ACTIVATION EFFECTS OF MAGNETISM ON REDUCED NICKEL SUPPORTED ON METALLIC OXIDES*

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A study was made of the magnetic susceptibility of the various metallic oxides used with varying quantities of nickel supported on them. It was shown that there is an increasing amount of evidence in favour of a direct relationship between the magnetic susceptibilities of the supports and their catalytic activities. An attempt was made to study the nature of the reduced nickel on the supports by the carbon monoxide chemisorption method, electron microscope and X-ray diffraction.

Several workers, notably Winger,[1] and Kalcher and Teller[2] have investigated a possible relationship between magnetism and catalysis. No single mechanism can possibly explain all catalytic activities, but catalysis and magnetic properties are often found together. In some cases, such as the ortho-para hydrogen conversion, there is a direct relationship between the activity of the catalyst and its magnetic moments. In others, the magnetic properties of a catalyst can be made use of in the determination of its structure. Diamagnetic gases do not catalyse, but diamagnetic solids such as charcoal are excellent catalysts. The heterogeneous ortho-para hydrogen conversion on paramagnetic oxides has been studied by Taylor and Diamond.[3] The effect is marked in that a 6 hours contact with diamagnetic lanthanum oxide produced only 17 percent conversion, whereas less than three minutes contact with strongly paramagnetic gadolium oxide produced nearly 100 percent conversion. This experiment is impressive because of the striking similarity in all the chemical as well as physical properties of these oxides. This magneto-catalytic effect was confirmed by Forestier [4] and Selwood.[5]

Conflicting reports, however, appear from time to time in the literature. For instance Olmer [6] failed to find any relationship between the catalytic activities of iron, nickel and cobalt and their magnetic properties. Ogawa, [7] on the other hand, claimed that the ortho-para conversion of hydrogen on a ferromagnetic catalyst is retarded by the magnetisation of the catalyst. The question as to whether there is an effect of a magnetic field on the reaction velocity and the chemical equilibrium has also been discussed by Bhatnagar and Mathur.[8]

Elements which show strong catalytic activity can be related more or less directly to their magnetic properties, d-band character and unpaired electrons. In recent years, Maxted [9] has pointed out that there exists considerable evidence that the catalytic activity is related to the d-band deficiency. In other words, the catalytic activity is proportional to the degree to which d-orbitals are filled with paired electrons. This is confirmed further by the observation that the poisons for such catalysts are substances which eliminate the d-band deficiency by contributing electrons. Such substances are atoms or groups having free electron pairs in the valency shell; metals with half filled or completely filled d-band or compounds with unsaturated bonds. An example can be cited in the poisoning action of dimethyl sulphide on palladium, which causes a decrease of paramagnetism, owing to the filling of the partially unoccupied d-band of the metal of electrons from the free pair in the sulphide.

The purpose of the present work was to use magnetic susceptibility measurements to study the structure of supported nickel and to relate the magnetic data to actual catalytic activity, as far as possible.

Preparation of Supports

Nickel supported on zirconia, thoria, titania and lanthanum oxide were prepared as follows:

The general experimental method of preparing reduced nickel on various oxide supports as laid down in detail in a previous publication [10] was followed. A fixed amount of support (4.5 g.) was taken in a narrow glass vessel and to this was added a varying amount of nickel formate (0.25 g. to 4.5 g.) dissolved in aqueous ammonia (0.88M). Ammonia was slowly boiled off the sample accompained by vigorous shaking in order to ensure a thorough impregnation of nickel formate on the metallic oxide. It was dried overnight (12 to 14 hours) in an oven at 65°.* The sample was then reduced under a current of hydrogen at 280° for

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*All temperatures are in degrees centigrade unless stated otherwise.

about 90 minutes, cooled and powdered in an agate mortar. The substance chosen for hydrogenation was ethyl oleate, containing one olefinic double bond and adds two hydrogen atoms to form stearate.

$$2H + C_8H_{17}CH : CH \ (CH_2)_7. \ COO. \ C_2H_5 \rightarrow$$
$$C_8H_{17}CH_2CH_2(CH_2)_7. \ COO \ C_2H_5.$$

