O} \\ | \text{O} \\ \diagdown \text{O} \end{array} -x\text{H}_2\text{O}$. The first was prepared by passing chlorine gas into a suspension of nickelous hydroxide, $\text{Ni}(\text{OH})_2$, in water, and by adding sodium hypochlorite to a nickel salt solution. The second was prepared by the action of hydrogen peroxide on nickelous hydroxide.

The oxide Ni_3O_4 was prepared by passing moist oxygen over nickel chloride for eight hours at 440° .

Preparation of Samples for X-Ray Analysis.—Although nickel catalysts are usually precipitated on a support, such as asbestos, diatomaceous earth, etc., before reduction in order to increase the area of exposed surface, it was not feasible to do this in the

² Ellis, "Hydrogenation of Oils," D. Van Nostrand Co., New York, 1914, p. 142.

present work because of the complications introduced into the spectra by the supporting substance. The reduced material was cooled and subjected to X-ray analysis in an atmosphere of nitrogen so that contact with air was avoided. However, the diffraction photographs of the sample exposed or unexposed to air could not be distinguished. For use in the spectrograph, sealed, capillary glass tubes, both stationary and rotating, brass holders for ribbon-shaped samples with mica, glass and paper windows and very thin collodion-bound ribbons were tried. The last gave by far the best results. Mica windows invariably produced extremely weird distorted lines, while glass and paper produced the broad bands near the center of the films typical for such substances.

Spectrograph.—The powder spectrograph was in large part developed during the course of this work in order to obtain, with minimum cost for construction, maximum dispersion and the spectrum on both sides of the direct beam for accurate measurement. It is shown in Fig. 1. The radius as measured directly and checked by measurement of standard diffraction films of powdered sodium chloride is 14.821 cm.

The X-ray tube was a standard Coolidge type, molybdenum target, water-cooled tube, operated at 35,000 volts and 20 milliamperes. Under these conditions, $K\alpha$ doublet and $K\beta$ radiations constitute the primary beam. In most cases a zirconium oxide filter was not used in order that the $K\beta$ lines might be utilized in accurate measurements. Under these circumstances the time of exposure was ten hours.

The spacings of the spectral lines on the films were measured to 0.02 mm. with a Brown and Sharpe precision vernier calipers with an attached fine tungsten wire as a hair-line. The experimental error is of the order of $\pm 0.2\%$.

Interpretation of Powder Photographs

The Space Lattice of Nickel Catalysts.—A typical analysis of one of the powder photographs, that of the alcohol-reduced catalyst, is presented in Table I. It gives the dimensions of the unit cell of the cubic crystalline metal as 3.536 Å.

All the other catalysts except that prepared by reduction from solution gave the same average value within ± 0.002 Å. Two powder photographs of the catalyst prepared by the reduction of a nickel salt in solution by means of sodium hypophosphite failed to show any definite spectrum

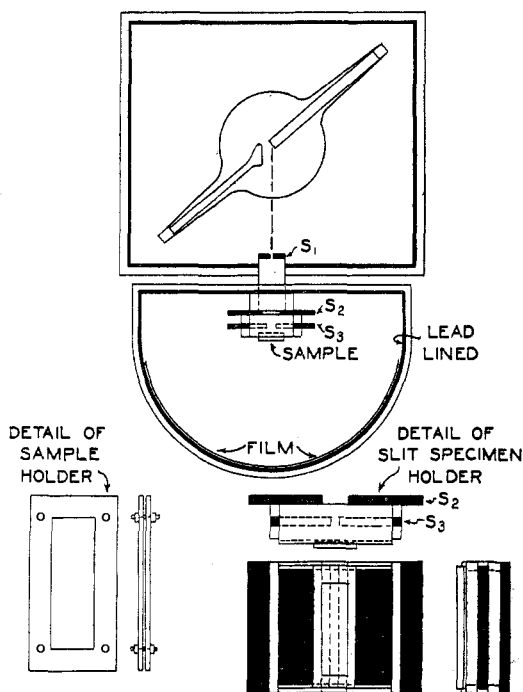


Fig. 1.—Improved powder spectrograph.

TABLE I
NICKEL REDUCED BY ALCOHOL
Radius of spectrograph, 14.821 cm.

