bulk and not of individual atoms or ions. In view of the very low ferromagnetism produced it must be concluded that no significant portion of the iron remains in aggregates larger than the minimum ferromagnetic domain.

The unique production of tetravalent iron in the iron–*rutile* system raises a number of interesting points. Iron is a common impurity in titania; such iron must generally be in the tetravalent state, and as such fit fairly well into the titania lattice. Perhaps this contributes to the difficulty in removing the last traces of iron from titania. It will also be observed that iron as a promoter in manganese dioxide catalysts probably also assumes a valence of four.

These considerations raise the possibility of using supported iron on *rutile* as a depolarizer in the Leclanché dry cell. Some cells were made up[4] according to standard practice, but using the iron–*rutile* instead of manganese dioxide as depolarizer. The sample was that containing 8.4% total iron, of which 40% was in +4 state. The number of coulombs withdrawn indicated that the iron was reduced to the +2 state. The performance of the cell seemed, within our limited experience, to be comparable to that of cells depolarized with manganese dioxide.

A second cell was made using iron–*rutile* containing 3.8% total iron of which 60% was in the +4 state. It was hoped that it would be possible to follow the valence changes of the iron by measuring the magnetic susceptibility of the cell during discharge. But no magnetic change was observed, possibly because the expected increase of susceptibility in going from +4 to +3 iron was accompanied by a decrease in going from +3 to +2 iron. For this reason, the experiments on tetravalent iron as a dry cell depolarizer were not continued.

Summary

Susceptibility isotherms have been measured for iron oxides supported on high-area *gamma*-alumina and on *rutile*. Iron oxide at low concentrations on *rutile* tends to assume an oxidation state of four.

EVANSTON, ILLINOIS RECEIVED OCTOBER 23, 1948

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[4] These experiments were performed by Mr. Robert P. Eischens, and will be described in a later paper.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE DEPARTMENT OF PHYSICS OF NORTHWESTERN UNIVERSITY]

Nuclear Induction and the Structure of Catalytically Active Solids

BY ROBERT B. SPOONER AND P. W. SELWOOD

Recent publications[1,2,3] from these laboratories have shown that the environment and oxidation state of a supported transition group element may, to some extent, be revealed by measurements of magnetic susceptibility. In the present paper it is shown how the nuclear induction experiment may be used to give additional information concerning catalyst structure: This additional information concerns the state of aggregation and the extent of active surface in the catalyst. But the chief application of nuclear induction to catalyst problems seems to be the promise of making rapid, *in situ*, observations during the actual time when the catalyst is promoting a chemical reaction.

The nuclear induction experiment has so far had only a few applications in chemistry. The principle of the method will, therefore, be outlined briefly.

It is well known that the familiar electronic paramagnetism is established almost instantly on application of an external field. This is not true of nuclear magnetism. The time for establishment of equilibrium in the nuclear case may be of the order of seconds, and is extremely sensitive to the structure and motions of the whole system. This time, necessary for the establishment of resolved nuclear moments in the applied field, is called the relaxation time.

For our present purpose the most interesting feature of the nuclear induction experiment is that the relaxation time, which it measures, may be greatly reduced by the use of paramagnetic catalysts. The phenomenon is similar to the use of paramagnetic catalysts in the spin isomerization of hydrogen. The nuclear induction experiment thus affords a method for measurement of paramagnetic moments, or of the concentration of paramagnetic substances of known moment. The method has been used[4] to measure the magnetic moments of copper, nickel and other ions in solution. The results depend to some extent on the distance of closest approach of a magnetic ion to the nucleus in question and hence give some information concerning the size and stability of any complex surrounding the nucleus or the paramagnetic ion. The nucleus used in all the experiments reported here was that of hydrogen, and the hydrogen was present in water, although any hydrogen compound, such as a hydrocarbon, would have been satisfactory.

The present paper reports relaxation measurements in which the catalysts were iron, and neodymium oxides, each supported on γ-alumina,

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[1] Eischens and Selwood, THIS JOURNAL, **70**, 2271 (1948).

[2] Selwood, Moore, Ellis and Wethington, *ibid.*, **71**, 693 (1949).

[3] Selwood, Ellis and Wethington, *ibid.*, **71**, 2181 (1949).

[4] Bloembergen, Purcell and Pound, *Phys. Rev.*, **73**, 679 (1948).

and manganese dioxide supported on *rutile*. These systems were chosen because complete susceptibility data were available, and because of the bearing the induction data would have on the interpretaion, previously presented, of the susceptibilities.

If such systems actually consist of microcrystals of the active oxide on the support surface[1,3] and if the size of the microcrystals varies with concentration, then the relaxation time in the nuclear induction experiment should be a function of the concentration of the active element. More specifically, the relaxation time, for equal weights of active elements, should decrease as the concentration decreases. This should be true because the more effectively the active element is dispersed on the alumina surface, the larger proportion of active element should be available to catalyze the relaxation of nuclear moments.

