[CONTRIBUTION FROM THE SCHOOL OF ENGINEERING RESEARCH, UNIVERSITY OF TORONTO]

Nickel Catalysts. I. The Effect of the Temperature of Preparation on the Crystal Size and Composition of Nickel Oxide[1]

BY M. C. BOSWELL AND R. K. ILER

It is generally recognized that the properties of near-amorphous solids such as solid catalysts and adsorbents, are profoundly influenced by the temperature of preparation, and that at higher temperatures crystal growth occurs with a corresponding change in the properties. In this investigation the sintering of nickel oxide has been followed by means of x-rays and more closely by a chemical method to be described later. The results indicate that the crystal size developed is an exponential function of the maximum temperature to which the nickel oxide has been heated.

Experimental

Preparation of Nickel Hydroxide.—The nickel hydroxide was precipitated at 60° from a solution of 40 g. per liter of C. P. hydrated nickel nitrate. Exactly the equivalent amount of a carbonate-free solution of 30 g. per liter of C. P. sodium hydroxide was added dropwise with mechanical stirring. The solution was boiled for four hours and washed by decantation. Every effort was made to have all materials free from carbon dioxide. Small amounts of sodium hydroxide were added during decantation to settle the material and the material was thus washed free from nitrate. The last trace of sodium hydroxide was removed by electrodialysis until the conductivity had fallen to that of a 0.0001 N salt solution. The sludge of hydroxide was dried in a vacuum at 100° and ground in air free from carbon dioxide.

Preparation of Nickel Oxide.—Samples of nickel oxide were prepared by heating nickel hydroxide in pure nitrogen at definite temperatures which were controlled within 5°. x-Ray examination showed that at 220° the nickel hydroxide was transformed in a few minutes to nearly amorphous nickel oxide which was found to contain water even after drying in nitrogen at the preparation temperature until the evolution of moisture was less than 2 mg. per twenty-four hours.

Analysis of Materials.—Nickel was determined by the standard dimethylglyoxime method. Water was estimated by determining the loss in weight of the sample on heating to 900° and checked by weighing the evolved water in U-tubes filled with sulfuric acid on pumice.

x-Ray Determination of Particle Size.—The Debye–Scherrer powder method was used with a water-cooled Coolidge tube having a molybdenum cathode, monochromatic radiation being obtained with a zirconium oxide filter.

The samples in the form of a powder were put into lithium glass tubes 1 mm. in diameter and placed over the defining slit which was 10 by 0.5 mm. in cross section and 9 cm. in length. A flat film holder was used at a distance of 9.35 cm. from the sample. Microphotometer traces were made of the resulting films and the line breadth measured at half the height of the peaks. There were two lines corresponding to each of the 111 and 100 planes, on each film.

The formula used to calculate the crystal size was

$$\frac{(B-b)}{2} = 0.94\,\frac{L}{D_1}\,\frac{1}{\text{Cos }A/2}$$

where B is the angular line width at half height, b the minimum angular line width, L the wave length (0.71 Å.), D_1 the length of side of cubic crystals in Ångström units and A the angular deviation. Substituting the camera constants it is found that $D_1 = 129/(B_1 - b_1)$ where B_1 and b_1 are in mm.

Determination of the Particle Size by Chemical Means

In an effort to find a reagent which would combine with the surface of nickel oxide crystals to form a surface complex, hydrogen peroxide, dimethylglyoxime and various alkaline sulfides were tried without success. Samples of nickel oxide were suspended in solutions of the reagents in both warm and cold solutions for various lengths of time, filtered on fine filter paper and washed with hot water until the filtrate was free from the reagent. In the case of hydrogen peroxide no oxidation of nickelous to nickelic oxide could be detected. Microscopic examination showed that in the case of dimethylglyoxime, separate crystals of the nickel salt were formed. With sulfides no definite oxide–sulfide ratio was found in the resulting materials.

Alkaline sodium hypochlorite solutions gave definite results. It was found that with a batch of nickel oxide which had been prepared at a definite temperature, the hypochlorite reagent could oxidize only a definite fraction of the nickelous oxide to the nickelic condition. With increasing temperatures of preparation this fraction decreased. It was important that the hypochlorite reagent should not be boiled with the sample of oxide as this treatment caused high and erratic results.

