chloric acid solutions under the assumption that $\gamma_{UO_2^{++}}/\gamma_{U^{+4}} = 1$ and $\gamma_{H^+} = \gamma_{\pm HCl} = 0.809$.

(4) Summary

Polarographic, *p*H and potential measurements on solutions of uranium pentachloride in water have been carried out.

It was found that uranium pentachloride reacts with water to yield initially uranium(IV) and uranium(VI) and that near *p*H 2 uranium(IV) and uranium(VI) react rapidly to yield appreciable concentrations of uranium(V).

Near *p*H 2 the species U^{+4}, UOH^{+3}, UO_2^+ and UO_2^{++} can exist in equilibrium with each other. Verification of the assignment of the species was obtained through *p*H measurements.

The potentials of the uranium(IV)/(V), uranium(IV)/(VI) and uranium(V)/(VI) couples have been determined near *p*H 2. Utilizing the available knowledge of the hydrolytic behavior of the species involved, the potentials of these couples were estimated for unit activities of oxonium ions. The values for the potentials of the uranium(IV)/(V) and uranium(IV)/(VI) couples at this acidity were found to be approximately −0.55 and −0.31 v., respectively.

OAK RIDGE, TENN. RECEIVED JANUARY 31, 1949

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Structure and Activity of Supported Nickel Catalysts

BY FRED N. HILL[1] AND P. W. SELWOOD

The purpose of this work was to use magnetic, and other, methods to study the structure of supported nickel; and to relate the structural information, so far as possible, to actual catalytic activity.[2] This work was carried on simultaneously with related studies on supported manganese and iron. During the course of all the work there emerged the principle of valence inductivity.[3] Applications of the principle to supported nickel are included in the present paper.

Preparation of Materials

Magnesia.—This material was prepared as follows: 290 g. of magnesium chloride hydrate was dissolved in 15 liters of distilled water. To this there was added a solution of 160 g. of potassium hydroxide in 3 liters of distilled water. The finely divided precipitate was allowed to settle for twelve hours. The supernatant liquid was removed, and a cycle of washings by decantation was begun. After three washings, the mixture was heated to 70° for ten minutes, and then allowed to cool. This procedure allowed a partial agglomeration of the finer particles, and decreased the difficulty of filtration. The mixture was filtered, the precipitate again washed by decantation, and once more filtered. No chloride ion could be detected in the final wash water. The precipitate was dried at 110° for two days, ground in an agate mortar, then finally ignited at 360° for fourteen hours.

The final product showed no X-rays lines except those due to magnesium oxide. The magnetic susceptibility of this material was approximately -0.3×10^{-6}, and independent of temperature. The surface area of the magnesia was 138 ± 2 sq. m. per g. as determined by low temperature nitrogen adsorption.

γ-Alumina.—This support was prepared by a standard procedure. Aluminum metal shot was dissolved in potassium hydroxide solution. The resulting solution was filtered, partially neutralized with nitric acid, then treated with carbon dioxide until precipitation was complete. The precipitate was decanted, washed until the wash water was neutral, then filtered, dried at 110°, ground, and finally ignited at 450° for sixteen hours.

The X-ray diffraction pattern of this material gave no lines other than those of γ-alumina, although traces of *boehmite* may have been present. The X-ray pattern was somewhat diffuse. The magnetic susceptibility of the alumina was approximately -0.3×10^{-6}, substantially independent of temperature down to −190°. The surface area of the alumina was 230 ± 5 sq. m. per g.

Rutile.—This material was obtained from the National Lead Company, Titanium Division. The X-ray pattern showed no lines other than those due to *rutile*. The magnetic susceptibility was approximately -0.3×10^{-6}, and was independent of temperature. The surface area was 126 ± 5 sq. m. per g. Neither the surface area nor the magnetic susceptibility of the *rutile* were appreciably altered by a twelve hour ignition at 450°.

Nickel Oxide on Magnesia.—This system was prepared by impregnation of the high-area magnesia with nickel nitrate solution. The mixture was then dried and ignited. Details of preparation were similar to those described more fully below for the nickel-alumina system. It was noted that quite dilute nickel nitrate solution sufficed for appreciable nickel concentrations in the finished catalyst. The supported oxide ranged in color from gray to black.

Nickel Oxide on Alumina.—Between 5 and 10 g. of *gamma*-alumina was stirred with nickel nitrate solution for five minutes. The volume of solution was usually 10 cc. per gram of support. This is much in excess of the amount of solution necessary to saturate the alumina. The slurry was filtered with suction, then dried at 110° and ignited for twelve hours at 450°. Samples were prepared in this way ranging from 2 to 24 weight per cent. of nickel. The nickel content was, of course, related to the nickel concentration in the solutions used for impregnation. For instance 5 g. of alumina impregnated with 50 cc. of 3.28 *M* nickel nitrate solution yielded an ignited sample containing 22.9% nickel.