Experimental

The Nuclear Induction Experiment.—The apparatus used was similar in principle to that described by Bloch, Hansen and Packard to whose paper reference should be made.[5] The principle of the apparatus will be outlined very briefly: A sample is placed in a magnetic field of a few thousand oersteds. This field is modulated at 20 cycles by coils, the axes of which are parallel to the field. A high frequency radio transmitter supplies energy to the system, and the nuclear magnetic moments oriented by the field are caused to precess by the driving field in a coil energized from the radio-frequency transmitter. The precessing nuclear magnetic moments induce voltages in a receiving coil. These induced voltages are amplified and detected on an oscilloscope. It should be pointed out that the signals obtained are very small; their detection is a matter of some difficulty owing to spurious effects.

Preparation of Samples.—The system neodymia-alumina was chosen because of the relatively strong paramagnetism of the neodymium ion and because this system could offer no complication such as change of oxidation state, exchange interaction, or anomalous magnetic moment. As pointed out some years ago,[6] dispersed neodymia shows virtually none of the magnetic effects shown by supported oxides of chromium, manganese, iron and other first transition series elements. This is, of course, a consequence of the 4f electronic structure of the rare earths.

γ-Alumina of surface area ~ 200 sq. m. per g. (BET nitrogen) was impregnated with pure neodymium nitrate solution. The mixture was then filtered, without washing, dried and ignited at 400°. The products were pale lavender, in some contrast to the characteristic blue of pure neodymia. The samples were analyzed by solution in nitric acid, followed by precipitation and ignition of the oxalate. Two samples were prepared, containing 3.8 and 6.8% neodymium.

The second series chosen was manganese oxide supported on high-area titanium dioxide (rutile modification). The manganese in this system has been shown to have a normal, spin-only moment, and a uniform oxidation state of four. But the susceptibility shows the dilution effect, namely, a large increase of susceptibility at low manganese concentrations. This effect is especially pronounced at low temperatures and has been shown to be due to changes in the Weiss constant which reflect a changing average environment for each manganese ion.

Preparation and analysis of the samples already has been described; in fact, several of the samples used were identical with those previously used for susceptibility measurements.[2]

The third and last system studied was iron-alumina prepared and analyzed as previously described.[3] The susceptibility and analytical measurements on this system show that the iron maintains an oxidation state of three but that intercation covalency reduces the moment to roughly 70% of the spin-only value. Hence it was thought that the induction experiment might reveal a change due to the changing moment, as well as the expected change caused by changing dispersion.

A further test was made by comparing the relaxation time produced by the same weight of iron oxide in true three-dimensional solid solution in alumina. For this test iron and aluminum were co-precipitated by addition of ammonium hydroxide to a dissolved mixture of ferric nitrate and aluminum nitrate. The mixture contained 0.4% iron as iron oxide after ignition for eighteen hours at 600°; at the end of this period the X-ray diffraction pattern gave only weak lines of γ-alumina. Samples were removed for susceptibility and nuclear induction measurements. The material was then further heated up to 1175° for about forty-eight hours until no X-ray pattern other than that of α-alumina was found. The iron oxide was at that time assumed to have gone into solid solution, a conclusion which was supported by the susceptibility and relaxation time data.

In all the nuclear induction tests it was desirable to have the same volume of water in contact with the same weight of catalyst within the receiving coil. These conditions were easily achieved by a technique previously used in the comparison of catalytic activities. The most dilute of several samples of each series was taken as the standard dilution. Then each of the more concentrated samples was diluted mechanically with pure γ-alumina until the concentration of the active element reached the standard dilution. Equal weights of samples thus diluted were chosen for each test. It will be clear that these samples after dilution contained the same weight of active element, but that they differed in the ratio of alumina used as support to that used merely as a mechanical diluent. In some cases the standard dilution was itself prepared by some mechanical dilution.

Freshly boiled water was used in each test, and the air in contact with the sample was displaced by pure nitrogen. This was done to reduce the small effect of oxygen on the relaxation time. In all tests 1.2 g. of diluted catalyst sample was used with 1.2 cc. of water, except the neodymium which was used with 1.5 cc. of water. The tests were carried out at 23°.

Results

Neodymia-Alumina.—Relaxation times and new susceptibility data for this system are shown in Table I. The very limited concentration range in this series was caused by the difficulty in obtaining satisfactory impregnation.

TABLE I

SUSCEPTIBILITY AND RELAXATION TIME FOR Nd_2O_3/Al_2O_3

Concentration	Susceptibility × 10^6 per g. neodymium 25°	−87°	−167°	τ sec. × 10^2
3.8/3.8	68	111	140	5.4
3.8/6.8[a]	66	101	131	6.2

[a] This means that the sample contained 3.8% neodymium but that this was prepared by mechanical dilution of a sample containing 6.8% neodymium.