A reasonable hypothesis is that only the nickel atoms which are situated on the surface of the oxide crystals, can combine with additional oxygen under these circumstances. If this be true, the particle size can be calculated from the ratio of the number of nickel atoms on the surface to the total number present in the sample, providing cubic crystals are assumed. x-Ray examination shows that no separate crystalline phase of higher oxide is formed.

Experimental Procedure.—The sample of nickel oxide which had undergone a known heat treatment was placed in a loosely stoppered flask with a large excess of molar solution of slightly alkaline sodium hypochlorite. This was let stand from twenty-four to forty-eight hours at 30°. The sample was then filtered on fine filter paper and washed first with cold and then with hot water until the filtrate

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(1) Abstract from a thesis presented by R. K. Iler to the School of Graduate Studies of the University of Toronto in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1933.

was completely free of reagent. The precipitate and filter paper were transferred to a flask in which an atmosphere of carbon dioxide was maintained. Dilute solutions of potassium iodide and hydrochloric acid were added. After ten minutes an equal volume of water was added and the liberated iodine titrated with 0.01 N sodium thiosulfate solution. Oxygen must be excluded from the flask because of the atmospheric oxidation of hydriodic acid in the presence of nickel oxide.

The ratio of the number of added oxygen atoms to the total number of nickel atoms in the sample will be called "x," the "surface ratio," since it will be assumed that each nickel atom on the surface can adsorb one oxygen atom.

Results.—Samples of the oxide previously prepared at 250° were heated in a stream of dry nitrogen for one, three and six hours at a definite temperature which was higher than the original preparation temperature, and the surface ratio was determined. These checked closely showing that the sintering action was substantially complete in one hour. Other experiments showed that the results did not depend on the amount of hypochlorite reagent used, providing it was present in a large excess.

It was found that nickel oxide prepared as described, contained about 0.005 atom of active oxygen per atom of nickel present in the sample, *before* treatment with hypochlorite. Whether this is a trace of higher oxide of nickel or whether it is adsorbed oxygen in an active condition, is not definitely known. When this gray-black oxide is heated at 100° with hydrogen there is a reaction with 0.006 mole of hydrogen per atom of nickel and then the reaction stops. At the same time the oxide changes from black to bright greenish-yellow. An equivalent amount of oxygen will instantly turn it black again even at room temperature. Also in a very high vacuum at 250° the black oxide is slowly changed to the greenish-yellow color which reverts to black in the presence of a trace of air or oxygen. These observations tend to show that the black color and the apparent presence of higher oxide may possibly be due to a small amount of adsorbed oxygen.

Since this small amount of "active oxygen," as it is termed by LeBlanc and Sachse,[2] seems to be more or less independent of the temperature of preparation of the oxide, it is assumed that it is not directly related to the particle size. In this connection it was observed that samples of oxide which had been strongly sintered at 1500° and were green and definitely crystalline, gave a surface ratio of 0.005 when treated with hypochlorite. As this fraction of the nickel atoms could not be on the surface when the crystallization was so complete, it bears out the idea that the surface ratio, as measured, should be corrected by subtracting 0.005 from it before using the results in calculating particles sizes. It is interesting to note that Klemm and Haas[3] report that above 400° nickel oxide has the composition $NiO_{1.005}$.

Hence $(x - 0.005)$ is a measure of the surface which can be destroyed by sintering and is the value to be used for calculating particle size. We think it may be possible to denote the degree of perfection of crystals, such as are being formed during sintering, by a number representing the average size of perfect crystals which would give an equivalent specific surface.

Let D_2 be the number of elementary crystal units along one edge of a cubic crystal, each element exposing two nickel atoms. If D be the number of nickel atoms across one edge of the crystal, $D = 2D_2$. In this crystal there are D^3 nickel atoms, and on the surface approximately $6D^2$ nickel atoms. By definition the surface ratio $= 6D^2/D^3 = (x - 0.005)$; or $D = 6/(x - 0.005)$.

It was found that $\log_{10} D = kT$ where k is a constant and T is the temperature of preparation in Å. Namely

$$\log_{10} 6 - \log_{10} (x - 0.005) = kT$$

It is quite possible that there is the more general relationship

$$\log_{10} (x - 0.005) = C - kT$$

and that in this particular case $C = \log_{10} 6$ by coincidence. More work must be done to decide this point.

