lenesulfonic acid and 8-amino-1-naphthol-3,6-disulfonic acid.

Acknowledgment.—The authors wish to acknowledge their appreciation for bacteriostatic determinations by Dr. P. A. Tetrault of the Purdue Bacteriology Department and to the Mallinckrodt Chemical Works for its generous support.

Summary

8-Quinolinol was coupled with twenty-eight diazotized amines to give azo dyes. A detailed table of properties and yields of these 8-quinolinol dyes is deposited with the American Documentation Institute.

LAFAYETTE, INDIANA RECEIVED AUGUST 4, 1943

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Magnetic Measurements on Some Catalytically Active Substances

BY HUMBERT MORRIS AND P. W. SELWOOD

It is well known that copper hydrogenation catalysts are activated by small amounts of nickel, and that these catalysts undergo thermal deactivation, poisoning, and activation by minute amounts of substances, such as lead, which normally act as poisons.[1,2] The system copper-nickel is peculiarly convenient for magnetochemical investigation, because nickel is ferromagnetic and copper is diamagnetic. The principal purpose of this work was to examine the environment and behavior of the nickel in such catalysts, by the aid of magnetic susceptibility measurements. The use of magnetic methods to study catalytically active substances has been described by several workers.[3-9]

Experimental Methods

Catalytic Measurements.—The reaction studied with all catalysts was the hydrogenation of benzene. Chemically pure benzene, thiophene free, was dried with sodium and fractionated through an efficient column, the middle third being used in the hydrogenation reaction.

The hydrogenation train consisted of copper gauze at 550°, followed by anhydrous calcium chloride, ascarite and anhydrone. The mixture of hydrogen and benzene was obtained by bubbling hydrogen through benzene contained in a spiral wash-bottle in a constant temperature bath at 25°. The catalyst was packed into a glass tube in a furnace held at constant temperature. The liquid catalysate was collected in two receivers which were cooled in a bath of toluene and solid carbon dioxide. In all the hydrogenation tests the catalyst was at 175°, except where otherwise stated.

The composition of the catalysate, a mixture of benzene and cyclohexane, was determined from its refractive index, according to the data of Ipatieff, Corson and Kurbatov.[1]

Typical treatment of the catalytic data is shown in Table I. The contact time in seconds was calculated as the free space divided by the gas rate per second. The gas volume was taken as the sum of the benzene and cyclohexane volumes plus the arithmetical mean of the inlet and outlet volumes of hydrogen. The free space was taken as the difference between the volume of the reaction tube and the volume of the catalyst as calculated from its weight, and the density of the metal. In those cases where it was desirable to compare the activity of a catalyst at different times it was convenient to calculate the proportion of cyclohexane that would have been produced in a given contact time by assuming a direct proportion between the time and the amount of cyclohexane. This was valid over short ranges only, so care was taken to have results which are so compared be of approximately the same contact time.

TABLE I

TYPICAL CALCULATION

Hours on test		0.5
Excess pressure at inlet, mm.		12.0
Temperature of benzene, °C.		25.0
Vapor pressure of benzene at 25.0°, mm.		94
Barometer (corrected), mm.		749
Average pressure in system, mm.		755
Hydrogen-benzene volume ratio		7.0
Liquid catalysate	Grams	0.5857
	$n^{20}D$	1.4300
Weight composition, 7% benzene and 93% cyclohexane		
Gas volumes at 175° and 755 mm.		
Benzene + cyclohexane, cc.		260
Inlet hydrogen, cc.		1830
Outlet hydrogen, cc.		1110
Average hydrogen, cc.		1469
Benzene + cyclohexane + average hydrogen, cc.		1729
Contact time, sec. (free space, 22 cc.)		23

Because the catalysts were very sensitive to impurities, all apparatus was scrupulously cleaned with hot concentrated nitric acid or a hot mixture of concentrated nitric and sulfuric acids, and then rinsed with distilled water.

Preparation of the several catalysts is more conveniently described *seriatim* below.

Magnetic Measurements.—The magnetic susceptibilities were measured by the Gouy method.[10] The sample tube was surrounded by a silica tube which could be heated electrically as desired. The details of this apparatus will be clear from Fig. 1. A few magnetic measurements were made on a more sensitive magnetic balance which has been described elsewhere.[11]

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[1] Ipatieff, Corson and Kurbatov, *J. Phys. Chem.*, **43**, 589 (1939).

[2] Corson and Ipatieff, *ibid.*, **45**, 431, 440 (1941).

[3] Welo and Baudisch, *Chem. Ztg.*, **49**, 661 (1925).

[4] Veiel, *Compt. rend.*, **180**, 932 (1925); **182**, 1028 (1926).

[5] Merck and Wedekind, *Z. anorg. allgem. Chem.*, **186**, 49 (1930); **192**, 113 (1930).

[6] Baudisch, *Ber.*, **68B**, 769 (1935).

[7] Hüttig, *et al.*, *Acta Physicochem. U. R. S. S.*, **2**, 1929 (1935), *et seq.*

[8] Bhatnagar, *et al.*, *J. Indian Chem. Soc.*, **17**, 125 (1940); **18**, 350, 371, 390 (1941).