The above procedure is believed to yield a more homogeneous product than the commonly used method of adjusting the volume of impregnation solution to that just necessary to saturate the support. Nevertheless, it is difficult to obtain microscopic homogeneity. There are always formed small clumps of massive nickel oxide, through drying and ignition of occluded solution. The magnetic data thus all tend to be low because dispersed nickel oxide has a much higher magnetic susceptibility than has the massive oxide.[4]

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[2] This is the seventh paper on the susceptibility isotherm from this Laboratory. The sixth appeared in THIS JOURNAL, **71**, 2181 (1949).

[3] Selwood, THIS JOURNAL, **70**, 883 (1948).

[4] The term "massive" oxide is here used to mean a well-crystallized, pure compound, in contrast to a dispersed or attenuated oxide such as a supported compound or a gel-like substance.

The preparations of supported nickel oxide described above were made by single impregnation steps. Samples were also made by the multiple impregnation procedure. The procedure was the same as that described except that the ignited, supported, oxide was used as a support through another impregnation. As many as nine impregnations were made with approximately 1% of nickel being added at each step. The single impregnation supported oxides ranged in color from very pale blue to gray. The multiple impregnation samples were a pronounced pale blue.

Nickel Oxide on Rutile.—The procedure for these preparations was similar to that described above except that much more concentrated nickel nitrate solutions were required. All the samples were bright yellow.

Analysis of Supported Oxides.—The alumina-supported samples were analyzed for nickel as follows: a sample to contain approximately 40 mg. of nickel was weighed out. With samples of high nickel concentration, conveniently larger samples were weighed and aliquot portions taken after solution. The weighed sample was dissolved in 1:1 sulfuric acid. Heating for twenty minutes was often necessary to effect solution. The solution was diluted to about 300 cc., and 5 cc. of saturated tartaric acid solution was added. This served to prevent precipitation of hydrous aluminum oxide in the next step. The solution was then neutralized with ammonium hydroxide, and slightly acidified with dilute sulfuric acid. The solution was heated to 70°, and 25 cc. of 1% dimethylglyoxime solution was added. The mixture was stirred and slowly made basic with ammonium hydroxide. The red precipitate was allowed to settle, and then collected on a porous porcelain crucible, washed, dried at 110°, and weighed. The reproducibility of analyses was excellent.

Analysis of the magnesia-supported samples was similar except that the samples were dissolved in hydrochloric acid, and that precipitation of magnesium hydroxide was prevented by ammonium chloride.

Analysis of the titania-supported samples proved much more difficult. Solution of the sample was effected by fusion with potassium bisulfate, of which 10 g. was added to 1 g. of sample. The mixture was fused until all the sample dissolved. It was then cooled and dissolved in 200 cc. of 6 *N* sulfuric acid. The solution was slowly made basic with ammonia, and a rough separation was accomplished owing to the solubility of the nickel ammonia complex and the insolubility of the titanium hydrous oxide. After being filtered and washed, the precipitate was redissolved in sulfuric acid, reprecipitated, and filtered. The process was repeated once more, after which the precipitate gave only a faint coloration with dimethylglyoxime. The combined filtrate was concentrated, and analyzed as described above. Several other procedures were investigated in an effort to find a less tedious method, but all proved less reliable.

Experimental Procedures

Magnetic, surface area, and X-ray procedures have all been described in earlier papers. A single measurement on the chemisorption of carbon monoxide by reduced nickel-alumina was made by the method described by Emmett and Brunauer.[5] There remain to be described in this section the quantitative reduction of the supported nickel oxide by hydrogen, the specific magnetization (ferromagnetism) of the reduced nickel, and the measurement of catalytic activity.

Quantitative Reduction in Hydrogen.—There are two reasons for obtaining quantitative data on the reduction of supported nickel oxides. The first reason is that it is idle to compare catalytic activities unless the extent of reduction is comparable in several catalysts. The second reason is that reduction in hydrogen offers the most convincing evidence for deviation of the maximum nickel oxidation state from two.

The obvious method for obtaining quantitative reduction data is to pass hydrogen over the sample and to weigh the evolved water. This method proved unsatisfactory because the pure supports all contained water which was slowly given up over very long heating periods. The method successfully used was a measurement of hydrogen used up during reduction. The apparatus is shown in Fig. 1. The sample weighing about 1 g. was placed in G and lightly plugged with glass wool. The entire apparatus was then evacuated while the sample was moderately heated. Pure hydrogen from reservoir B was admitted to the buret system A, in which the temperature and volume of the gas was measured. The measured volume was then admitted to the sample through stopcock D. The sample tube was heated to any desired temperature in an electric furnace. Evolved water was frozen in trap F. The hydrogen was circulated by a Toepler pump, the action of which was made automatic by a mercury valve described by Maass.[6] The Toepler pump also served to exhaust the residual hydrogen into the buret system for measurement. This apparatus gave satisfactory service for runs as long as three weeks. For example 65.2 cc. of hydrogen were passed over 1.2 g. of pure alumina for thirty hours at 350°, and at the end of that time 65.2 cc. of gas was recovered.