TABLE I

Temp. of prepn., °C.	x	D	$\log_{10} D$	T°, Abs.	k
330	0.088	72.3	1.86	603	0.00308
370	.066	98.3	1.99	643	.00309
410	.051	130	2.12	683	.00311
430	.046	146	2.17	703	.00309
500	.030	240	2.38	773	.00308
630	.0145	632	2.80	903	.00310
670	.0115	922	2.97	943	.00315
750	.0092	1432	3.15	1023	.00308
				Average	0.00310

Results of x-Ray Measurements of Crystal Size.—For comparison with the above results obtained by the chemical method, the particle size measurements by x-rays are given in Table II.

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(2) LeBlanc and Sachse, *Z. Elektrochem.*, **32**, 58 (1926).

(3) Klemm and Haas, *Z. anorg. allgem. Chem.*, **219**, 82 (1934).

TABLE II

Temp. of prepn., °A.	$B_1 - b_1$	D_1	D_2	D	Log D	k
590	0.68	190	46	92	1.96	0.0033
720	.50	260	62	124	2.09	.0029
800	.26	500	120	240	2.38	.0030
1020	.13	1000	240	480	2.68	.0026
					Average	0.0030

The value of D for the sample heated to 1020° in Table II is uncertain because of the small value of $(B_1 - b_1)$. No variation in the lattice constant was observed with these samples.

The agreement in the particle size measurements by the two methods would seem to justify the assumption that the hypochlorite adds one atom of oxygen to each nickel atom on the surface. The results are given graphically in Fig. 1.

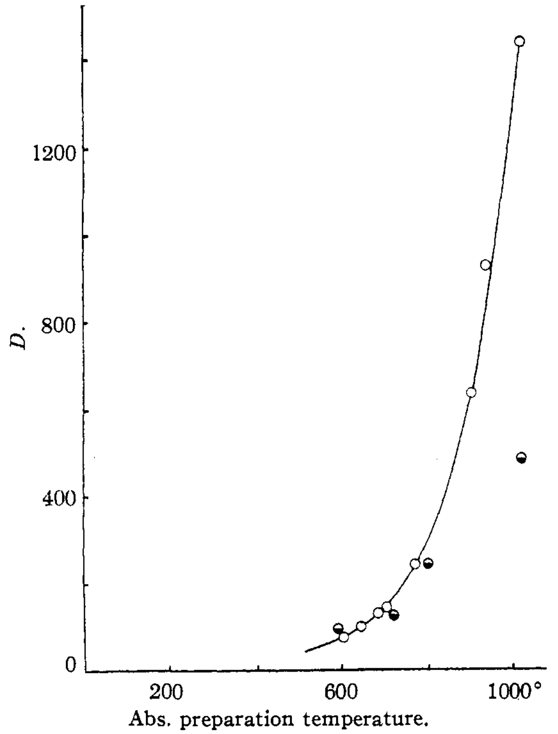

Fig. 1.—○, D determined by chemical method; ◒, D by x-rays.

Discussion.—The objection may be offered that the sintering action at any one temperature will proceed slowly but definitely over long periods of time and hence that the apparent relation between particle size and preparation temperature is only accidental. However, our experience has shown that all the sintering which will take place at any one temperature is substantially complete within an hour. A similar phenomenon has been noted by others. Fajans[4] states that when a nickel catalyst is sintered for ten minutes at a definite temperature, further sintering at the same temperature does not cause a further decrease in activity. Furthermore, for each sintering temperature a definite activity was reached regardless of the initial activity of the catalyst.

Apparently the aging of freshly prepared lead sulfate as studied by Rosenblum and Kolthoff[5] is a phenomenon similar to the sintering of nickel oxide. They state ". . . it is to be expected that after a certain time of heating at a given temperature, a final state of (crystal) perfection corresponding to that particular temperature will be found. In order to obtain a further aging the temperature has to be raised."

We believe that we have discovered a fundamental relationship between the size of crystals, or perfection of crystals, and the sintering temperature.

The Relationship between the Water Content of Nickel Oxide and the Particle Size.—The decomposition of nickel hydroxide has been studied by Hüttig[6] and Cairns and Ott[7] but no particular attention has been paid to the water content of the oxide when prepared from the hydroxide above 250°.

We have carried out many experiments decomposing the hydroxide in porcelain boats and in drying tubes of special design, in a stream of pure dry nitrogen in a thermostatically controlled electric furnace. The results may be summarized by saying that the decomposition of the hydroxide began to be rapid at 200°. At each temperature above this point, there remained a certain amount of water in the oxide which could not be removed in dry nitrogen at that temperature.