[9] Woodman, Taylor and Turkevich, THIS JOURNAL, **62**, 1397 (1940).

[10] Selwood, *ibid.*, **61**, 3168 (1939).

[11] Preckel and Selwood, *ibid.*, **63**, 3397 (1941).

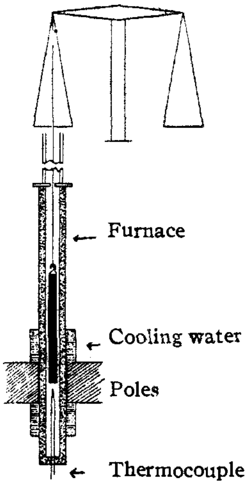

Fig. 1.—Gouy magnetic balance.

The apparatus was calibrated at several field strengths with Mohr's salt, the susceptibility of which was taken as 31.6×10^{-6} at 27°.[12] For ferromagnetic substances at sufficiently high fields the magnetic susceptibility is a linear function of the reciprocal field strength. The relationship between χ, the specific susceptibility, and σ, the specific magnetization, is $\chi H = \sigma$, where H is the field strength. The specific magnetization, σ, is also, of course, equal to $\mathfrak{I}/d$ where $\mathfrak{I}$ is the intensity of magnetization and d the density.

Results

Pure Copper.—Metallic copper is diamagnetic with a susceptibility presumably independent of field strength. Nevertheless, commercially available samples of copper and of copper compounds almost invariably contain ferromagnetic impurities. These impurities find their way into catalytic preparations containing copper, unless elaborate precautions are taken to exclude them. For instance, some purified copper oxide made available through the courtesy of Drs. Ipatieff and Haensel showed, after reduction in hydrogen, a susceptibility markedly dependent on field strength. This is shown, together with data for other samples of copper, in Fig. 2. It was suspected that the ferromagnetic impurity in this case was iron. Iron is not soluble in copper at room temperature, but it is soluble at high temperatures. If the hot mixture is rapidly cooled, some of the iron remains in solution. But if the sample is now annealed the iron precipitates and the mixture becomes more ferromagnetic. That this reasoning is correct was shown by heating the copper to 550° for twenty-two hours to anneal it. The increase in ferromagnetism after this treatment was between five- and ten-fold. It was obvious that a sample of copper which was so ferromagnetic, and the ferromagnetism of which varied so much with thermal history, would not be suitable for the experiments to be undertaken in this study. Further purification of the copper was therefore attempted.

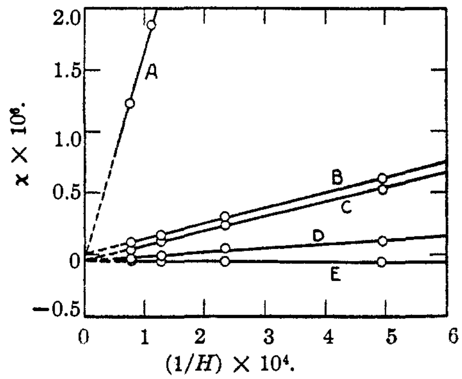

Fig. 2.—Susceptibility plotted against reciprocal field strength for some samples of copper, purified as follows: B, by reduction of "C.P." CuO; A, same, after annealing; C, commercial electrolytic copper wire; D, recrystallized as $CuSO_4$; E, repeated electrolysis.

Passage of carbon monoxide over copper powder at 120° was tried in an effort to remove ferromagnetic impurities in the form of volatile carbonyls. Little or no reduction in ferromagnetism was achieved in this way.

Copper purified by repeated crystallization of the sulfate gave greatly improved results.

Best results were obtained as follows.

Chemically pure copper sulfate was electrolyzed, with the use of tantalum electrodes. A potential difference of about two volts was used. The copper deposit was dissolved in redistilled chemically pure nitric acid and once more electrolyzed. The second deposit was dissolved in nitric acid and, after precipitation with ammonium hydroxide, ignition, and reduction, was found to be almost entirely free from ferromagnetism. The actual data obtained on several different batches over a period of ten months are shown in Table II.

TABLE II

SUSCEPTIBILITY OF COPPER PURIFIED BY REPEATED ELECTROLYSIS

Field strength in oersteds	Susceptibility × 10⁶ for batch number 1	2	3	4	5	6
1050	0.18	0.19	..	..	..	..
2020	.17	.08	..	..	..	..
2050	..	..	− .17	− .09	− .09	− .03
2940	..	..	− .12	− .04	− .04	− .03
3600	..	..	− .08	− .06	− .03	− .04
4250	.00	.00	..	..	..	..
4750	..	..	− .08	− .07	− .07	− .05
8620	− .03	− .03	..	..	..	..
12670	− .05	− .05	..	..	..	..

These results emphasize the astonishing power of the magnetic method of analysis as applied to the detection of ferromagnetic impurities. The sensitivity is such that less than 1 part of iron in 10^9 parts of copper is readily detected, and, in favorable cases, quite accurately estimated. The method does not, of course, respond to the ferromagnetic elements unless they happen to be in the ferromagnetic condition.