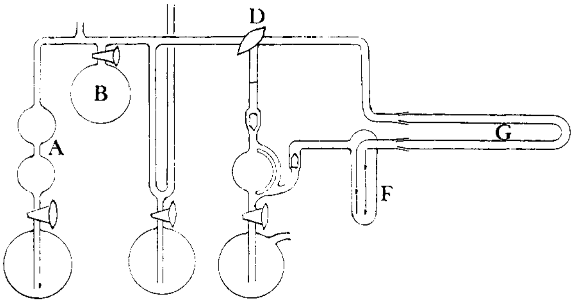

Fig. 1.—Apparatus for quantitative reduction of samples in hydrogen.

Specific Magnetization.—The fact that nickel metal is ferromagnetic makes it interesting to measure the ferromagnetism developed when the supported oxides are reduced. Measurements were made with a simple primary coil surrounding opposed secondaries which were connected through a ballistic galvanometer. Reduced catalyst samples were placed inside one of the secondaries, the current in the primary was reversed, and the galvanometer deflection was observed. It was realized that this method is open to objection in that saturation is probably never attained, and hence the results are qualitative only. But pending the construction of an apparatus employing a saturating field, it was felt that the measurements would be of interest and would suggest directions for future work, as actually proved to be the case. It should be mentioned that all reduced samples were handled in absence of air.

Catalytic Activity.—The reaction chosen for the activity tests was the hydrogenation of benzene. The measurements were restricted to the nickel–alumina series. The reason for this was that quantitative reduction of nickel–magnesia and of nickel–titania proved impossible.

Comparison of catalytic activities for samples containing different percentages of nickel was done by a method which had previously proved convenient for testing the dehydrocyclization of *n*-heptane over chromia–alumina. In all activity tests the total nickel concentration was set at 3.33% nickel. In all but the most dilute sample this was achieved by making a mechanical dilution of the original prepared catalyst. The diluting agent was γ-alumina identical with that used for impregnation. In this way a series of catalyst samples was prepared. They differed from each other, not in total nickel, but in the ratio of alumina used as support to that used merely as a mechanical diluent.

In all tests 3 g. of catalyst was used. Each then contained 0.1 g. of nickel. The samples were reduced *in situ*

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(5) Emmett and Brunauer, THIS JOURNAL, **59**, 1553 (1937).

(6) Maass, *ibid.*, **41**, 54 (1919).

at 510° for sixteen hours. This reduction procedure was adequate to insure quantitative reduction, but not so drastic that irreversible changes of any magnitude occurred. A few comparable measurements were also made using different reduction temperatures and times.

Catalytic activity was measured as follows: pure hydrogen was bubbled at about 200 cc. per min. through two benzene saturators, in series, held at 25°. The gas mixture was then passed into the catalyst chamber where it went through a porous glass disk directly into the powdered catalyst. The reaction chamber was maintained at 125° for all runs.

The reaction mixture was passed through a Dry Ice trap from which samples were removed for analysis by refractive index. Catalytic activities are expressed as moles per cent. of cyclohexane per mole of benzene feed.

Results

Magnetic Susceptibilities.—Table I gives susceptibility data on the unreduced nickel-magnesia system. Following the system used in presenting data for other systems there are given the measured susceptibility of the unreduced catalyst at several temperatures. Directly under each measured susceptibility there is given the calculated susceptibility per gram of nickel, on the assumption that the susceptibilities of alumina and of oxide ion remain unchanged.

TABLE I

SUSCEPTIBILITY DATA ON NICKEL OXIDE–MAGNESIA

Ni, %	Susceptibilities × 10⁶ 298°K.	186°K.	102°K.
1.70	0.65	1.15	2.1
	56	81	141
2.77	1.15	1.95	5.0
	55	82	180
3.22	1.6	2.3	5.5
	58	82	180
3.48	1.8	2.6	5.4
	60	85	164
4.25	2.1	3.3	6.8
	57	85	167
4.83	2.5	4.0	8.8
	57	89	189
6.00	2.9	4.8	9.4
	54	85	156
6.24	3.2	5.2	10.0
	56	88	165
7.23	3.4	5.4	10.2
	51	79	145
7.33	3.7	5.9	11.2
	53	85	157
9.55	4.5	7.1	13.6
	51	77	145
11.2	5.5	8.1	16.8
	52	75	152
12.8	6.1	9.7	17.3
	50	80	137
14.5	6.8	10.6	18.2
	49	75	127
16.6	6.7	11.3	19.7
	42	70	120
23.2	9.2	13.0	23.0
	41	58	100
25.7	9.6	13.5	26.3
	39	54	103
26.8	9.8	13.7	22.7
	38	52	86
31.2	10.5	14.5	28.7
	35	48	93
32.0	10.7	14.1	25.0
	34	45	79

Corresponding data for nickel–alumina and for nickel–titania are shown in Tables II and III, respectively.

