[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Structure Studies on Chromium–Aluminum Oxide and Related Catalyst Systems

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This paper describes further applications of the susceptibility isotherm[2] to chromia–alumina catalysts. The work is extended to catalysts prepared by impregnation, precipitation, and coprecipitation. Supports other than γ-alumina have been investigated. Magnetic measurements have been made on supported catalysts containing molybdenum, tungsten, and uranium. X-Ray diffraction results have been correlated with the magnetic data.

Experimental Part

The magnetic susceptibility measurements, and the general features of the susceptibility isotherm were described in the first paper on this subject. X-Ray data given below were obtained on a Norelco Recording X-ray Spectrometer. Surface areas were obtained by low temperature nitrogen adsorption and the BET equation.

Impregnated Chromium.—As previously described, this catalyst system was made by impregnating the support in chromic acid solution, drying, and reducing in hydrogen at 360°. Impregnations were made on γ-alumina, on *boehmite*, on α-alumina (*corundum*), and on silica gel. The method of analysis for chromium has already been described.

Precipitated Chromium.—γ-Alumina was suspended in 25% ammonium hydroxide solution. The mixture was stirred rapidly while chromic nitrate solution was added from a buret. The mixture was treated in the same manner as the impregnated chromium. Four concentrations were prepared.

Co-precipitated Chromium.—Ammonium hydroxide was added to a solution containing aluminum nitrate and chromic nitrate. The precipitate was treated in the same way as the impregnated chromium. A single catalyst was prepared in this way.

Impregnated Molybdenum.—Molybdenum trioxide was dissolved in dilute ammonium hydroxide. γ-Alumina was impregnated with this solution. The mixture was dried and reduced in hydrogen at 500°. Five catalysts were made.

Two further molybdenum impregnation catalysts were made using titanium dioxide and thorium dioxide respectively as supports. Reasons for the choice of these supports will be given below.

The analytical procedure for all molybdenum catalysts is based on precipitation with α-benzoin oxime. The sample is fused with sodium peroxide in a nickel crucible, the melt dissolved in water, boiled to decompose excess peroxide, and filtered to remove nickel hydroxide. The filtrate is made slightly acid with sulfuric acid, and the molybdenum is precipitated with α-benzoin oxime. The precipitate is ignited at 500° and molybdenum weighed as the trioxide.

Coprecipitated Molybdenum.—Molybdenum trioxide was placed in hydrochloric acid. The mixture was boiled for thirty minutes, then cooled and filtered to remove insoluble material. Aluminum turnings were added slowly. During this addition the mixture turned green, then black. After reduction was complete the solution was rapidly filtered and then neutralized with ammonium hydroxide until the mixed hydrous oxides precipitated. The mixture was dried, washed, and reduced in hydrogen at 500° A single catalyst was made.

A second coprecipitated molybdenum catalyst was made containing a larger proportion of alumina, and all drying operations were carried out in hydrogen to prevent possible reoxidation. A portion of this was dried, washed and redried without heating over 110°.

Impregnated Tungsten.—γ-Alumina was impregnated with tungstic acid solution. The mixtures were dried at 500°, then reduced in hydrogen and steam at 780°. After being put into solution by peroxide fusion the sample was analyzed for tungsten by precipitating the tungsten from dilute hydrochloric acid solution as tungstic acid and cinchonine tungstate. The precipitate was ignited at 750° and weighed as WO_3.

Impregnated Uranium.—γ-Alumina was impregnated with a solution of uranyl acetate hydrate in ethyl alcohol. The mixture was filtered, dried at 500°, then reduced in hydrogen at 650°. Two samples were made.

The uranium catalysts were analyzed for uranium by the following procedure. The sample was fused in a platinum crucible with potassium pyrosulfate, and the melt was dissolved in dilute sulfuric acid. The cooled solution was passed through a Jones reductor. After reduction the solution was aerated and titrated with standard dichromate.

Results

For convenient reference the susceptibility isotherm for impregnated chromium at liquid nitrogen temperature is given in Fig. 1. This is based on data previously reported.[2] Several new results are presented in the same figure.