This "magnetically pure" copper was completely inactive as a catalyst for the hydrogenation of benzene under the experimental conditions described. This was true even though the reduction of the copper oxide was carried out very slowly at a temperature not in excess of 150°.

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[12] Jackson, *Trans. Roy. Soc.* (London), **A224**, 1 (1923).

This finding is contrary to that of Pease and Purdum,[13] but in agreement with those of Sabatier and Senderens,[14] of Ipatieff, Corson and Kurbatov,[1] and of Emmett and Skau.[15]

Preparation of Copper–Nickel Catalysts.—In all preparations the starting material was metallic copper purified by repeated electrolysis as described above. Cupric hydroxide was precipitated from cupric nitrate solution by dilute ammonium hydroxide. The amount of ammonium hydroxide was adjusted so that the supernatant liquid was just faintly colored by the copper–ammonia complex ion. The precipitate was filtered with suction and washed with water. Nickel nitrate in aqueous solution was now added in the proportion desired, and the mixture was stirred to a paste of even consistency. It was dried at 95°, then heated at 180° for thirty-six hours, and finally at 400° for twenty hours. The black powder so prepared was poured into the reaction tube of the hydrogenation train where it was reduced at 150° by a stream of hydrogen for twenty hours.

Thermal Deactivation.—A catalyst containing 1% of nickel and prepared as described gave 15% of cyclohexane in contact time 115 seconds at 100°. It was also, as expected, strongly ferromagnetic, with a specific magnetization, σ, of 2.60×10^2. Catalysts such as this readily undergo thermal deactivation, which has sometimes been ascribed to a sintering process. This catalyst, after heat treatment in a stream of dry nitrogen at 400° for thirteen hours was inactive, giving 0% cyclohexane in eighty-five seconds. The specific magnetization simultaneously fell to about $^1/_{10}$ of its original value. The magnetic data are shown in Fig. 3 in which susceptibilities before and after thermal deactivation are plotted against the reciprocal field strength.

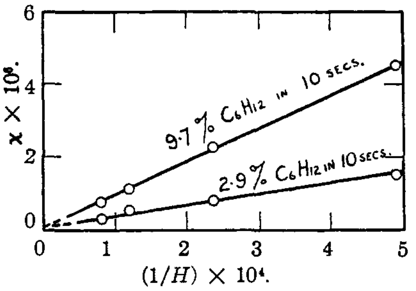

Fig. 3.—Effect of thermal deactivation on magnetic susceptibility of a nickel-activated copper catalyst.

These results suggest that there may be a relationship between the magnetization of a catalyst and its activity. A series of measurements was therefore made on a single catalyst containing 2% of nickel. The catalyst was divided into two parts. One of these was used for the hydrogenation tests, and the other for the magnetic measurements. Both samples were subjected to the same heat treatment between successive measurements. The results of these tests are summarized in Fig. 4. This figure shows that there is a linear relationship between magnetization and catalytic activity for this catalyst. Similar results were obtained with other catalyst preparations. The slopes of the lines differed for different preparations, but in all cases the intersection of the axes was near the origin, indicating substantially zero magnetization for zero catalytic activity.

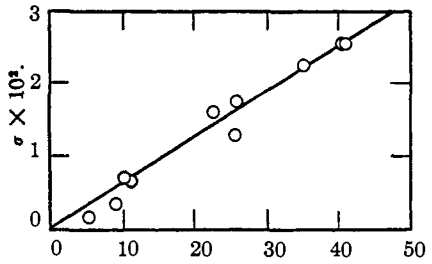

Fig. 4.—The activity and specific magnetization of a nickel-activated copper catalyst.

This is not to be interpreted as meaning that catalytic activity is related to specific magnetization and to nothing else. It is well known that surface is of prime importance in many active substances. It is possible that loss of surface may take place concurrently with loss of magnetization, although no one would suggest that there is necessarily a relationship between the two.

There is a temptation to interpret the phenomena thus far described as a process of diffusion in the solid state. It seems as though the active catalyst masses must contain metallic nickel, and that during thermal deactivation the nickel diffuses into the copper to form dilute solid solutions which are known to be paramagnetic rather than ferromagnetic.[16] That this interpretation with respect to the metallic nickel is not entirely accurate is shown by the Curie point determinations to be described now.

Curie Points of Copper–Nickel Catalysts.—It is well known that ferromagnetic substances suffer an abrupt reversible change of magnetization at the Curie point. For pure nickel this temperature is near 358°. The Curie point of a copper–nickel alloy is approximately a linear function of the concentration.[17,18] The specific magnetization is also a linear function of the concentration.[17] These two useful facts enable us to find the actual composition of the catalytically active mass. For reference, Marian's data on the variation of Curie point with composition are reproduced in Fig. 5. The magnetization–temperature curve for a homogeneous alloy is of the same shape as that for a pure ferromagnetic metal, but for a non-equilibrium[19] alloy the different compositions all have different Curie points, the superposition of which may give a curve differing widely from that of a pure substance.