TABLE II

SUSCEPTIBILITY DATA ON NICKEL OXIDE–ALUMINA

Ni, %	Susceptibilities × 10⁶ 298°K.	186°K.	102°K.
1.85	1.0	1.8	4.3
	70	116	248
2.22	1.20	2.4	5.1
	69	120	240
2.91	1.45	3.0	5.8
	62	113	209
3.24	1.9	...	...
	68		
3.39	2.0	...	...
	68		
3.75	2.0	3.8	7.0
	62	109	195
4.65	2.3	4.4	9.5
	57	100	204
5.15	2.6	4.9	9.7
	56	101	194
5.5	2.7	5.6	10.3
	55	107	192
6.45	3.1	5.8	11.4
	53	95	182
6.75	2.9	6.6	12.0
	48	102	180
7.30	3.2	...	...
	48		
8.15	3.3	...	...
	45		
9.1	4.1	...	...
	47		
10.0	3.8	...	...
	41		
11.3	4.4	9.5	17.8
	42	87	160
12.0	4.9	8.9	20.0
	43	78	168
14.9	5.2	...	...
	38		
17.4	6.2	14.0	23.5
	37	82	137
19.5	6.5	13.4	26.0
	35	75	135
21.2	7.1	...	...
	35		
22.9	7.8	...	...
	36		

Table IV gives magnetic data on a nickel oxide–alumina sample prepared through multiple impregnation.

TABLE III

SUSCEPTIBILITY DATA ON NICKEL OXIDE–TITANIA

Ni, %	Susceptibilities × 10^6 298°K.	186°K.	102°K.
3.86	3.1	5.2	9.0
	88	145	240
4.45	3.7	6.0	10.5
	90	141	242
6.9	5.1	8.0	14.2
	78	120	210
10.1	8.0	12.4	21.2
	82	127	213
11.3	8.3	12.7	21.8
	76	115	196
15.1	10.7	18.0	29.4
	73	121	193

TABLE IV

SUSCEPTIBILITY DATA ON MULTIPLE IMPREGNATION NICKEL OXIDE–ALUMINA

Impregnation step	Ni, %	Susceptibilities × 10^6 298°K.	186°K.	102°K.
1	1.85	1.0	1.8	4.3
		70	116	248
4	5.63	3.9	...	...
		73		
6	7.70	5.1	9.6	16.0
		70	128	212
9	10.5	6.65	12.0	20.5
		66	117	198

It is of interest to compare the susceptibility of supported nickel with that of nickel in massive crystalline nickel oxide prepared by ignition of pure nickel nitrate. The nickel in this compound has a susceptibility per gram of about 16 $\times 10^{-6}$, and this value is virtually independent of temperature. It is clear, therefore, that all series of supported nickel oxide show the large increase of susceptibility at low concentrations, as already reported for supported chromium, tungsten, uranium, copper, manganese, and iron in recent papers from this Laboratory.

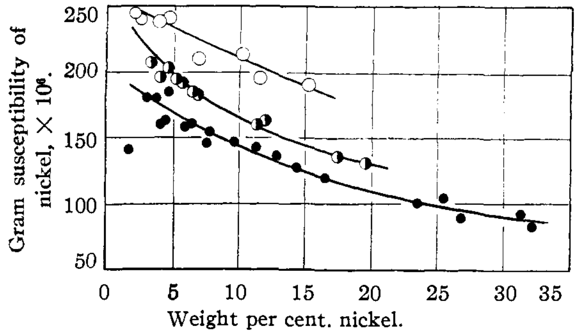

Fig. 2.—Susceptibility isotherms for nickel oxide supported on: ○, titania; ◑, alumina; and ●, magnesia; all at −171°.

Figure 2 shows susceptibility isotherms for nickel oxide supported on magnesia, on alumina, and on titania, all at 102°K. Figure 3 gives magnetic moments as a function of concentration for each of the three series, throughout the rather limited low concentration range in which the Curie–Weiss law applies.

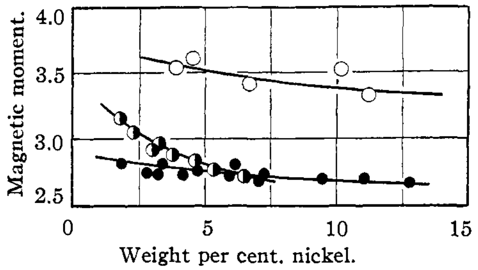

Fig. 3.—Magnetic moment as a function of concentration for nickel oxide supported on: ○, titania; ◑, alumina; and ●, magnesia.