Impregnated Chromium on *Boehmite*.—The area of the *boehmite* used was 170 sq. m./g. The area of the γ-alumina used for Fig. 1 was 423 sq. m./g. The susceptibilities found for the *boehmite* series are indicated in Fig. 1. The effect of reducing the carrier area by over 50% is shown to have little effect on the susceptibilities. The effect of carrier surface area on the susceptibility isotherm is, therefore, seen to be negligible within this range of area.

This conclusion is surprising but it is understandable when we recall that at point "1" (the critical point in the susceptibility isotherm) only about one-ninth of the carrier surface area is actually covered by chromia. A two-fold reduction of the carrier area still leaves large expanses of exposed carrier when the concentration of chromia corresponds to point "1," namely, about 6% by weight of chromium.

A further test of the effect of carrier area is shown by the results obtained by using α-alumina (*corundum*) as carrier. The area of this carrier is only about 5 sq. m./g. The susceptibility of the chromia on this support is greatly reduced as indicated by point Δ in Fig. 1. The susceptibility of the chromium in this catalyst at $-190°$ was 86×10^{-6}. The chromium concentration was 5.45%. By contrast, the chromium concentration on a high area alumina would have to be five times greater before the susceptibility would be reduced to 86×10^{-6}. It is clear, therefore, that gross changes in carrier area have a large effect on the

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[2] Eischens and Selwood, THIS JOURNAL, 69, 1590 (1947)

susceptibility isotherm provided we are working in a region where most of the surface is covered by chromia. The magnetic susceptibility could be used for rough surface area determinations if there were any point in so doing.

Impregnated Chromium on γ-Al_2O_3; Effect of Impregnation Temperature.—The view previously expressed regarding catalyst structure was that as at point "1" the chromia is aggregated into very small crystals having only about three oxide ion layers, and that most of the carrier area remains uncovered. This view suggests that raising the impregnation temperature will modify the distribution of chromium by increasing the number of chromia crystallites, and decreasing their size. These changes may be caused by breaking up any tendency toward isopolychromate ion formation in the solution used for impregnation.

The correctness of this general view is shown by carrying out the impregnation at 90° instead of as usual at room temperature. The susceptibility of the chromium at liquid air temperature for hot impregnation is 184 and 188 $\times 10^{-6}$, respectively, for catalysts containing 7.24 and 5.67% chromium. Catalysts of the same concentration but made by room temperature impregnation would have susceptibilities of 140 and 150 x 10^{-6}. One might say that the chromium is about twice as effectively dispersed by impregnation at 90° as compared with 25° if one considers the concentrations necessary to give equivalent dispersions.

It might be expected that hot impregnation would, therefore, yield a more effective finished catalyst than would room temperature impregnation. This expectation is confirmed by relative activity studies. The reaction used was the dehydrocyclization of *n*-heptane. The hot impregnation catalyst was about 25% more effective than the cold. The catalytic measurements were made by Dr. A. S. Russell of the Aluminum Research Laboratory, Aluminum Company of America.

Impregnated Chromium on γ-Al_2O_3; Weiss Constant at Infinite Dilution.—In our previous paper we based our interpretation of the susceptibility isotherm on the Weiss constant, Δ, approaching zero at infinite dilution of the chromium. Magnetic measurements below 1% chromium are difficult because the susceptibility is so close to that of pure alumina, and because ferromagnetic impurities present to the extent of 1 part in 10^8 have a marked effect on the observed susceptibilities. In an effort to go to very low concentrations we have measured chromium on γ-alumina on a sensitive magnetic balance designed for work on organic free radicals. A chromium concentration of 0.106% gave chromium susceptibilities of 103 and 151 $\times 10^{-6}$ at 25 and at $-70°$, respectively, after suitable corrections for ferromagnetic impurities. It is clear from these results that $\Delta = 0$, within the experimental error at this concentration. We interpret this to mean that at this low concentration no appreciable fraction of chromium ions are at the normal minimum chromium–chromium distance of 2.80 Å. The chromium may be considered at this concentration to be in true two-dimensional solid solution on the alumina support.