Figure 6 shows the magnetization as a function of temperature for a catalyst consisting of copper plus 2% nickel, identical with the catalyst described for thermal deactivation studies as shown

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(13) Pease and Purdum, THIS JOURNAL, **47**, 1435 (1925).

(14) Sabatier and Senderens, *Ann. chim. phys.*, **4**, 368 (1905).

(15) Emmett and Skau, THIS JOURNAL, **65**, 1029 (1943).

(16) Ross, *Phys. Rev.*, **46**, 46 (1934).

(17) "International Critical Tables," Vol. VI, p. 405.

(18) Marian, *Ann. Phys*, **7**, 459 (1937).

(19) There does not seem to be any word commonly used to describe a system which consists of a one-phase continuous series of solutions of variable composition. "Heterogeneous" as applied to alloys has the definite implication of more than one phase. We shall use the term "non-equilibrium" to describe these alloys.

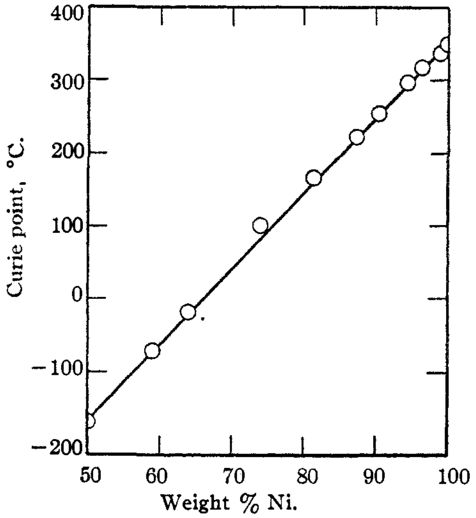

Fig. 5.—Curie points of copper–nickel alloys (after Marian).

in Fig. 4. Curves are shown (in Fig. 6) for the fresh active catalyst, and for the same catalyst after it had suffered partial and complete thermal deactivation. For reference the curve for a roughly equivalent amount of pure nickel is also shown.

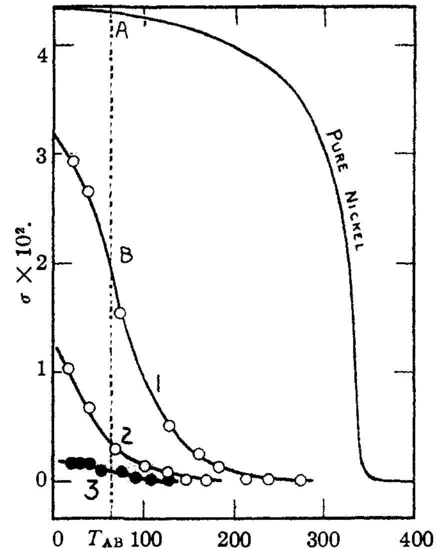

Fig. 6.—Magnetization and Curie point of a nickel-activated copper catalyst: (1) fresh catalyst; (2) heated three hours at 300°; (3) heated four hours more at 350°. The ordinate for pure nickel is reduced.

The conclusions to be drawn from these data are surprising. At the temperature of the hydrogenation reaction, 175°, the fresh catalyst was only a little ferromagnetic, and the partially deactivated ones were not ferromagnetic at all. It is clearly not essential that the active mass should be ferromagnetic at the temperature of the reaction.

It appears that the active catalyst contains no unalloyed metallic nickel. This must be true, because all ferromagnetism disappears nearly 100° below the Curie point of nickel. This observation disposes of the suggestion made by Emmett and Skau[15] that the catalytic effect may be caused by nickel collecting preferentially on the surface of the copper. If we take the highest temperature at which ferromagnetism appears as 275°, then, from Fig. 5, we see that the most concentrated nickel alloy present contains no more than 92.5% of nickel. Most of the catalyst mass contains a much lower percentage of nickel. It is clear also that the bulk of the active mass is by no means homogeneous because the magnetization suffers no abrupt change, but rather falls slowly as the temperature is raised.

This evidence, taken with that of Corson and Ipatieff[2] (that the same amount of nickel is much less efficient as a catalyst when a support like aluminum oxide is used instead of copper), makes it seem probable that the catalytic activity is due, not to the nickel as such, but to copper–nickel alloys.

A number of studies,[20–24] chiefly by Hedvall, have indicated that there is a sharp increase in the temperature coefficient of velocity for hydrogenation, and other reactions, at the Curie point of the catalysts used. If this is generally true it may mean that the most active catalysts are those whose Curie points lie below the temperature of the reaction. For the present study this would indicate that alloys containing less than 82.5% nickel, corresponding to Curie points below 175°, are the ones showing maximum activity. On the other hand, the fact that the catalysts are ferromagnetic at room temperature shows that they must contain not less than 66% of nickel.