The magnetic moment of nickel in the most concentrated sample prepared by multiple impregnation was 3.1. This sample contained 10.5% nickel.

In all samples of supported nickel oxide the Weiss constant was found to be zero within the limits of experimental error (±20°); and the form of the susceptibility isotherm is due to (1) more or less rapidly changing moment with concentration, and (2) deviations from the Curie–Weiss law.

In the case of the titania-supported samples it was felt that there was a remote possibility of some unexpected chemical change having taken place in the support itself. A sample of high area *rutile* was impregnated with sodium nitrate solution, then dried and ignited as in the preparation of the nickel–titania samples. The product containing sodium–titania proved to be white and to have a diamagnetism indistinguishable from that of the pure support.

Quantitative Reduction in Hydrogen.—As previously pointed out, the attempted reduction of nickel–magnesia and of nickel–titania was unsuccessful because even after very long periods little more than half the nickel oxide present was reduced. The reason for this failure must be related to the way in which the nickel ions tend to build themselves into the support lattice. By contrast, the reduction of nickel–alumina was completely successful and will be described in detail.

In Table V there are given reduction times, volume of hydrogen used, and equivalents of

TABLE V

Reduction time, hours	H_2 volume used (S. C.), cc.	Equivalents H_2 per gram atom Ni
16	5.7	0.62
24	11.2	1.21
54	15.4	1.68
77	16.0	1.74
128	17.0	1.83
131	18.1	1.97
150	18.2	1.98
174	18.2	1.98

hydrogen used per gram-atom of nickel. The sample weight was 0.746 g. and the concentration of nickel was 6.45%.

Data for a second sample weighing 1.546 g. and containing 3.4% nickel are shown in Table VI.

TABLE VI

Reduction time, hours	H_2 volume used (S. C.), cc.	Equivalents H_2 per gram atom Ni
3.5	18.9	1.88
5.2	20.2	2.02
8.7	22.3	2.22
10.2	23.2	2.32
23	25.1	2.50
45	26.8	2.68
59	26.8	2.68
69	26.8	2.68

Figure 4 shows apparent oxidation states of nickel oxide supported on alumina, as a function of nickel concentration. For comparison purposes the apparent oxidation state of nickel in massive nickel oxide (NiO) was found by this method to be 2.04, that of nickel in a multiple impregnation sample supported on alumina was found to be 2.56 when the nickel concentration was 6.9%.

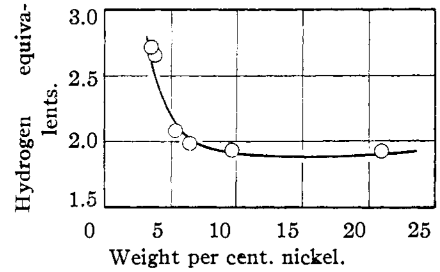

Fig. 4.—Hydrogen equivalents required for reduction of nickel oxide supported on alumina, as a function of nickel concentration.

As might have been expected the X-ray diffraction pattern yielded nothing of interest in the supported systems because no lines due to anything but the support could be found until the nickel concentration exceeded 12%, above which crystalline nickel oxide (NiO) was present in abundance.

One other point to be mentioned in this section is the magnetic properties of nickel–alumina samples after reoxidation. Several samples were reduced quantitatively in hydrogen, then reoxidized by heating in air for twelve hours at 450°. The magnetic susceptibilities per gram of sample are shown in Table VII.

TABLE VII

Wt. % Ni	Susceptibility × 10^6 Original	Susceptibility × 10^6 After reoxidation
7.9	3.3	4.1
11.3	4.4	5.5
17.8	7.4	8.0
21.2	7.1	8.6

Estimation of Exposed Metal Surface.—Only one sample was studied by the Emmett and Brunauer method for exposed metal. This sample was that containing 10.5% nickel, and prepared by multiple impregnation. The nitrogen area of the reduced sample proved to be 187 sq. m. per g. The volume of chemisorbed carbon monoxide was 5.4 ± 0.4 cc. per g. Complete monolayer formation per gram of catalyst would have required 43 cc. of carbon monoxide. The exposed metal surface may then be estimated as 5.4/43 = 13% of the total surface.

While this determination is approximate only, yet it is instructive to compare the area with that which could be covered by a monolayer of close-packed nickel atoms. Assuming that the radius of a nickel metal atom is about 1.2 Å., a sample of nickel weighing 0.105 g. could cover a minimum area of $(0.105/58.7) \times 6.03 \times 10^{23} \times (10/9) \times \pi(1.2 \times 10^{-10})^2$ sq. m. = 54 sq. m. Normal packing as on the (111) face of crystalline nickel would raise this to 58 sq. m. On the other hand 13% of 187 sq. m. is 24 sq. m.