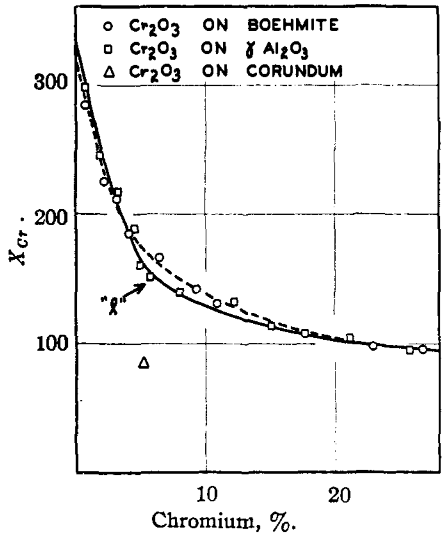

Fig. 1.—Susceptibility isotherm for impregnated chromium oxide on γ-alumina and on *boehmite*. Point Δ corresponds to a single measurement on chromia supported on α-alumina. All measurements are at liquid air temperature.

Impregnated Chromium on γ-Al_2O_3; Effect of Heating.—Chromia–alumina catalysts are often used at temperatures in the neighborhood of 600°. Such catalysts slowly decrease in activity, although they may be reactivated in part.

A catalyst containing 7.0% impregnated chromium on γ-alumina was heated for two weeks at 600° in air. The catalyst was then cooled and reduced in hydrogen in the usual manner. The susceptibility of the chromium in this catalyst at $-190°$ rose from about 165 $\times 10^{-6}$ to 265 $\times 10^{-6}$. The Weiss constant fell from 100 to 30°. The magnetic moment rose from $\sim$ 3.25 to 3.5 Bohr magnetons indicating a drop of average oxidation state from $\sim$ 3.5 to $\sim$ 3.2. We conclude that prolonged heating at 600° causes the chromium to dissolve in the support. The chromium is obviously more thoroughly dispersed after the heat treatment. We believe that the dispersion is three dimensional rather than two. If the chromium merely spread out on the surface we might expect the catalytic activity to rise rather than fall.

Impregnated Chromium on Silica Gel.—Two catalysts containing chromia supported on silica gel revealed that this support may contain somewhat variable amounts of ferromagnetic impurities. After appropriate corrections are made a 1.6% chromium catalyst has a chromium susceptibility of 403 × 10^{-6}, and a 2.70% catalyst has a susceptibility of 310 × 10^{-6}, both at −190°. These values are higher than those for chromium on γ-alumina at corresponding concentrations. Although the error in these calculations is large, it is safe to conclude that chromium disperses on silica to at least as great a degree as it does on alumina.

Precipitated Chromium.—The magnetic data obtained on the precipitated chromium series of catalysts (on γ-Al_2O_3) are given in Table I.

TABLE I

MAGNETIC SUSCEPTIBILITIES OF PRECIPITATED CHROMIUM-ALUMINUM OXIDE CATALYSTS

	Susceptibilities × 10^6					
	85°K.		190°K.		295°K.	
Wt. %Cr	$\chi_{cat.}$	χ_{Cr}	$\chi_{cat.}$	χ_{Cr}	$\chi_{cat.}$	χ_{Cr}
4.00	7.2	187	4.1	109	2.9	81.0
6.86	9.8	147.5	6.3	96.3	4.5	69.9
9.74	11.3	119	8.1	85.2	6.3	67.8
12.30	11.7	98.1	9.1	76.4	7.5	62.6

Magnetic moments and Weiss constants for the precipitation series are shown in Fig. 2. For comparison, Fig. 2 also shows moments and Weiss constants for the previously reported impregnation series on γ-alumina. The most striking magnetic difference between the precipitated and the impregnated series is that for the former the Weiss constant shows no critical point corresponding to point "1" in the susceptibility isotherm. The layering, characteristic of impregnated catalysts, is absent. In the impregnation series each chromium ion has a fairly uniform environment at each concentration. But in the precipitation series the chromia particles must vary widely in size from substantially isolated chromium ions to macrocrystals. This view is supported by the X-ray studies reported below.