Figure 6 shows that thermal deactivation is attended, not only with a general loss of ferromagnetism, but also with a recession of the Curie point to below room temperature. Thermal deactivation must, therefore, consist of a diffusion process whereby the nickel gradually becomes uniformly distributed throughout the mass which is then, of course, paramagnetic at room temperature. The process is essentially one of dilution by copper of the nickel rich copper–nickel alloys. Furthermore, catalysts subjected to thermal deactivation gradually become more stable, requiring higher temperatures and longer heating times to bring about more deactivation. This effect is now seen to be associated simply with a loss of the high concentration gradients which are essential for rapid diffusion.

Still another observation which may be made

[20] Hedvall, "Reactions in the Solid State," J. A. Barth, Leipzig, 1938, p. 164; *Atti X° congr. intern. Chim.*, **2**, 255 (1938).

[21] Hedvall and Gustavson, *Svensk. Kem. Tids.*, **46**, 64 (1934).

[22] Hedvall, Hedin and Persson, *Z. physik. Chem.*, **B27**, 196 (1934).

[23] Hedvall and Byström, *ibid.*, **B41**, 163 (1938).

[24] Aoyama, Matsuzawa and Takahashi, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **34**, 957 (1938).

is that a large part of the nickel must remain in the form of nickel oxide. This must be true, because the total magnetization observed is only about 5% of that expected for complete reduction to the metal. That this reasoning is correct is shown by the very much higher magnetization obtained when powdered metallic nickel is added to magnesium oxide as described later. It is well known that the most active catalysts of the type described are prepared by prolonged reduction at quite moderate temperatures. The reason for this is now clear. If the temperature is too high, thermal deactivation takes place owing to diffusion. But if the temperature is low, long times are necessary to obtain appreciable reduction.[25]

Thermal Deactivation of Nickel on Magnesium Oxide.—The fact that thermal deactivation of the copper–nickel catalysts is accompanied by dilution of the nickel-rich alloys suggests that more stable, even though less active, catalysts may be prepared by supporting the nickel on an inert substance such as magnesium oxide, in which nickel is not soluble.

Chemically pure nickel carbonate was reduced to nickel in a stream of hydrogen at 200° for twenty-four hours. To a weighed amount of the nickel so prepared was added a weighed amount of chemically pure magnesium oxide, to make a catalyst which had 1% by weight of nickel. The catalyst was thoroughly mixed and used in the following tests.

Corson and Ipatieff[2] have shown that nickel is less efficient as a catalyst if an oxide such as magnesia is substituted for copper. This fact was confirmed, but surprisingly the catalyst underwent deactivation when it was heated for a few hours at 300°.

TABLE III

ACTIVITY OF NICKEL–MAGNESIA CATALYST

	%C_6H_{12} in 10 sec.
Fresh catalyst	8.1
Heated 4 hours at 300°	3.6
Heated 3 hours more at 300°	0.9
Heated 3 hours more at 300°	0.7

The magnetic data on this catalyst are given in Fig. 7, which shows the magnetization as a function of temperature for the fresh catalyst and for the catalyst after it had been heated in vacuum at 300° for thirty-five hours. These results show that the catalyst initially contained metallic nickel, which was scarcely surprising, and that, contrary to the case of the copper–nickel catalyst, the Curie point did not change even after prolonged thermal deactivation. What may be the mechanism of deactivation here we can only conjecture. But it is clear that supporting the nickel on a substance with less pronounced solvent characteristics than copper does not render the catalyst more stable. The really surprising feature of these results, however, is that heating the nickel–magnesia mixture caused the loss not only of the major part of its catalytic activity, but also of nearly a third of its magnetization at room temperature. It might be thought that sintering of the nickel powder could account for the change, but sintering is accompanied by an increase in size of crystal aggregates, and this would increase the magnetization or leave it unchanged. This curious effect will receive further study.

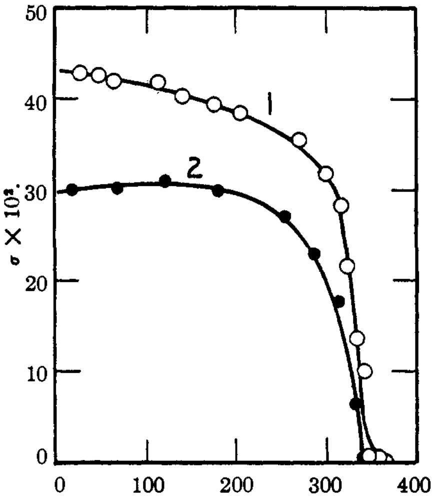

Fig. 7.—Magnetization and Curie point of nickel supported on magnesia: (1) active catalyst; (2) same heated at 300° for 35 hours.

Poisoned Catalysts.—Nickel-activated copper catalysts are poisoned by hydrogen sulfide, carbon monoxide, mercury and lead. Parallel catalytic and magnetic measurements were made on each of these in turn. In each case the active mass contained 1% of nickel.