Distance from C. L., cm.	θ	$2 \sin \theta$	h, k, l	$n\sqrt{h_2^2 + k_2^2 + l_2^2}$	λ	a_0 in Å.
4.605	8°54'	0.30942	111(1) β	1.732	0.63110	3.535
5.184	10°2.4'	.34868	111(1) α	1.732	.70783	3.515
5.994	11°35.4'	.40182	100(2) α	2.000	.70783	3.522
7.546	14°36'	.50414	110(2) β	2.828	.63110	3.535
8.534	16°30'	.56804	110(2) α	2.828	.70783	3.522
8.915	17°13.8'	.59240	311(1) β	3.135	.63110	3.531
10.028	19°22.2'	.66334	311(1) α	3.315	.70783	3.531
10.475	20°15'	.69224	111(2) α	3.460	.70783	3.536
11.801	22°48'	.77504	331(1) β	4.358	.63110	3.550
12.118	23°25.2'	.79592	210(2) β	4.470	.63110	3.545
13.413	25°54.6'	.87392	331(1) α	4.358	.70783	3.531
13.733	26°31.2'	.89302	210(2) α	4.470	.70783	3.542

Av. 3.536

lines, but merely a broad blur where the (111) lines might have appeared. These facts suggest that the nickel is in a practically amorphous condition, for if it were a crystalline colloid it should have produced definite, though broad, spectrum lines.

Certain investigators have endeavored to explain the differences existing in the behavior of nickel catalysts by a fundamental difference in the crystal structure of the nickel. Thus Adkins and Lazier^{1d} explain the difference between a hydrogen-reduced and an alcohol-reduced catalyst as a change in "the resultant distribution of nickel atoms." Our measurements show conclusively that the structure of these catalysts, as well as those prepared by reduction with hydrogen and carbon, and by mechanical pulverization, is the same, each having a face-centered cubic lattice of exactly the same dimensions. Differences in activity are not to be ascribed, therefore, to differences in the type or dimensions of the crystal lattice.

The values obtained by ourselves and others for the lattice constant of nickel fall into two groups. A. W. Hull,³ H. Bohlin,⁴ and ourselves found, respectively, 3.54, 3.53 and 3.536 Å. F. Wever⁵ and L. W. McKeehan⁶ found the value to be 3.51 Å., and Davey⁷ determined it as 3.499 ± 0.003 Å. Very recently (April, 1925) Lange and Wever, working independently, have determined the value to be 3.518 Å., while Sacklowski⁸ obtained 3.54 Å.; Lange and Sacklowski obtained the same value for copper. This

³ Hull, *Phys. Rev.*, **14**, 540 (1919); **17**, 571 (1921).

⁴ Bohlin, *Ann. Physik*, **61**, 421 (1920).

⁵ Wever, *Mitt. Kaiser Wilhelm Inst. Eisenforsch*, **3**, 17 (1922).

⁶ McKeehan, *Phys. Rev.*, **21**, 402 (1923).

⁷ Davey, *ibid.*, **27**, 292 (1924).

⁸ Sacklowski, *Ann. Physik*, **76**, 491 (1925).

discrepancy between 3.54 and 3.50 Å. suggests that something more than mere inaccuracies of measurement are involved, since the agreement on other metals is much better. However, it hardly seems possible that nickel exists in two forms, each with a face-centered cubic structure, the lattice constant of one being different from that of the other.

No lines appeared on any of the several films taken of each sample which could not be ascribed to nickel; there were no traces of oxide lines although exposure was ample to bring these out as shown by one sample in which reduction was known to be incomplete.

The Oxides of Nickel.—The powder photograph of nickel oxide (NiO) exhibits a face-centered cubic structure with respect to the nickel atoms, the oxygen atoms filling up the remaining positions at the mid-points of the edges of the unit cube. The compound lattice is, therefore, simple cubic. A careful analysis of the powder photograph gives as the dimension of the unit cell, 4.16 Å. Davey and Hoffman⁹ obtained a value of 4.20 Å., and Davey⁷ gives another value of 4.14 Å. Brentano¹⁰ in the standardization of his new focusing method has just found 4.172 ± 0.004 Å.