0.5 g. of reduced nickel supported on metallic oxide was used as the catalyst and this was mixed with 5 ml. of ethyl oleate in a reaction pipette, which was connected to the hydrogenation apparatus. The apparatus was flushed with hydrogen, the oil bath temperature raised slowly to 160°, and the shaker switched on. The hydrogen taken up was followed in a gas burette. The experimental details have been described earlier. The results are shown in Fig. 1.
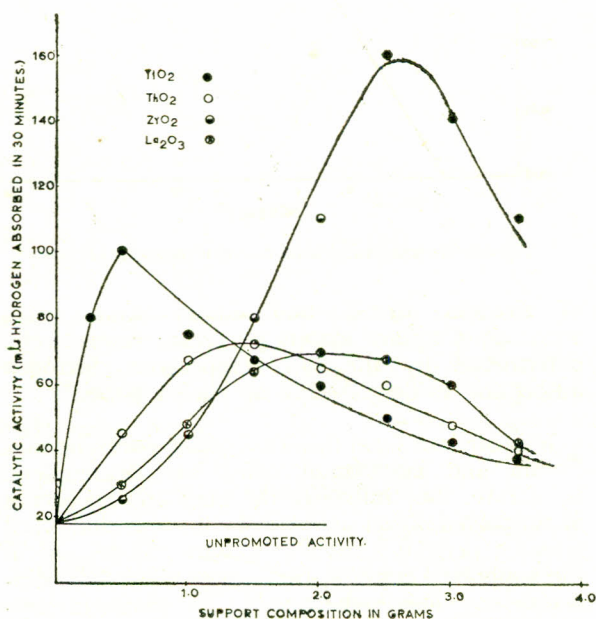

Fig. 1.—Showing activity isotherms of reduced nickel with varying quantities of support.

Experimental

In spite of the repeated powdering and mixing done to yield a homogeneous product, nevertheless it was difficult to obtain a microscopic homogenity. There were always formed small lumps of massive nickel, due to drying and decomposition of the occluded powder. The magnetic data thus all tend to be low because dispersed nickel has a much higher magnetic susceptibility than the massive oxide.* The preparation of supported nickel was made by impregnation. The supported oxides varied in colour from pale blue to black.

All the samples were weighed for magnetic susceptibility in a thin glass tube about 21 cm. in length, of which 15 cm. was filled with the sample. The reproducible uniform filling of the sample was extremely tricky. The sample powder was poured into the tube through a small piece of polythene tubing which was attached to the sample tube. The glass tube was then taped on the bench until all the powder fell into the tube, when the polythene tube was filled with more powder. When the powder level reached the 15 cm. mark, the taping was continued until the powder stayed level at the 15 cm. mark. Dropping of the tube from a height of about 10 cm. on the bench for about 100 times was adopted as the standard procedure. Polythene tubing having been removed, the sample tube was suspended through a piece of steel wire such that the lower end of the tube hung between the two poles of the electromagnet.

The magnetic balance used was of the conventional Gouy type. According to Stoner,[11] if a cylinderical sample of matter is suspended between the poles of a magnet so that one end of the sample is in a region of a large field intensity and the other in a region of small field, then the sample will experience a force along its length. The magnitude of this force, f, is given by the expression:

$$f = \tfrac{1}{2}(K_1 - K_2) \ (H_1^2 - H_2^2)A,$$

where K_1, K_2, are the volume susceptibilities of sample and surrounding atmosphere respectively; H_1, H_2 are the maximum and minimum fields to which the sample is subjected; and A is the crosssectional area of the sample. In practice H_2 was made negligible, and by making corrections for the magnetic susceptibilities of the atmospheric air, K_2 was also made negligible: f was therefore measured in its convenient form of:

$$f = \tfrac{1}{2}K_1 \ H_1^2 \ A = g \ \Delta w,$$

where g is the gravitational constant, and Δw the apparent change in weight of the sample on application of the magnetic field. It was found convenient to use a magnetic field of 1,500 to 2,500 oersteds. A Stanton microbalance was used throughout the measurements as Δw was in the region of milligrams. A newport electro-

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*The term 'massive oxide' is used here to mean a well crystallized pure compound, in contrast to a dispersed oxide such as a supported substance.

magnet unit using D.C. was used with about 2 cm. in between the flat surfaces of the poles; and water jackets spaced between the coil layers. This cooling mechanism was installed not only to protect the magnet from injury, but also because the strength of the field depends on the temperature of the iron core. The control of strength of the field was achieved by passing the current through a 0.1 ohm resistance. Wires leading from this resistance were connected to a potentiometer which in turn was connected to a galvanometer.