Hydrogen sulfide was chosen as the first poison. The hydrogen sulfide was produced by the reaction of dilute hydrochloric acid on ferrous sulfide. It was then bubbled through sodium sulfide solution and dried in a trap cooled in solid carbon dioxide and toluene. The volume of gas passed over the catalyst was measured by displacement of mercury in a buret. The catalyst was poisoned by a stream of hydrogen sulfide for an hour at −77°. After the poison had been put in, hydrogen was passed through the catalyst for an hour. The effluent gas was passed through lead acetate

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(25) An inspection of Fig. 6 will show that it is possible to compute what percentage of the whole catalyst mass contains nickel in any given concentration. The line AB (in Fig. 6) represents approximately that part of the magnetization belonging to alloy concentrations whose Curie points are below temperature, T_{AB}. Both magnetization and Curie point are linear functions of concentration, hence we may say that point B tells us what fraction of the catalyst mass consists solely of alloys having less than a certain definite concentration of nickel. It is scarcely worth while to make this computation for the present case, because we have no accurate measure of the rather large fraction of nickel remaining as unreduced nickel oxide. But such "distribution" curves of two metals in non-equilibrium solid solution have obvious applications to metallurgical problems, particularly to powder metallurgy. Methods for obtaining such curves will be dealt with more fully in a subsequent publication.

solution, but no trace of lead sulfide was observed. The catalytic and magnetic results are summarized in Table IV.

TABLE IV

MAGNETISM AND CATALYTIC ACTIVITY OF A NICKEL-ACTIVATED COPPER CATALYST POISONED BY HYDROGEN SULFIDE

Field strength in oersteds	Susceptibility × 10^6 at 25° Fresh catalyst	Poisoned by 10 cc. of H_2S	Poisoned by 43 cc. of H_2S
2050	33.2	29.4	26.8
2940	25.0	21.9	19.4
3600	21.2	18.7	16.4
4750	16.8	14.8	13.1
$\sigma \times 10^2$	6.08	5.28	4.92
%C_6H_{12} in 10 sec.	75.6	31.8	1.6

These data will be discussed below, but it is interesting to notice that there is once more a linear relationship between specific magnetization and catalytic activity.

Carbon monoxide as a poison was chosen next. The gas was prepared by reaction of formic acid with hot phosphoric acid. It was dried in a trap cooled with solid carbon dioxide, and then passed through the catalyst at 270° for one hour. The results are shown in Table V.

TABLE V

MAGNETISM AND CATALYTIC ACTIVITY OF A NICKEL-ACTIVATED COPPER CATALYST POISONED BY CARBON MONOXIDE

Field strength in oersteds	Susceptibility × 10^6 at 26° Fresh catalyst	Poisoned by CO
2050	9.93	9.17
2940	7.44	7.10
3600	6.46	6.01
4750	5.14	4.85
$\sigma \times 10^2$	1.72	1.70
%C_6H_{12} in 10 sec.	20	5.5

Mercury was used as a poison by adding the mercury, then passing a stream of hydrogen through the catalyst at 175° for three hours. The results are shown in Table VI.

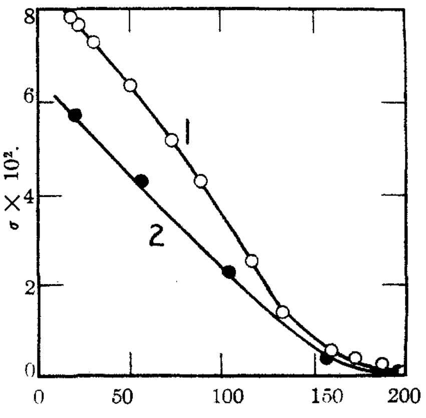

Fig. 8.—Magnetization and Curie point of a copper-nickel catalyst poisoned with lead: (1) fresh (inactive) catalyst; (2) same after seven hours of heating at 200°.

TABLE VI

MAGNETISM AND CATALYTIC ACTIVITY OF A NICKEL-ACTIVATED COPPER CATALYST POISONED BY MERCURY

Field strength in oersteds	Susceptibility × 10^6 at 26° Fresh catalyst	Poisoned by Hg
2050	11.26	2.64
2940	8.45	1.86
3600	7.16	1.60
4750	5.57	1.23
$\sigma \times 10^2$	2.08	0.50
%C_6H_{12} in 10 sec.	71	0.0

Corson and Ipatieff[2] have shown that nickel-activated copper catalysts containing minute amounts of lead show higher hydrogenation activity than when the lead is absent. This effect was confirmed, but no significant differences were discovered in the magnetization of these catalysts. Whatever the cause of this enhanced catalytic activity may be, it is not paralleled by the customary increase in magnetization.

Larger amounts of lead, of the order of 1%, effectively poison the catalyst. Two series of tests were made. In one of these the lead was added in the form of the nitrate to the copper hydroxide. In the other test the lead was added in the form of tetraethyllead directly to the catalyst. The tetraethyllead was added to the nickel–copper catalyst in the proportion of 0.188 g. of $Pb(Et)_4$ to 17 g. of active catalyst. The catalyst was then allowed to stand at room temperature for four hours, at 90° for one hour, and finally at 250° for one hour. Results for one of the tetraethyllead poisoned catalysts, which are characteristic, are shown in Table VII.