Manganese-Titania.—Relaxation times for this system are shown in Table II. For comparison, previously published susceptibility data are included in the table. For this system it

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(5) Bloch, Hansen and Packard, *Phys. Rev.*, **70**, 474 (1946).

(6) Selwood, THIS JOURNAL, **53**, 3161 (1931).

Table II

Susceptibility and Relaxation Time for MnO_2/TiO_2

Concentration	Susceptibility × 10^6 per g. manganese 25°	τ sec. × 10^2
0.5/1.3	292	1.58
.5/3.9	167	2.70
.5/7.9	119	6.06
.5/12.5	96.8	11.0
.5/18.8	78.7	16.0

was possible to choose a standard dilution so that the relxation time fell in a region convenient for measurement. The results are hence considerably more significant than are those for neodymium.

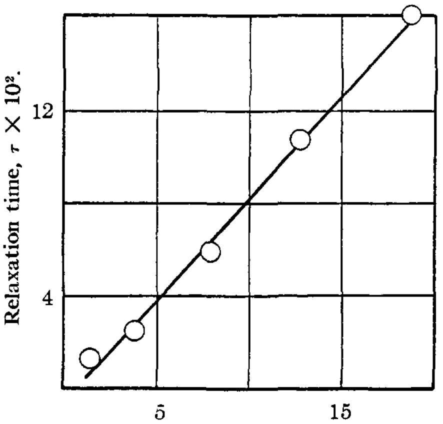

Fig. 1.—Relaxation time as a function of manganese concentration in manganese dioxide/rutile.

Iron–Alumina.—Relaxation times for this system are shown in Table III. Previously published susceptibilities at 25° are shown for comparison.

Table III

Susceptibility and Relaxation Time for Fe_2O_3/Al_2O_3

Concentration	Susceptibility × 10^6 per g. iron 25°	τ sec. × 10^2
0.1/0.54	148	1.21
.1/1.65	135	1.81
.1/2.6	115	2.24
.1/3.6	110	2.34
.1/5.1	118	2.77
.1/7.1	111	3.33

The results on the iron oxide/aluminum oxide solid solution are compared with those on a supported oxide of the same concentration in Table IV.

Table IV

Susceptibility and Relaxation Time for 0.4% Fe_2O_3/Al_2O_3

Ignition temp. and time	Susceptibility × 10^6 per g. iron 25°	−87°	−167°	τ sec. × 10^2
600° (18h), supported oxide	500	825	1200	1.8
1050 (+18h)	550	875	1320	2.1
1175 (+48h) solid solution	...	...	1470	7.2

It may be pointed out that after the 1050° ignition the sample gave a large number of X-ray lines, indicating some intermediate structure for the alumina.

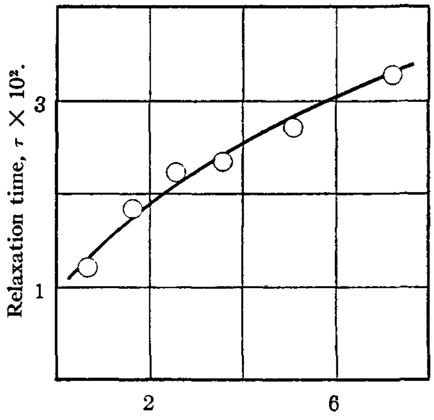

Fig. 2.—Relaxation time as a function of iron concentration in iron oxide/aluminum oxide.

Discussion of Results

The results on supported neodymia are limited in accuracy because of impregnation difficulties. But the point is definitely established that in this relatively simple system the relaxation time increases with increasing initial neodymium concentration, even though the susceptibility is constant within the probable experimental error. It is difficult to see how this result could be achieved unless the more dilute catalyst sample actually offered a greater proportion of its neodymium ions for mutual contact with water molecules.

Somewhat more satisfactory results are obtained in the manganese–alumina system. Here it is clearly shown that the relaxation time is directly proportional to the initial manganese concentration. It has already been shown that the alumina surface is too large to be covered by a single atom layer of manganese oxide in this concentration range. The nuclear induction experiment rules out the possibility of single atom layers occurring in discrete widely separated patches. If such patches occurred it would be impossible for the relaxation time to vary as it does, because all manganese ions would be equally well located to act as catalysts. The relaxation times support rather the conclusion reached from susceptibility measurements, namely, that the active element is aggregated in microcrystals a few atom layers thick. As the concentration is lowered, more manganese ions are exposed, fewer act merely to support other manganese ions.