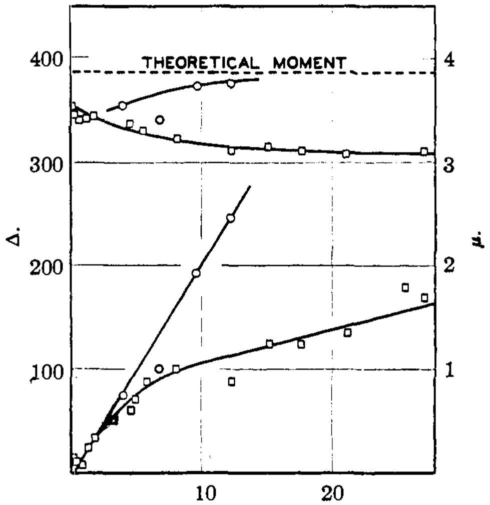

Fig. 2.—Magnetic moments and Weiss constants for precipitated chromium on alumina: ○, precipitation series; □, impregnation series.

Another interesting feature of the precipitation series is that the magnetic moment corresponds almost exactly to an oxidation of +3 for the chromium, except at the lowest concentrations where the moment falls slightly, indicating a slight rise in average oxidation state. At the lowest concentrations the average oxidation state for both impregnation series and precipitation series seems to be the same, namely, about 3.25. Higher chromium concentrations in the impregnation series showed an oxidation state of about 3.5. These oxidation states are confirmed by direct chemical analysis.

It should be pointed out that there is nothing startling about an abnormal oxidation state on a surface. In the center of a crystal, valence anomalies may only be achieved by the creation of lattice defects. But on the surface of an oxide, the addition of a few oxygen ions produces no distortion in the lattice, but merely adds slightly to it.

Coprecipitated Chromium.—The single catalyst prepared by coprecipitation contained 35.0% chromium on γ-alumina. The susceptibility of the chromium in this catalyst was 142 × 10^{-6} at liquid air temperature. It is of interest to note that this catalyst itself has a greater susceptibility (49.6 × 10^{-6}) than has pure chromia (~22.8 × 10^{-6}) at the same temperature. The susceptibility of the chromium is also much larger than that found in the impregnation series. The 35% coprecipitation catalyst contains chromium in approximately the same degree of dispersion as does a 7% impregnation catalyst. We attribute this great difference to the presence of three-dimensional dispersion in the coprecipitation catalyst, as compared with two-dimensional dispersion in the impregnation series.

Impregnated Molybdenum.—Success of the susceptibility method with chromia catalysts suggests trying the method with supported molybdenum. The results with molybdenum must all be classed as failures, in that no appreciable paramagnetism could be developed. However, these results raise some interesting questions regarding the structure of molybdenum compounds.

In a series of five impregnated molybdenum catalysts on γ-alumina the suceptibilities were substantially independent of concentration and all near zero. The molybdenum concentrations ranged from 4.6 to 29.2%.

It was thought that the structure of the support might have some effect on the tendency for molybdenum (+4) ions to disperse. With a view of providing a support more in line with the natural crystallographic tendency of molybdenum dioxide, there was prepared an impregnation catalyst on titanium dioxide. This also failed to yield any appreciable paramagnetism.

A further attempt in the same direction was made by supporting the molybdenum on thorium oxide. This also failed to produce much paramagnetism, although the susceptibility of the molybdenum at liquid air temperature did rise to 14 × 10^{-6}. The surface area of the thoria was not very large, and it is possible that the approach of supporting the molybdenum on a high area support of the rutile or fluorite structure might succeed in producing a higher paramagnetism.

Coprecipitated Molybdenum.—The tendency of molybdate ion to isopolyanion formation is well known and it was thought that reduction prior to precipitation might be more effective in dispersing the molybdenum. But in the three samples tested the susceptibility of the molybdenum was negligibly low.