TABLE VII

MAGNETISM AND CATALYTIC ACTIVITY OF A NICKEL-ACTIVATED COPPER CATALYST POISONED BY TETRAETHYLLEAD

Field strength in oersteds	Susceptibility × 10^6 at 26° Fresh catalyst	Poisoned by $Pb(Et)_4$
2050	15.8	10.3
2940	11.8	7.8
3600	9.8	6.6
4750	8.1	5.2
$\sigma \times 10^2$	2.8	2.1
%C_6H_{12} in 10 sec.	35	0

In each of these poisoning experiments the loss of activity is accompanied by some loss of specific magnetization. It was therefore felt that Curie point data should be obtained on at least one of the poisoned catalysts. A copper catalyst was prepared containing 1% of nickel and 1% of lead, both introduced as nitrates in solution to the copper hydroxide. After the usual drying and reduction the mass proved to be completely inactive. Its magnetization as a function of temperature is shown in Fig. 8. The same graph shows the effect of prolonged heating at 200°. Although the catalytic activity of this substance was zero, the response of its magnetization to heat treatment is about the same as for an active catalyst.

Poisoned catalysts do not show the great change in magnetization attendant on thermal deactivation. Poisoning does not consist of promotion of mutual diffusion of the nickel and the copper. The fact that the Curie point for the lead poisoned catalyst is nearly the same as for the active catalyst indicates that the original active copper–nickel alloys are not greatly modified during the poisoning process. In contrast to the effect of heat, which alters the whole catalyst mass, poisoning must affect only a small part of the mass. During poisoning no large part of the catalyst suffers solution, dilution or chemical change. These conclusions from the magnetic data simply confirm, of course, beliefs generally held by catalytic chemists.

Nevertheless, there is in all cases some change of magnetization during poisoning, and the loss of catalytic activity is linear with the loss of magnetization. This effect is very clearly shown in Fig. 9 in which the susceptibility of the hydrogen sulfide-poisoned catalyst is plotted as a function of reciprocal field strength. It may therefore be concluded that the active microcrystals in the catalyst are of such dimensions that the surface atoms are an appreciable fraction of the whole. The partial loss of ferromagnetism with poisoning is not uniform, but it may be very roughly estimated that about 10% of the nickel atoms are on the surface of each microcrystal. On the other hand Winkel and Haul,[26] and Haul and Schoon[27] have determined the limiting dimension of certain ferromagnetic particles as not less than 30 to 40 Å. on a side. If catalytic activity is actually associated with small ferromagnetic crystals, as is suggested by all these experiments, then these crystals must be approximately codimensional with the ultimate ferromagnetic domain.

The possibility has been considered that some of the nickel may be present in a state of atomic subdivision, and that it is this nickel which is catalytically active. Such nickel would not be ferromagnetic. If thermal deactivation consists of loss of surface by such atomically dispersed nickel, then it should be attended by an increase in magnetization. But in all cases thermal deactivation resulted in a great loss of ferromagnetism. We can only conclude, therefore, that loss of surface is unimportant or that there was no appreciable quantity of atomically dispersed nickel present to begin with. An improbable alternative is that the loss of surface is overbalanced by the opposite effect of diffusion and that this complicated process takes place so as to give an apparent linear relation between activity and magnetization.

The fact that different poisons have different effects on the magnetization of the catalysts is readily explained. Mercury, which produced the greatest loss of magnetization, is able to penetrate into the body of the microcrystals. Carbon monoxide, which produced the smallest magnetic effect, acts only on the surface layer of atoms.

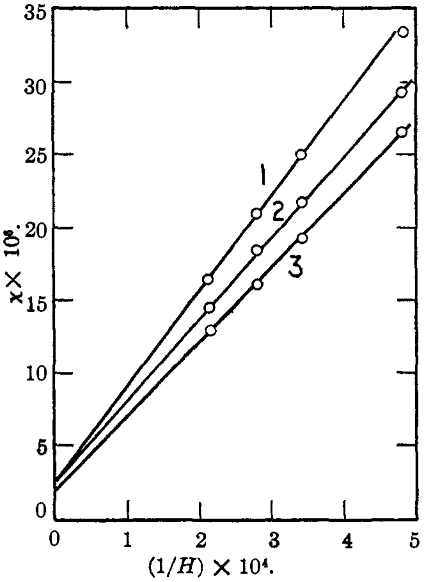

Fig. 9.—Susceptibility plotted against reciprocal field strength for a nickel-activated copper catalyst: (1) fresh catalyst giving 75.6% C_6H_{12} in 10 sec.; (2) after 10 cc. H_2S, 31.8% C_6H_{12}; (3) after 43 cc. of H_2S, 1.6% C_6H_{12}.

Nickel-Activated Molybdenum Oxide.—The last experiment to be described concerns a catalyst prepared by the roasting and reduction, in hydrogen, of ammonium nickel molybdate. This catalyst has been studied by Woodman, Taylor and Turkevich,[9] who considered the ferromagnetism and catalytic activity to be due to metallic nickel. In view, however, of the results already described, and of the possibility of ferromagnetic spinel formation, it seemed worthwhile to determine the Curie point of this substance.