The powder photograph of nickel sesquioxide coincides exactly with that of nickel monoxide, giving a lattice constant of 4.16 Å. This leads us to the conclusion that nickel sesquioxide is a mixture of nickel monoxide and dioxide; the nickel dioxide structure does not appear in the photograph. The individual photographs of the dioxides of nickel (and also Ni₃O₄) prepared as stated above, failed to show any distinct lines due to the finely divided character of the material. It is reasonable to assume that in the case of the nickel sesquioxide the nickel dioxide present was also in an extremely finely divided state, thus explaining the non-appearance

TABLE II
NICKEL MONOXIDE (NiO) AND NICKEL SESQUIOXIDE (Ni₂O₃)

Distance from C. L., cm.	θ°	$2 \sin \theta$	h, k, l	$n\sqrt{h^2 + k^2 + l^2}$	λ	$a_0, \text{Å.}$
3.889	7.52	0.26174	111(1) β	1.732	0.63110	4.17
4.404	8.51	.29594	111(1) α	1.732	.70783	4.14
5.080	9.82	.34112	100(2) α	2.000	.70783	4.16
6.350	12.27	.42504	110(2) β	2.828	.63110	4.19
7.188	13.89	.48014	110(2) α	2.828	.70783	4.16
7.518	14.53	.50180	311(1) β	3.315	.63110	4.16
8.453	16.33	.56222	311(1) α	3.315	.70783	4.17
9.058	17.10	.58808	111(2) α	3.460	.70783	4.16
9.926	19.18	.65706	331(1) β	4.358	.63110	4.19
10.238	19.80	.68076	210(2) β	4.470	.63110	4.14
11.270	21.75	.74112	331(1) α	4.358	.70783	4.16
11.587	22.40	.76214	210(2) α	4.470	.70783	4.15

Av. 4.160

⁹ Davey and Hoffman, *Phys. Rev.*, **15**, 333 (1920).

¹⁰ Brentano, *Proc. Phys. Soc. London*, **37**, 184 (1925).

of the characteristic lines. Caven and Lander in their "Systematic Inorganic Chemistry" state that nickel sesquioxide is a mixture of nickel monoxide and dioxide, and may be written $\text{NiO} \cdot \text{NiO}_2$.

A complete tabulation of the calculations for the determination of the lattice constant of nickel monoxide and sesquioxide appears below. The lines on both photographs coincide exactly. The calculations follow those outlined under the alcohol-reduced catalysts.

Relation between Degree of Dispersion and Width of Line

Debye and Scherrer have worked out the following relation for colloidal cubic crystals: $B = 2\sqrt{\log_e 2/\pi(\lambda/D)(1/\cos \theta)} + b$, where B is the angular

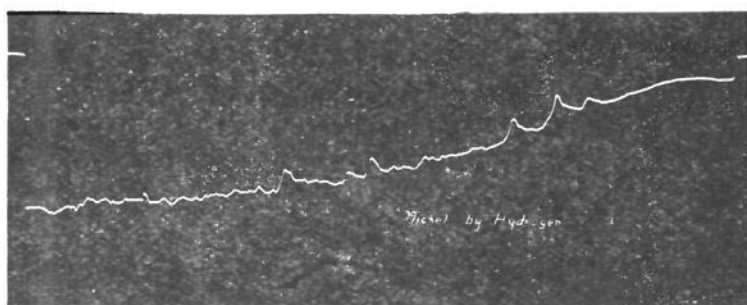


Fig. 2.

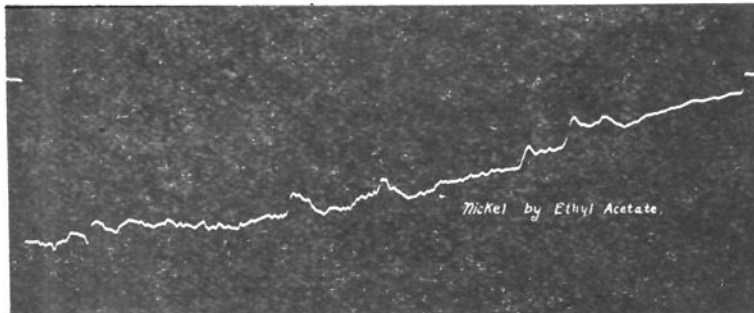


Fig. 3.