Calibration of the Magnetic Balance.—Various substances of known magnetic susceptibility have been used to calibrate the magnetic balance. Many authors have used a solution of nickel chloride as a calibrating agent with excellent results. A 30 percent solution of nickel chloride by weight, at 20°, was carefully prepared thus: 30 g. of nickel chloride was dissolved in distilled water and the solution was boiled for about one hour. This was transferred to a measuring flask and made up to 100 ml. at room temperature. The precaution of boiling the solution for one hour was taken to free the solution from dissolved air, since oxygen dissolved in water has an appreciable susceptibility, and also to avoid the bubbles of air collecting on the surface or on the walls of the tube during measurements.

Molar susceptibility of nickel chloride at 20° is $(4433 \pm 12) \times 10^{-6}$, and this value is independent of concentration around 30 percent $NiCl_2$; the susceptibility being a linear function of the concentration is given by the relationship:

$$\lambda = \frac{4433}{129.6} \ p\text{-}0.720 \ (\text{1-p}) \times 10^{-6}$$

where p is the proportion of $NiCl_2$ present by weight. The calibration curve is shown in Fig. 2, current against varying field strengths. Using the value of the field strength H, obtained from this graph, the magnetic susceptibility per unit mass, λ, was calculated for all the samples from the relationship;

$$\lambda = \frac{2 \ g \ \Delta \ w \ l}{m \ H^2}$$

where m is the mass, and l is the length of the cylinderical sample.

Results and Discussion

The magnetic susceptibility measurements for reduced nickel supported on various metallic oxides are given in Table 1. The surface areas
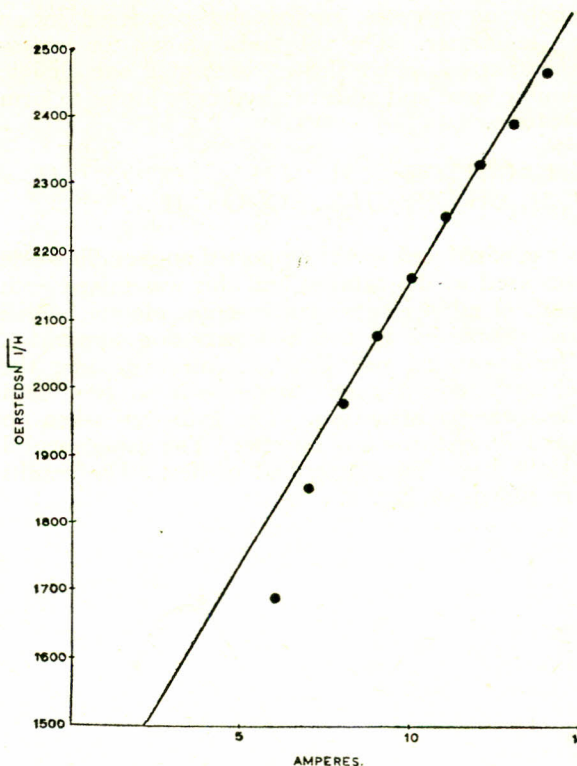

Fig.—2. Showing calibration curve of magnetic balance.

of zirconia, thoria, and titania were 11.9, 20.9, 95.5 square meters per gram respectively, determined by the low temperature nitrogen adsorption as described in an earlier paper.[12]

It is obvious from this Table that since zirconia, titania and lanthanum oxide are diamagnetic by nature, they influence the magnetic properties of supported nickel strongly; so much so that until about 5 percent nickel by weight was present in the supported catalyst, the overall effect was diamagnetic. The highest value for magnetic susceptibility was 12.178×10^{-6} when the proportion of nickel/zirconia was 20 percent nickel by weight. Incidentally this was the proportion at which the catalytic activity also was heighest, being 5.4 ml. per minute. With thoria as a support the susceptibility value was highest at 11.41×10^{-6}, when only 3 percent nickel was present. Once again this was near the highest value of catalytic activtity. When 10 percent nickel by weight is present in the nickel/titania catalyst; the highest values are obtained both for susceptibility and catalytic activity, being 2.634×10^{-6}, and 17.5 ml. per minute, respectivily. However, when lanthanum oxide was used as a support, the highest catalytic

TABLE I.