The catalyst was prepared exactly according to the directions of Woodman, Taylor and Turkevich.[9]

The results obtained are shown in Fig. 10. The last trace of ferromagnetism disappears at about 240°, over 100° lower than the Curie point of nickel. The catalyst contains, therefore, no metallic nickel as such. The slope of the magnetization curve suggests a non-equilibrium aggregate similar to that found for the copper-nickel catalysts. Whether the mass contains some form of nickel in solid solution, or a spinel or other ferromagnetic compound, is not known. The discontinuity in the neighborhood of 200° is believed to be real, but what it may signify is not clear. It is quite obvious, however, that this and similar catalytically active mixtures present a rich field for magnetochemical investigation.

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(26) Winkel and Haul, *Z. Elektrochem.*, **44**, 420 (1937).

(27) Haul and Schoon, *ibid.*, **45**, 663 (1939).

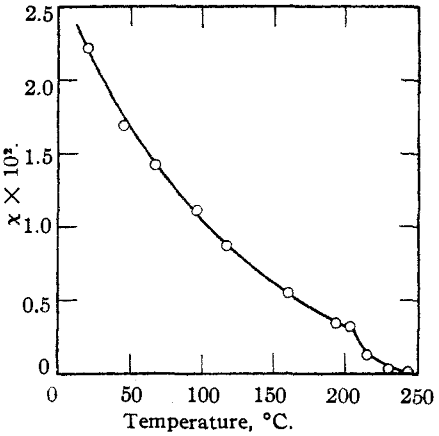

Fig. 10.—Magnetization and Curie point of a catalyst derived from nickel ammonium molybdate.

Summary

Magnetic susceptibility measurements, over a range of temperature and field strength, have been made on a series of nickel-activated copper hydrogenation catalysts, on nickel supported on magnesia, and on a catalyst derived from ammonium nickel molybdate.

Active copper–nickel catalysts consist of a continuous series of solid solutions ranging in composition from about 66 to 92.5% nickel. Pure metallic nickel is not present.

Thermal deactivation is accompanied by diffusion of copper into the nickel-rich alloys.

Thermal deactivation of nickel supported on magnesia must proceed by a different mechanism because, while the magnetization is lowered, the Curie point remains the same.

Poisoning experiments indicate that the poisons affect a small but measurable fraction of the nickel atoms, presumably those on the surface of the active microcrystals. It may be conjectured from this that the active microcrystals are approximately codimensional with the ultimate ferromagnetic domain.

The catalyst derived by heating and reducing ammonium nickel molybdate contains no metallic nickel.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF SOUTH CAROLINA]

Alkyl *p*-Nitrobenzoates[1]

BY MARVIN D. ARMSTRONG AND J. E. COPENHAVER

Henstock[2] has suggested the use of the alkyl *p*-nitrobenzoates as derivatives for use in the identification of alcohols and has prepared the first six members of the series. The purpose of this investigation was to extend this series and to study the physical properties of these compounds.

The esters were prepared by refluxing an excess of the lower alcohols with the acid chloride and by heating the higher alcohols with a 10% excess of *p*-nitrobenzoyl chloride. The reaction proceeded rapidly with the alcohols through the butyl but it was necessary to heat the others for two hours or longer to carry the reaction to completion. The crude esters were dissolved in ether and washed with a 10% sodium carbonate solution until free from nitrobenzoic acid. The ethereal solution was then washed with water, the ether evaporated and the esters recrystallized from petroleum ether, usually two or three times, until they showed constant melting points. The liquid esters, amyl through nonyl, were rapidly distilled *in vacuo* until a constant index of refraction was secured (see Table I) and in general a yield of 70–90% was obtained. The melting points of the esters with analytical data for nitrogen are given in Table II and are plotted in Fig. 1.

TABLE I

PHYSICAL PROPERTIES OF THE LIQUID *p*-NITROBENZOATES

Ester	B. p., °C.	*P*, mm.	n^{20}_D	d^{20}_{20}
Amyl	144–146	3	1.5186	1.1452
Hexyl	175–177	8	1.5153	1.1193
Heptyl	147–155	5	1.5122	1.0973
Octyl	170–175	5	1.5094	1.0817
Nonyl	175–185	5	1.5074	1.0719

The esters are light yellow through nonyl; from decyl through eicosyl, white crystalline solids. From Fig. 1 it can be seen that, beginning with the hexyl ester, the melting points exhibit regular alternation, the esters containing an even number of carbon atoms in the alkyl group having the higher melting points. The lower members exhibit a very irregular melting point pattern.

The *p*-nitrobenzoates may be used for the identification of the aliphatic alcohols except for the few which have melting points too close together. They are easily prepared and purified, and melt sharply.

The melting points were taken, with mechanical stirring in a 200-cc. bulb, fitted with a side-arm for the thermometer and melting point tube. Standard Anschütz thermometers were used.

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[1] Original manuscript received July 17, 1941.

[2] Herbert Henstock, *J. Chem. Soc.*, 216 (1933).