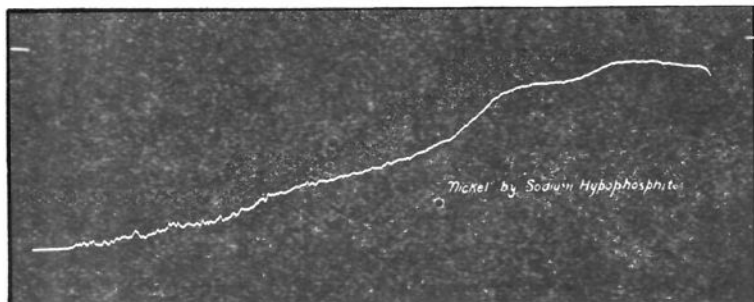


Fig. 4.

breadth of halo measured between points where the intensity has fallen to half its maximum value; 2θ is the angle through which the rays are diffracted; λ is the wave length of the monochromatic X-rays, D is the

thickness of the crystal parallel to a cubic axis, and b is the minimum breadth of halo determined by dimensions of the X-ray beam and the ribbon of powder.

By measuring B photometrically and plotting it against the reciprocal of cosine θ , a value for the constant $2\sqrt{\log_e 2/\pi} \times (\lambda/D)$ can be found and D determined. This method is used in our work to study the size of the particles in various nickel catalysts. Since in every case the catalyst was prepared from the same oxide, the results are comparable.

Since under a microscope a line on a photographic negative becomes a diffuse blur and visual measurement of its width is impossible, the lines were measured photometrically. This was done by means of the sensitive and precise photodensitometer developed by Dr. George R. Harrison, Research Fellow at the Jefferson Physical Laboratory of Harvard University.¹¹ Examples of the curves are shown in Figs. 2, 3 and 4.

Interpretation of Photometric Prints.—Perpendiculars drawn from the peak of each line to the base line on these photometric prints were taken as a measure of the intensities of the lines. By referring the intensities of all the observable lines to the 111 α (1) line, which is the most intense, a ready comparison of intensities may be made. The intensity of the reference line was taken to be 10.

The plot of the intensities given in Table III is shown in Fig. 5. The

TABLE III
DATA ON INTENSITY OF LINES
Catalysts reduced by

h, k, l	Alcohol	Carbon	Ethyl acetate	Hydrogen	Calcd.
111(1) β	4.7	4.4	4.7	4.2	...
111(1) α	10.0	10.0	10.0	10.0	10.0
100(2) α	6.2	6.2	6.0	6.8	5.4
110(2) β	4.1	3.8	2.7	2.8	...
110(2) α	8.0	7.3	7.7	6.8	4.7
311(1) β	5.3	3.8	3.6	3.2	...
311(1) α	9.2	6.4	9.1	7.1	6.5
111(2) α	3.3	2.6	3.3	2.7	1.9

¹¹ *J. Opt. Soc. Am.*, **10**, 157 (1925). The principle on which this photometer works is, briefly, as follows. A beam of light is passed through a photographic film and focused on a bismuth-silver thermocouple connected to a sensitive D'Arsonval galvanometer which is influenced by the different light intensities registered as the photographic film passes over the beam of light. Another beam of light is reflected by a mirror attached in lieu of an indicating needle to the galvanometer and focused by a lens on a rotating strip of sensitized paper. Since the deflections of the galvanometer are closely proportional to the light intensities, the plate can be moved across the slit and automatic registrations of the galvanometer deflections will give an opaque curve indicating the relative intensity of each point along the film. The plate is moved over the source of light by a carriage provided with a screw drive run by a synchronous motor. Since the drum carrying the sensitized paper is also motivated by a synchronous motor there is a definite ratio between the linear dimensions on the original film and on the sensitized paper.

intensities of the lines for all the samples are nearly the same and, except for a large intensity for $110\alpha(2)$, are in good agreement with the calculated values for a face-centered lattice.

In measuring the widths of the lines we were interested in finding the linear dimension at points of half intensity. To do this, the mid-point of the perpendiculars already referred to was determined, that being the point of half intensity. Lines were drawn through these points parallel to the base line, and the distance between the intersection of this line and the intensity curve was taken as the breadth.

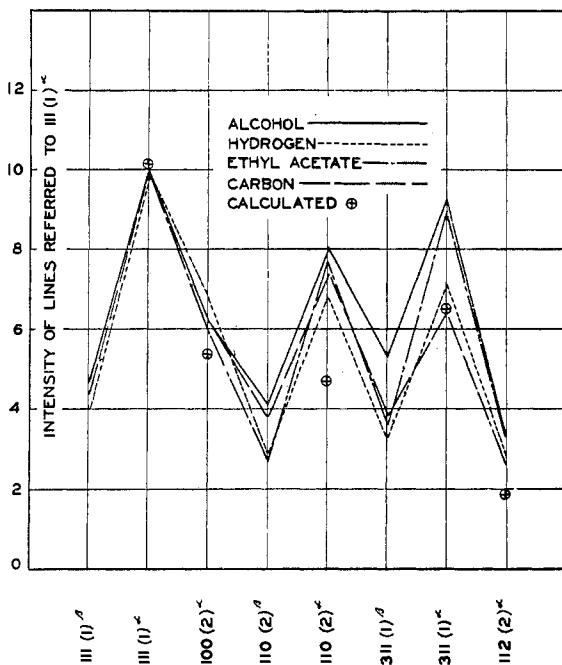


Fig. 5.—Relative intensities for different catalysts.