The iron–alumina system is interesting not only because it exhibits the same magnetic effects as shown by the manganese–titania system, but because, superimposed on the normal dispersion effect there is a strong change of moment caused by interaction covalency. It is particularly gratifying to note that this effect is reflected in a peculiar change, with concentration, of the relaxation times for iron–alumina. Instead of relaxation times appearing linear with concentration as for manganese–titania there is a marked increase of catalytic effect at low concentrations. This parallels the increase of magnetic moment which occurs in this region owing to diminished numbers of iron ions being adjacent to each other in positions to exhibit a diminution of normal moment.

These results all show a definite parallelism between susceptibility and relaxation time. This is not surprising in a supported system when it is recalled that increased dispersion is generally attended by increased susceptibility, and not infrequently also by increased catalytic activity.

The sharp difference, however, between the kinds of information from susceptibility measurements and nuclear induction measurements is shown by the data on the iron–alumina solid solution.

The iron in the supported system has a very high susceptibility owing to the highly dispersed nature of a sample containing only 0.4% iron. As the sample is ignited to form a three-dimensional solid solution the degree of dispersion tends to became even greater, finally reaching infinite magnetic dilution. Hence the susceptibility also increases somewhat, tending toward a maximum. But the relaxation time behaves quite differently. In the supported system a large fraction of the iron ions are in a position to exert catalytic activity. Hence the diminution of relaxation time is very great. But as the sample is ignited, the iron atoms leave the surface to go into solid solution where they are no longer available for catalytic action. The relaxation time correspondingly increases.

It may be argued that all this could be surmised from a combination of susceptibility and surface area measurements. (The area of the sample decreases greatly during the ignition process.) This is, of course, true, but it also illustrates what promises to be a most useful application of the nuclear induction experiment, namely, that the measurements may be made on a catalyst *in situ*, that they may be completed in a few moments, and that almost any compound containing hydrogen may be used as the proton carrier.

It is a pleasure to acknowledge the invaluable assistance of Professor Arnold J. F. Siegert in connection with this work. The authors are also indebted to Marylinn Ellis and to Lorraine Lyon for assistance with the preparations and analyses.

Summary

Relaxation times as found by the nuclear induction experiment are used to extend information on solid catalyst structures.

EVANSTON, ILLINOIS RECEIVED JANUARY 22, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN]

The Distribution of Rare Earth Nitrates between Water and *n*-Hexyl Alcohol at 25°

BY CHARLES C. TEMPLETON

The possibility of the use of organic solvents for the fractionation of mixtures of rare earth salts was proposed by Fischer, Dietz and Jübermann.[1] They claimed the existence of 50% differences between neighboring rare earths in the distribution of their chlorides between an aqueous phase and an organic solvent (ether, alcohol or ketone). Although Fischer and later co-workers have given detailed reports concerning the use of solvent methods for the purification of scandium[2] and the separation of hafnium from zirconium,[3] none of the actual data for the rare earths was ever published. Appleton and Selwood[4] reported a separation factor of 1.06 in favor of neodymium for extracting an aqueous solution of neodymium and lanthanum thiocyanates with *n*-butyl alcohol. Recently Templeton and Peterson[5] substituted *n*-hexyl alcohol and nitrates in this process and obtained a separation factor of 1.5. The complete data for these distributions must be available before one may judge whether solvent extraction will either compete with or supplement other methods of separating the rare earths. Certainly it is not inconceivable that there may develop some special application for which liquid–liquid extraction will surpass even ion-exchange methods.

The study, for its own theoretical interest, of the distribution of salts between immiscible liquids has been much neglected. S. A. Voznesenskii (Wosnessensky)[6] did some work of this sort in connection with the investigation of electrolytic cells involving non-aqueous solvents. The only recent reports appear to be those of Nachtrieb, Conway and Fryxell[7] on the distribution of ferric chloride between isopropyl ether and aqueous hydrochloric acid solutions,

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[1] Fischer, Dietz and Jübermann, *Naturwissenschaften*, **25**, 348 (1937).

[2] Fischer and Bock, *Z. anorg. allgem. Chem.*, **249**, 146 (1942).

[3] Fischer and Chalybaeus, *Z. anorg. Chem.*, **255**, 79 (1947), and Fischer, Chalybaeus and Zumbusch, *ibid.*, **255**, 277 (1948).

[4] Appleton and Selwood, THIS JOURNAL, **63**, 2029 (1941).

[5] Templeton and Peterson, *ibid.*, **70**, 3967 (1948).

[6] Wosnessensky, *Z. physik. Chem.*, **104**, 46 (1923), and **115**, 405 (1925); Voznesenskii and Chmutov, *J. Russ. Phys.-Chem. Soc.*, Chem. Part, **57**, 343 (1925).

[7] Nachtrieb and Conway, THIS JOURNAL, **70**, 3547 (1948), and Nachtrieb and Fryxell, *ibid.*, **70**, 3552 (1948).