Specific Magnetization.—The data obtained on reduced samples (all handled in complete absence of air) are conveniently expressed as deflection produced on the ballistic galvanometer divided by deflection produced by an equal weight of pure nickel. All samples were diluted mechanically so as to contain the same weight of nickel, and care was taken to see that reduction was complete. For obvious reasons the nickel–alumina system was the only one which could be studied in this way.

The data are shown in Fig. 5, in which relative deflection is plotted against original nickel concentration. For comparison, the sample prepared by multiple impregnation, and containing 10.5% nickel, gave a relative deflection of only 21% as compared with 44% deflection for a sample of the same nickel concentration but prepared by a single impregnation step.

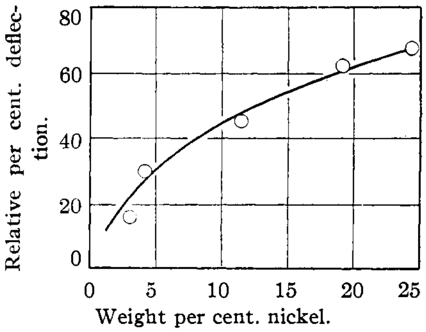

Fig. 5.—Relative specific magnetization (ferromagnetism) as a function of nickel concentration for reduced nickel/alumina.

Catalytic Activity.—Activities in mole per cent. cyclohexane per mole of benzene feed are shown in Fig. 6 as a function of nickel concentration. These data are for a series reduced at 510° for sixteen hours. Changing the reduction temperature altered the activity levels but did not change the great decrease in activity in the neighborhood of 8% nickel. For comparison, a sample prepared by multiple impregnation and containing 10.5% nickel had an activity of only 3% as compared with 26% for a single impregnation catalyst of the same concentration.[7]

Discussion of Results

The susceptibility isotherm for nickel oxide supported on γ-alumina has been shown to have the same general form as those already reported for chromia–alumina, and for low-ignition manganese–alumina, although the critical point (point "l") is not so sharply defined as in the case for the other systems. This general form for the susceptibility isotherm has now been demonstrated for supported chromium, manganese, iron, nickel and copper. Preliminary results indicate that similar isotherms will be obtained for supported tungsten, uranium, vanadium and cobalt. On the other hand, supported molybdenum and rhenium show practically zero susceptibility through the concentration range. It will be shown below that this difference with molybdenum and rhenium probably is one of degree rather than of kind.

Analysis of the nickel oxide–alumina system magnetic data shows that the Curie–Weiss law holds only within a rather low concentration range, and that the deviation at higher concentrations contributes to the form of the isotherm. Within this narrow concentration range the Weiss constant is so small as to be negligible. This is not surprising when it is considered that the exchange integral, the number of nearest paramagnetic neighbors, and the spin vector are all probably smaller for nickel oxide than is the case in any of the systems previously reported.

The magnetic moment for nickel in the nickel oxide–alumina system is seen to change rapidly with changing nickel concentration. The form of the susceptibility isotherm in the low concentration region is obviously determined by this change of magnetic moment. Nickel–alumina is thus seen to make an interesting comparison with several of the systems previously reported. For chromia–alumina the isotherm was almost wholly determined by a large change in the Weiss constant, indicating change in ionic environment. For the low-ignition manganese oxide–alumina system the isotherm was determined by a combination of changes occurring in both Weiss constant and in moment. In nickel oxide–alumina the isotherm is determined largely by a change of moment.

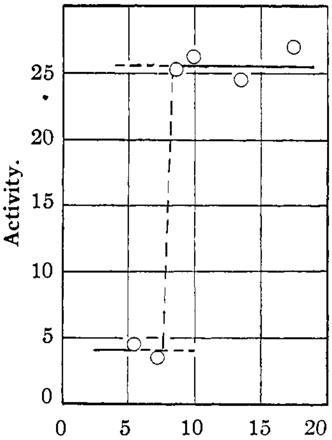

Fig. 6.—Catalytic activity as a function of nickel concentration for nickel/alumina.

It is clear from these results that the susceptibility isotherm cannot give much information concerning the state of aggregation of the nickel ions in this system. On the other hand the isotherm reveals the hitherto unsuspected fact that the magnetic moment, and hence the oxidation state of the nickel, is larger than could be accounted for if the nickel had a valence of two.

This result is such that independent confirmation was felt necessary, and experiments were conducted on the equivalents of hydrogen necessary to reduce the nickel. A fortunate coincidence makes it possible to reduce all the nickel in this system, although this is not true of nickel on other supports.