The average width of the lines was determined by measuring each side of the negative. This was then plotted against the reciprocal of $\cos \theta$, as previously explained. If the equation of Debye and Scherrer were true for the nickel particles in the catalysts, such a plot should give a straight line. However, our plots for the $K\alpha$ lines in Fig. 6 show a tendency to start high, drop, slope up and again drop, somewhat in the fashion of the graphic expressions of a cubic equation. Two of the four catalysts for which lines appear, namely, carbon- and alcohol-reduced nickel have very similar curves. The curves for the hydrogen- and ethyl acetate-reduced catalysts are similar to the others, but the second points of inflection occur at greater values of the reciprocal of $\cos \theta$. The mini-

mum point of inflection for the hydrogen-reduced sample comes at a higher value than the other three.

These results, which are tabulated in Table IV, suggest that the nickel catalyst particles are larger than 10^{-6} cm. in diameter (but smaller than 10^{-3} cm., since a larger size would produce streaked spectrum lines), that the equation developed by Debye and Scherrer holds only for the limiting case of particles of colloidal size ($< 10^{-6}$ cm.) and that the relation

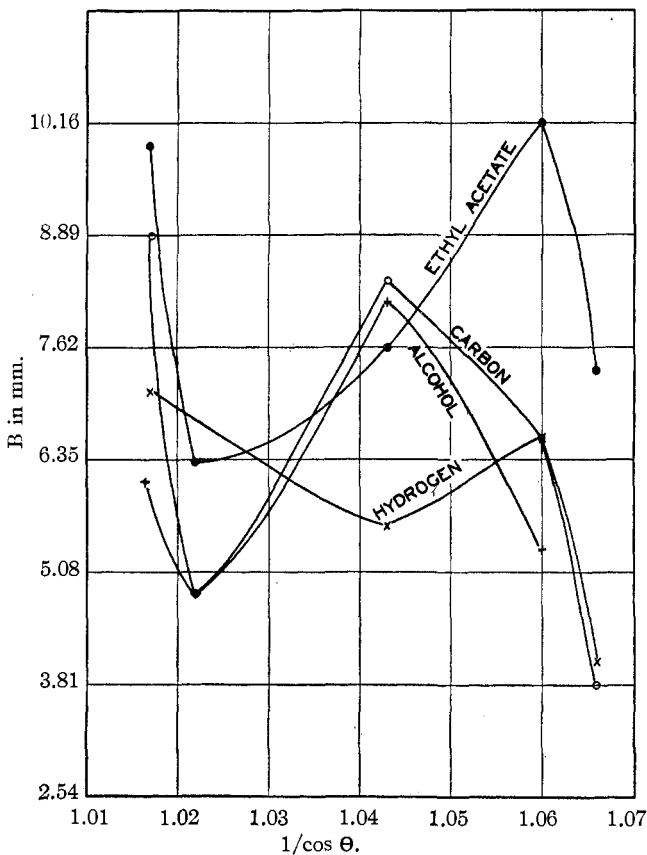


Fig. 6.

between the width of line produced on the photographic film and the size of the particle is more complex.

An attempt was made to determine in general which catalyst had the widest lines. A plot of width of line against the four catalysts was made for each line in Fig. 7. In general, this plot suggests that the gradation in particle size from smallest to greatest is as follows: catalysts reduced by sodium hypophosphite, by carbon, by ethyl acetate, by hydrogen and by alcohol,

TABLE IV
DATA ON WIDTH OF LINES
Obtained from photometer prints
Catalyst reduced by

$\frac{1}{\cos \theta}$	Carbon width of lines in millimeters			
	Hydrogen	Carbon	Alcohol	Ethyl acetate
1.014	7.62	10.92	6.35	7.87
1.017	7.11	8.89	6.10	7.11
1.022	6.86	4.83	4.83	6.35
1.034	5.84	5.33	5.08	5.59
1.043	5.59	8.38	8.13	7.62
1.047	5.33	7.37	7.62	8.13
1.060	6.60	6.10	5.33	9.91
1.066	4.06	3.81	...	7.37

This is, in general, the order of increasing activities of the catalysts if the results of Armstrong and Hilditch^{1a,1b} and Adkins and Lazier,^{1d} using catalysts prepared as those here studied, are accepted. This order is exactly the reverse of what might *a priori* be expected for the influence of particle size.