Sample	Support	Nickel %	Catalytic activity ml. of H_2 absorbed per minute	Magnetic suscepti-bility $\lambda \times 10^{-6}$	Corrected value $\lambda \times 10-6$
1	—	100	6.2	+35.7	+35.5
2	ZrO	0.6	0.7	— 1.140	— 1.252
3	ZrO²	1.6	0.9	— 1.240	— 1.422
4	ZrO²	3.0	1.8	— 1.50	— 1.622
5	ZrO²	6.0	3.9	+ 1.77	+ 1.658
6	ZrO³	10.0	2.4	+ 3.51	+ 3.398
7	ZrO²	13.0	1.2	+ 6.60	+ 6.488
8	ZrO²	16.0	4.7	+ 6.93	+ 9.818
9	ZrO²	20.0	5.4	+12.39	+12.178
10	ZrO²	23.0	3.8	+12.00	+11.188
11	ThO²	0.6	2.9	+ 5.7	+ 5.41
12	ThO²	1.6	5.7	+10.8	+10.51
13	ThO²	3.0	6.3	+11.7	+11.41
14	ThO²	6.0	6.7	+10.2	+ 9.91
15	ThO²	10.0	—	+ 5.7	+ 5.41
16	ThO²	13.0	3.1	+ 2.7	+ 2.41
17	ThO²	16.0	2.5	+1.14	+ 0.85
18	ThO²	20.0	—	+ 1.11	+ 0.82
19	ThO²	23.0	—	+0.93	+ 0.64
20	TiO²	0.6	6.7	— 0.6	— 0.666
21	TiO²	1.6	7.4	— 0.6	— 0.666
22	TiO₂	3.0	13.6	+ 1.2	+ 1.134
23	TiO₂	6.0	19.6	+ 2.4	+ 2.334
24	TiO₂	10.0	17.5	+ 2.7	+ 2.634
25	TiO₂	13.0	12.5	+ 1.2	+ 1.134
26	TiO₂	16.0	8.5	+ 0.9	+ 0.834
27	TiO₂	20.0	8.4	+ 0.6	+ 0.534
28	TiO₂	23.0	6.2	+ 0.294	+ 0.288
29	La₂O₃	0.6	2.6	— 0.3	— 0.70
30	La₂O₃	1.6	3.3	— 1.8	— 2.20
31	La₂O₃	3.0	3.7	— 2.4	— 2.8
32	La₂O₃	6.0	4.5	+ 4.2	+ 4.6
33	La₂O₃	10.0	4.9	+ 4.2	+ 4.6
34	La₂O₃	13.0	6.6	+ 4.8	+ 5.2
35	La₂O₃	16.0	5.0	+ 5.4	+ 5.8
36	La₂O₃	20.0	4.3	+ 7.2	+ 7.6
37	La₂O₃	23.0	4.1	+13.98	+14.3

activity was obtained when only 13 percent nickel was present; whereas the highest susceptibility value was obtained at 14.3×10^{-6}, when 23 percent nickel by weight was present.

Estimation of Exposed Metal Surface.—Only one sample was studied during the BET determinations[12] for the exposed metal. This was done by attaching a carbon monoxide bulb to the dilatometer apparatus used for the measurements of pore volume. The sample* used contained 10 percent by weight of nickel. The nitrogen area of the reduced sample

*The sample used as a support for this determination was an alumina specimen obtained from a United States source through Peter Spence Ltd. The physical properties of this pure substance were: surface area=215 m²/g. pore volume=0.296 ml./g; mean pore radius=27.5 A°; and X-ray crystallite size=200 A°.

proved to be 187 square meters per gram. The volume of chemisorbed carbon monoxide was 4.5 ± 0.6 ml. per gram. Complete monolayer formation per gram of the catalyst would have required 43 ml. of CO. The exposed metal surface was estimated to be $4.5/43 = 10$ percent of the total surface.