This water is believed to be associated with the surface of the nickel oxide because: (1) x-ray examination failed to show the presence of any nickel hydroxide. Only nickel oxide appeared to be present. The water cannot be in the lattice of the oxide and so must be on the surface. (2) As the oxide was sintered at successively higher temperatures, the water content decreased somewhat in proportion to the surface ratio as determined by the hypochlorite method.

The dehydration curves of various batches of oxides varied considerably, especially in the

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(4) Fajans, *Z. physik. Chem.*, **B28**, 239, 252 (1935).

(5) Rosenblum and Kolthoff, THIS JOURNAL, **57**, 2575 (1935).

(6) Hüttig, *Z. anorg. Chem.*, **189**, 183 (1930).

(7) Cairns and Ott, THIS JOURNAL, **55**, 527 (1933).

temperature range below 300°. Above 300° the results were fairly consistent. In Table III are given the results of the dehydration, and the water contents of the sample is compared with the surface ratio of nickel oxide prepared at the same temperature.

TABLE III

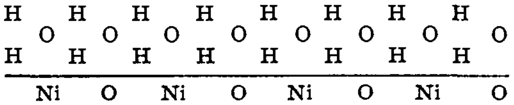
Temp., °C.	y, (mole H_2O per Ni atom)	x, (surface ratio)	y/x
250	0.26	0.14	1.85
330	.17	.088	1.9
375	.14	.064	2.2
400	.125	.055	2.3
450	.095	.040	2.4
		Average	2.1

The results show that the evolution of water becomes remarkably slow when a point has been reached corresponding approximately to two molecules of water adsorbed on the surface for each atom of oxygen that the surface can take up from sodium hypochlorite solution.

It must be made clear that by drying the sample of oxide in a high vacuum over phosphorus pentoxide at the same temperature as was used while drying in nitrogen, a further amount of water was slowly evolved but the rate fell off as the dehydration proceeded. Upon adding water vapor, and drying again in nitrogen, the original water content was found. Also when the vacuum-dried material was treated alternately with hydrogen and oxygen at 150° the water content rose approximately to the nitrogen-dried value. It is believed that the water was evolved rapidly until a monomolecular layer was formed and then further only with great difficulty.

It is thought that after oxidation by a cold sodium hypochlorite solution, one atom of oxygen is present on the surface for each atom of nickel. If so, the surface holds two molecules of water for each nickel atom on the surface.

A cross section of the hydrated surface might be represented as follows



$$\begin{array}{cccccccccccccccc} \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & \\ & \mathrm{O} & & \mathrm{O} & & \mathrm{O} & & \mathrm{O} & & \mathrm{O} & & \mathrm{O} & & \mathrm{O} & & \mathrm{O} \\ \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & \\ \hline & \mathrm{Ni} & & \mathrm{O} & & \mathrm{Ni} & & \mathrm{O} & & \mathrm{Ni} & & \mathrm{O} & & \mathrm{Ni} & & \mathrm{O} \end{array}$$

Discussion

Nickel oxide was prepared by LeBlanc and Sasche[2] by heating nickel carbonate in a vacuum at different temperatures. Their results are given in Table IV.

TABLE IV

Temp. of prepn., °C.	Active O atoms per Ni atom	y H_2O mols per Ni atom	x	y/x
250	0.046	0.50	0.11	2.3
300	.036	.25		
360	.031	.15	.074	2.0
475	.012	.06	.034	1.8
550	.006	.05	.028	1.8
675	.003	.025	.012	2.1
725	.002	.017	.010	1.7
800	.001	.013	.008	1.6
			Average	1.9

It is seen that y, the moles of water per atom of nickel, is also about twice the surface ratio of the nickel oxide prepared at the same temperature by us. Instead of an active oxygen content of as high as 0.04, as above, we found only 0.006 or less. The reason for this difference is not known.

Prasad and Tendulkar[8] have measured the catalytic activity of nickel oxide for the decomposition of hydrogen peroxide. Table V gives the ratio of catalytic activity, as measured by Prasad and Tendulkar, to the "surface ratio" as determined by our hypochlorite reaction on oxide prepared at a similar temperature.

TABLE V

Temp. of prepn., °C.	Catalytic activity	Surface ratio	Catalytic activity/surface ratio
400	81	0.055	1480
500	46	.0304	1510
800	16	.0079	2000
1000	8	.005	1600

Considering the range of the values of the activity and surface ratio, the ratio of the two are reasonably constant and show that in this case at least the activity of the catalyst may be proportional to its surface area.