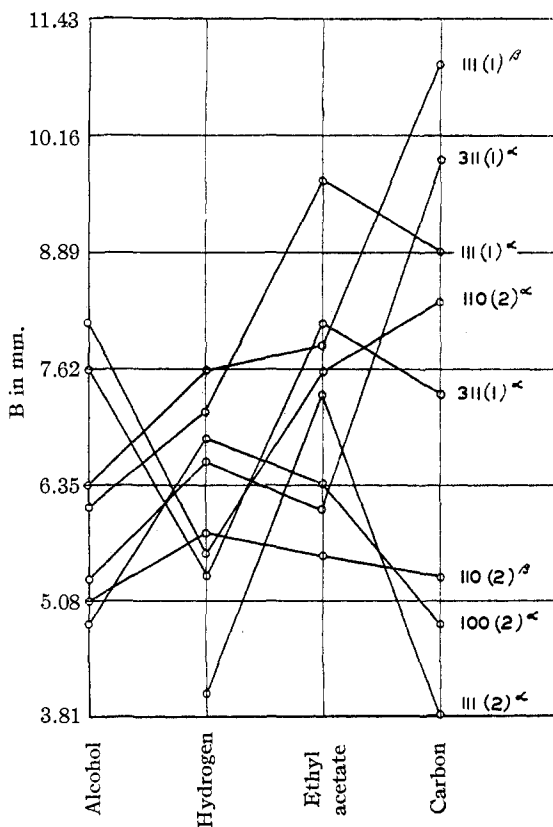


Fig. 7.

It is obvious that the X-ray method does not reveal the condition of the surface of the catalysts. By the process of elimination and in agreement with the generally accepted view, it must be concluded that the condition of the surface predominatingly determines activity.

Summary

1. Powder diffraction photographs in a new, inexpensive, but precise spectrograph have been taken of nickel catalysts of widely different hydrogenation and dehydrogenation activities, prepared by reduction with carbon, alcohol, ethyl acetate, hydrogen and sodium hypophosphite. Except for the last, which appeared colloidal, all give identical lines for nickel, $d_{100} = 3.536 \text{ \AA}$. Hence the difference in activities is not to be ascribed to a difference in lattice type or dimensions.

2. Precision photodensitometer curves from the films were prepared and used to measure relative intensities and widths of lines. The intensities for all were approximately the same and in fair agreement with the calculated values for a face-centered lattice.

3. The nickel catalysts do not obey the Debye-Scherrer equation connecting line width with particle size, defined for colloidal dimensions. A rough parallelism is found between decreasing line width and increasing catalytic activity.

4. X-rays give no information concerning the surface of catalysts.

5. Precision measurements on nickel monoxide (simple cubic) gave $d_{100} = 4.16 \text{ \AA}$. Nickel sesquioxide, Ni_2O_3 , gave only the lines of the monoxide, proving it to be $\text{NiO}\cdot\text{NiO}_2$. Photographs of the dioxide in its two forms gave no diffraction lines, explaining the non-appearance of these lines on the sesquioxide film. Nickelo-nickelic oxide, Ni_3O_4 , was also amorphous.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF IOWA STATE COLLEGE]

VANADIUM OXYTRICHLORIDE AS A SOLVENT

By F. E. BROWN AND J. E. SNYDER

RECEIVED JULY 9, 1925

PUBLISHED NOVEMBER 5, 1925

Introduction

Lenher¹ has shown that selenium oxychloride is a remarkable solvent. It was thought that oxychlorides of other elements near selenium in the periodic table might also be good solvents. Vanadium oxytrichloride is liquid between -15° and $+127.19^\circ$. It is light yellow, transparent and could be prepared in large quantities at a moderate cost. It may be refluxed over sodium for several days without suffering appreciable reduction or decomposition.

¹ Lenher, *THIS JOURNAL*, **43**, 29 (1921).