This failure of the susceptibility isotherm method with molybdenum is disturbing. The method has been demonstrated in this Laboratory to work well for supported chromium, nickel, cobalt, copper, tungsten and uranium. Failure with molybdenum must mean either that effective dispersion of the molybdenum ions is not being achieved, or else that the molybdenum–oxygen bond has much more covalent character than is found in any of the other metallic oxides studied by this method. Tetravalent molybdenum complexes, involving molybdenum–bromine bonds, seem to have a definite paramagnetism.[3,4]

Impregnated Tungsten.—A single catalyst on γ-alumina shows a tungsten susceptibility of 15.9 × 10^{-6} at $-190°$. The tungsten concentration was 6.3%. Tungsten, therefore, shows the dispersion effect, but not to quite the same degree as chromium.

Impregnated Uranium.—The susceptibility of the uranium in two catalysts on γ-alumina was respectively 33.6 × 10^{-6} and 26.6 × 10^{-6}. The corresponding uranium concentrations were 4.85 and 6.2%. Uranium, therefore, shows the dispersion effect. It may appear that the susceptibilities given for uranium are small compared with those for chromium. However, it must be recalled that tetravalent uranium contains, presumably, only two unpaired electrons, as compared with three for trivalent chromium. Furthermore, owing to the large atomic weight of uranium the susceptibility for two unpaired electron spins could reach a maximum at $-190°$ of only 41.5 × 10^{-6} as compared with 352 × 10^{-6} for trivalent chromium. It is clear, therefore, that uranium shows the dispersion effect to at least as great a degree as does chromium.

X-Ray Diffraction.—In the X-ray work on chromium the 1.67 Å. line is used as the reference line because it is the most intense, and the other lines give the same general results. Figure 3 shows the results of this work. The intensity (height) of the 1.67 line is plotted against chromic oxide concentration. In each case the intercept on the abscissa gives the approximate concentration at which the 1.67 line first appears on the X-ray pattern. This value is a rough measure of chromic oxide dispersion.

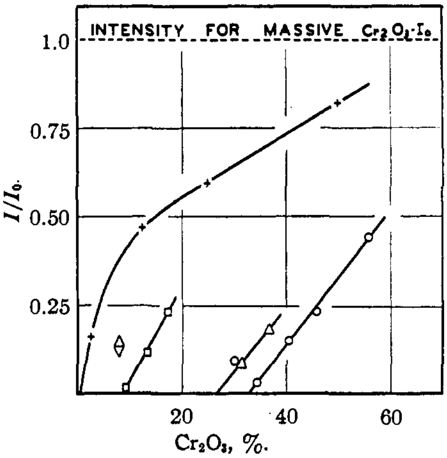

Fig. 3.—Relative X-ray intensities for the 1.67 Å. line for several chromia catalysts: ○, impregnation on γ-Al_2O_3; ⦵, impregnation on corundum; □, precipitation on γ-Al_2O_3; △, impregnation on *boehmite;* +, mechanical mixture.

It is apparent that all the catalysts show some dispersion when compared to a mechanical mixture. The catalyst on α-alumina shows less dispersion than any of the others. On this support the first trace of the 1.67 line would appear at about a 5% chromium concentration. The low dispersion indicated by the X-ray pattern is in accord with the results obtained from the magnetic measurements and the low area of the corundum.

With the X-ray data a comparison may be made between the impregnation and precipitation methods of catalyst precipitation. It can be seen that the precipitation series shows the 1.67 line at a chromium concentration of about 10%, while the line is not evident in the impregnation catalyst until the concentration is about 30%. This supports the view that the precipitation catalyst contains chromia crystals of all sizes from almost single chromium ions to those large enough to give X-ray diffraction patterns. The impregnation series, on the other hand, contains microcrystals of chromia of roughly equal size for each chromium concentration.

All the observed lines in the chromia–alumina catalysts were identified as being due to either chromia in the corundum structure, or to γ-alumina. This supports the view previously expressed that chromia assumes the corundum structure in the catalysts.