Nickel Oxide Promoted by Alumina

A suspension of aluminum hydroxide was mixed with one of nickel hydroxide and the mixture was separated and dried in the same manner as with pure nickel hydroxide. After drying in nitrogen at 300° the composition was NiO : $0.0204Al_2O_3$: $0.11H_2O$. A similarly prepared pure nickel oxide was NiO : $0.19H_2O$. The effect of treating the sample with different amounts of reagent and for different lengths of time is shown as follows.

Sample, g.	NaClO solution 1 molar cc.	Hours at 25° C.	Atoms of active oxygen per atom of nickel
0.0575	20	48	0.0508
.0907	20	24	.0507
.1703	20	24	.0505

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[8] Prasad and Tendulkar, *J. Chem. Soc.*, 1403 (1931).

The final result is not affected either by the excess of reagent or the longer time of treatment.

The material was heated to various temperatures, cooled and oxidized by hypochlorite. The results are given in Table VI.

TABLE VI

Heated, min.	Temp., °C.	Active O/Ni	Active O/Ni for pure NiO
180	300	0.0507	0.100
90	370	.0420	.066
180	370	.0417	.066
90	570	.0172	.020
90	900	.0172	.006

At lower temperatures the oxide surface is partially covered by alumina, judging from the lower active oxygen values. However at 900° the growth of crystals and hence the decrease in surface area is quite evidently prevented, thus illustrating the role of a promoter in preventing the sintering of a catalyst at high temperature.

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Summary

1. Nickel oxide is composed of very small crystals when prepared at lower temperatures from the hydroxide.

2 By treating the nickel oxide with cold sodium hypochlorite solution, the surface takes up oxygen in an "active" condition which can be determined later by iodimetry. No separate phase of higher oxide is formed and, assuming a monomolecular layer, the particle size of the oxide can be calculated.

3. The x-ray determination of particle size makes it appear likely that after oxidation by hypochlorite there is one atom of active oxygen to each atom of nickel on the surface.

4. The particle size increases with increasing temperatures of preparation according to the equation $\log D = kT + C$ where D is the diameter of crystal, T the temperature, and k and C are constants.

5. The possible structure of the adsorbed water film on nickel oxide has been given.

6. The presence of aluminum oxide in nickel oxide retards sintering at high temperatures.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND PLANT LABORATORIES, URAL INSTITUTE OF FERROUS METALS]

New Oxidation–Reduction Indicators. I. Phenylanthranilic Acid (*o*-Diphenylamine Carbonic Acid)

BY W. S. SYROKOMSKY AND V. V. STIEPIN

After studies made by Walden[1] and his coworkers on the indicator properties of nitro- and amino-derivatives of diphenylamine, A. V. Kirsanov,[2] suggested as possible indicators carboxylic derivatives of diphenylamine the ortho, meta and para diphenylamine carbonic acids.

The first of these compounds was prepared by A. V. Kirsanov and V. M. Cherkasov[3] according to Ullmann.[4] These two investigators conducted some preliminary qualitative experiments with this compound as an indicator. The other two derivatives have never been prepared, but are now in the course of preparation for investigation. The molar oxidation potential of *o*-diphenylamine carbonic (phenylanthranilic) acid was determined by us, using the method described by Walden, Hammett and Chapman.[5] The results gave a value of 1.08 volts, referred to the hydrogen electrode (the mean from eight well-checked titration curves). Such a high oxidation potential is quite unexpected in the diphenylamine series of indicators, and places it in an exceptional position in this series.

A stock solution of indicator was used (0.005 *M* solution of the sodium salt of phenylanthranilic acid, prepared by dissolving the acid in an equivalent quantity of sodium carbonate).

From 3 to 5 drops are satisfactory for most titrations. As might be expected from the value of the oxidation potential, the indicator works quite

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(1) Walden, Hammet and Edmonds, THIS JOURNAL, **56**, 350 (1934).

(2) Laboratory of Organic Chemistry, Ural Geological Trust.

(3) Kirsanov and Cherkasov, *Bull. soc. chim.* (in press).

(4) Ullmann, *Ann.*, **355**, 312 (1907).

(5) Walden, Hammett and Chapman, THIS JOURNAL, **55**, 2649 (1933).