The quantitative reduction of nickel oxide–alumina by hydrogen proves beyond doubt that in this system a substantial fraction of the nickel enjoys an oxidation state higher than two. The fraction of nickel in the higher oxidation state may be increased by resort to multiple impregnation in the preparation step. In this way up to 10% nickel may be obtained, nearly all in the +3 state. Our view of the phenomenon is that the alumina exerts an inductive action on the nickel, leading it to assume a radius, and oxidation state, such that it may fit naturally as a simple extension of the alumina lattice. This effect of valence inductivity has now been demonstrated for manganese and for iron, as well as for nickel. The effect carries the implication that vestiges of *chemical imitation* may be found in the simplest inorganic systems, as well as in the most complicated organic compounds.

Further examples of the valence inductivity effect are to be found in the results on nickel

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(7) The activity results suggest so strongly that a minimum aggregation of nickel atoms is necessary for catalytic activity in this system, that they were repeated on entirely new preparations by Mr. John Mooi, in this Laboratory. Mr. Mooi's results confirm in detail the effect found, namely, that there is a major change in activity at low nickel concentrations. The precise position of this change depends on conditions of impregnation, ignition, and reduction, but there seems little doubt that catalysts containing less than 3% nickel are almost always virtually inactive for this reaction, while those containing more than 10% nickel are generally highly active. It will be repeated that the method for making these tests involves using the same weight of nickel in each run, so that it is difficult to see how poisoning effects could affect the results.

oxide–magnesia, and on nickel oxide–titania. These systems, unfortunately, resist quantitative reduction in hydrogen. The nickel in nickel oxide–magnesia has a magnetic moment corresponding exactly with that expected for +2 nickel. The color is gray to black. For nickel oxide–titania the magnetic moment is much lower than expected for +4 nickel. However, the moment is higher than that found for nickel on alumina which proved to have a valence of three; and the hydrogen reduction, although incomplete, was carried beyond two equivalents. Furthermore, the color is a rich yellow, as compared with a clear pale blue for +3 nickel. It must be admitted that the evidence for +4 nickel is more tenuous than that for the other oxidation states. But it may be recalled that iron which was shown chemically to have an oxidation state of +4 on titania had also a magnetic moment considerably lower than expected. The difficulty seems to be, not in the induced valences, but rather in the subnormal magnetic moments. A possible explanation for this effect is presented in the following paragraphs.

The idea that covalent bonds may exist between adjacent metal ions is not new, but so far no method has been available for the definition of such bonds. In several recent papers from this Laboratory it has been pointed out that observed magnetic moments may be less than theoretical moments based on the spin-only formula, and it has been assumed that these diminished moments were caused by partial or complete covalent bonds between adjacent ions. A possible definition of *intercation* covalency is to be found in the diminution of magnetic moment from that theoretically probable. For instance, suppose that trivalent iron under certain conditions is found to have a moment of 3.6 instead of the spin-only value of 5.9. The degree of intercation covalent bond formation may be expressed as the percentage $(5.9 - 3.6)/5.9 = 39\%$.

It is probable that intercation covalency depends on several factors among which are the number of unpaired electrons (in the free ion), and the minimum distance between ions. It may be convenient to prepare a table showing those ions with equal numbers of unpaired electrons, and to indicate after each symbol the percentage covalency defined as above. Some magnetic moments change with changing concentration of supported oxides. We shall arbitrarily calculate the intercation covalency for 5% supported oxides; all the necessary magnetic data being obtained from this and earlier publications from this Laboratory.

TABLE VIII

Unpaired electrons	Ion and its intercation covalency in 5% supported oxide
1	Cu^{+2}(0)
2	Mo^{+4}(100), Ni^{+2}(0), U^{+4}(0?), W^{+4}(50?)
3	Cr^{+3}(10), Mn^{+4}(0), Ni^{+3}(29), Re^{+4}(100)
4	Co^{+3}(–), Fe^{+2}(–), Fe^{+4}(28), Mn^{+3}(0), Ni^{+4}(27)
5	Co^{+4}(–), Fe^{+3}(27)

This table may prove to be of some value in estimating the minimum distances of cation–cation approach in supported oxides. For instance, it might have been predicted that the molybdenum ions in the dioxide would be unusually close together. This is shown by Magnéli[8] to be actually the case. Similarly, it may be predicted that rhenium ions in the dioxide are quite close together.

We turn now to a brief discussion on a possible state of aggregation for the supported nickel ions on alumina. As pointed out, the Weiss constant gives no aid in understanding the structure of this system. But several lines of evidence suggest that the structure assumed by supported chromia, namely, an aggregation into microcrystal nuclei, is also the structure assumed by nickel. The experiments on nickel clearly show that the greater proportion of trivalent nickel on alumina is obtained when the nickel concentration is low, that is when each nickel ion tends to be in contact with, and under the influence of, alumina rather than of nickel oxide. This suggests that a maximum of valence inductivity would be obtained for infinite magnetic dilution, and this actually seems to be the case. The multiple impregnation experiments may be interpreted as approaching the condition of infinite dilution because in any one step the population density of nickel is so low that the chance of an incoming ion striking bare alumina is much greater than that of striking nickel oxide. At least this is true until the alumina surface becomes fairly well covered.