The above magnetic susceptibility studies show the manner in which nickel is aggregated on the surface of the supports. It may be concluded that a typical catalyst containing 10 percent nickel does not contain enough nickel to cover the promoter surface even in the thinnest possible continuous layer, the so-called monatomic layer. This view of the surface leaves large portions of the promoters bare of the catalyst. It may be concluded that the nickel/promoter catalyst consists of islands of nickel microcrystals relatively far apart. There is also a substantial amount of evidence that a certain 'minimum demain' is essential for activity. This has also been demonstrated by Selwood.[13]

Electron microscope studies are shown in Figs. 3 and 4. The Fig. 3 shows the electron microphotograph of a sample of nickel supported on thoria and Fig. 4 shows that of nickel on titania. With a microscopic specimen and an enlargement of the order of 10,000 to 30,000, it
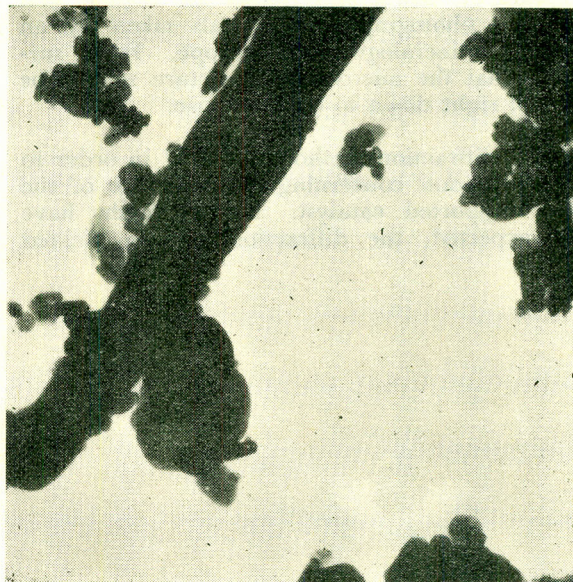

Fig. 3.—Showing electron microphotograph of nickel supported on thoria
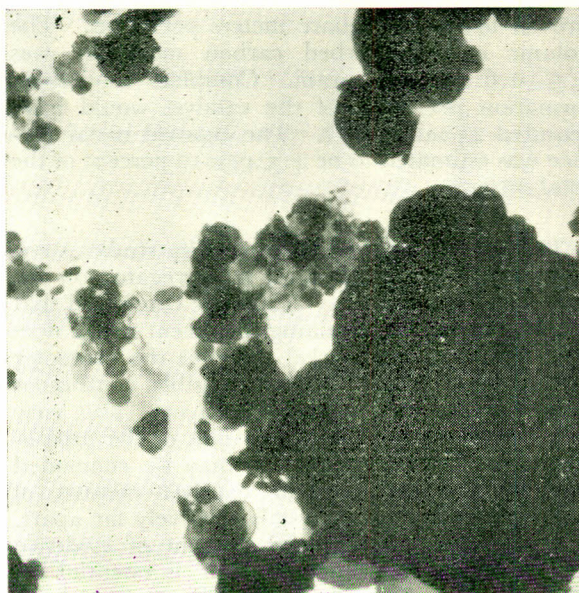
×5,000

Fig. 4.—Showing electron microphotograph of nickel supported on titania.

×5,000

was extremely tricky to ensure a truly representative portion of the sample. In general, the shapes of small particles found by the electron microscope are much the same as had been already suspected by indirect evidence. Thus the particles of nickel on thoria and titania are regular and look like photographs of crystals taken by an ordinary mineralogical microscope. It is surprising that the microscopic structure should be retained right down to colloidal size.

X-ray diffraction method was used in order to get information concerning the structure of the nickel supported catalyst. But as might have been expected, the diffraction pattern yielded nothing of interest in the supported catalysts because no lines due to anything but the support could be found until the nickel concentration exceeded 15 percent, above which crystalline nickel oxide was present in abundance.

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