Furthermore, prolonged heating, or reduction followed by reoxidation, seems to have no structural effect other than to promote some three-dimensional solid solution, as shown by a tendency for the susceptibility to rise slightly during these operations. If the nickel were at infinite magnetic dilution as first prepared on the support, then it is difficult to see how the susceptibility could rise, even slightly, during further processing. These results also show that the nickel atoms have no tendency to aggregate during catalyst use or other change. This is a result found to be true of all supported systems so far studied, namely, that the tendency is for further dispersion to take place by a process of solid solution, and that aggregation into larger crystallites does not take place.

The unlikely possibility that the nickel oxide is at any concentration spread on the alumina in a monatomic layer is easily excluded by a comparison of total nickel and of alumina area, together with the magnetic data as described above.

Supporting evidence for these views is found in the single observation on carbon monoxide chemisorption which was made on a 10.5% multiple impregnation sample. A monatomic

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(8) Magnéli, *Ark. Kem. Mineral. Geol.*, **24A**, Nr. 2 (1946).

layer of reduced nickel may be thought of simply as a close-packed layer of spheres, of radius about 1.2 Å. It was shown above that such a layer could cover only about 30% of the alumina surface in the catalyst of 10.5% nickel concentration. The actual nickel area found was 13% of the total catalyst area. The chemisorption experiment therefore gives further evidence that the nickel is dispersed to a very high degree, but that the average nickel particle still contains roughly two atom layers. Presumably the inductive effect on the valence could not be expected to extend much farther than two atom layers.

Still further support to this general picture of the surface is given by the results on specific magnetization. It is well known that ferromagnetism is a property of matter in the bulk although some uncertainty still exists concerning the size of the minimum ferromagnetic domain. The results obtained show that at low nickel concentrations few nickel particles reach the minimum size necessary to produce ferromagnetism. As might have been expected, the sample prepared by multiple impregnation shows that this procedure results in a substantial diminution of size or number, or both, of such ferromagnetic particles. It may be expected that careful preparation of a low nickel catalyst might produce one completely free from ferromagnetism.

We turn now to the results on catalytic activity. As is not infrequently the case, it proved difficult to reproduce activity results on different samples of the same concentration, although consecutive runs on the same sample gave results in very satisfactory agreement. The significant feature of the activity results is that low nickel concentrations consistently gave activities between ten to thirty-fold less than high nickel concentrations. The demarcation between high and low activities seems to be fairly sharp, but is not reproducible within several per cent. A reason for this lack of reproducibility is readily found if it is granted that a minimum catalytic domain is essential for activity.

Adsorption of a gas on to a solid is generally readily attainable under strictly isobaral conditions, but adsorption from a solution under the corresponding condition is virtually impossible. This is because the rate of diffusion is very low in solution, as compared with that in gases. Consequently, even though a large excess of impregnating solution is used, it is impossible to avoid having some alumina surfaces reached by more depleted nickel nitrate solution than others. This leads to inhomogeneity in the distribution of nickel in the finished catalyst.

In general the catalysts containing below 3% nickel had slight activity, those above 10% were almost always highly active. By proper procedures it might be possible to make an active catalyst containing less than 3% nickel, just as by multiple impregnation it is possible to make a low activity catalyst containing more than 10% nickel. The activity clearly depends on the nickel crystal size, and the size may be modified by appropriate procedures.

We come, therefore, to the conclusion that the geometrical aggregation of metal atoms is a major factor in the catalysis of benzene hydrogenation. This is, of course, in agreement with at least one well-known theory of catalysis.[9,10] The result is in sharp contrast to those on the dehydrocyclization of *n*-heptane on chromia–alumina, in which activity increased with dispersion through the whole available concentration range.

Summary

Susceptibility isotherms have been determined for nickel oxide supported on high area magnesia, γ-alumina, and *rutile*. The phenomenon of valence inductivity has been shown to apply in these systems, leading to nickel oxidation states of two, three and four. A quantitative definition is proposed for intercation covalency. The structure of nickel–alumina catalysts is discussed and related to activity for the hydrogenation of benzene. In agreement with current theories, a minimum geometrical aggregation of nickel atoms is shown to be required for the catalysis of this reaction.

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(9) Balandin, *Z. physik. Chem.*, **B2**, 289 (1929).

(10) Taylor, "Chemical Architecture," ed. Burk and Grummitt, Interscience Publ., Inc., New York, N. Y., 1948, pp. 1–22.