The coprecipitated chromium shows no X-ray

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(3) Klemm and Steinberg, *Z. anorg. allgem. Chem.*, **277**, 193 (1936).

(4) Recent X-ray work by Magnéli, *Ark. Kem. Mineral Geol.*, **24A**, Nr. 2 (1946), on crystals of molybdenum dioxide have shown the presence of covalent bonds between adjacent molybdenum atoms. This is probably the explanation of the anomalous magnetic effects reported in this paper.

lines at 51% chromium. This supports the view that the chromium dispersion is three-dimensional and very great in this method of preparation. It should be noted that three-dimensional dispersion does not mean that the preparation is necessarily a more effective catalyst.

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Summary

Magnetic susceptibilities have been used, together with X-ray and surface area studies, to elucidate the structure of supported oxides of chromium, molybdenum, tungsten and uranium.

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The Non-Equilibrium Theory of Absolute Rates of Reaction[1]

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Introduction

In every formulation of a theory of reaction rates, two distinct problems are involved, the one dealing with the forces acting between the particles participating in the reaction, *i.e.*, the activation energy, and the other, with the calculation of the specific rate constants assuming the first is known. Furthermore, to make the latter calculation possible, a basic assumption is made which finds its origin in S. Arrhenius's[1b] classical proposal that an equilibrium exists between normal and activated molecules. This is equivalent to the alternate assumption made in the quantum mechanical formulation of rate theory that an equilibrium exists between the various internal degrees of freedom of the initial configuration. The applicability of the equilibrium theory to chemical reactions or to any rate process, in which rearrangement of matter involves surmounting a potential barrier, requires further consideration in view of a complete formulation of the theory of absolute rates of reaction.[2]

The simplest example of the inapplicability of the simple equilibrium theory is shown for the case of homogeneous gas reactions, where for sufficiently low pressures molecular collisions are inadequate for maintaining an equilibrium concentration in the activated state. For most measurable reactions occurring under normal conditions of temperature and pressure, the assumption appears to be correct. Discussions of this matter are to be found in papers by Marcelin,[3] Wynne-Jones and Eyring,[4] Guggenheim and Weiss[5] and others.[6] The success of the crude collision theory and more so of the theory of absolute rates of reaction, which satisfactorily interprets chemical reactions and many diversified physical phenomena, is strong evidence for the correctness of the equilibrium hypothesis. All this, however, is *a posteriori* evidence that an adequate supply of energetic or activated molecules is maintained during all stages of the reaction and more direct quantitative reasoning is desired. Our present knowledge of chemical dynamics is not sufficiently advanced for a detailed investigation of the individual collision processes which give rise to a very great variety of energetic molecules and to determine what fraction of these fortuitously propitious collisions determine the concentration in the activated state. An ingenious approach to this complex problem was made by H. A. Kramers.[7] To elucidate the applicability of the absolute rate theory for calculating the velocity of chemical reactions, he considered the effect of the Brownian motion of a medium on the probability of escape of a particle (caught in a potential hole) over a potential barrier. Kramers' results indicate that the theory of absolute rates of reaction gives results correct within 10% over a wide range of viscosity values. Since he employed classical mechanical diffusion theory in the study, it is of interest to take into account the quantized nature of molecular levels.

Method

Consider reactants passing by a series of molecular collisions from a set of energy levels to a subsequent set of levels corresponding to the final states of the products. It is assumed that the values for the specific rate of transition k_{ij} from level i to level j are known, which, in principle at least, are calculable from the quantum mechanical theory of collisions.[8] Restricting ourselves to reactions where we can neglect the concentration changes in

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[1] Abstract from a dissertation submitted in May, 1947, to the Graduate School of Princeton University in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Presented at the Atlantic City meeting of the American Chemical Society, April, 1947.

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[1b] S. Arrhenius, *Z. physik. Chem.*, **4**, 226 (1889).

[2] Also referred to as the "transition-state" method. See M. Polanyi and M. G. Evans, *Trans. Faraday Soc.*, **31**, 875 (1935).

[3] A. Marcelin, *Ann. Phys.*, **3**, 158 (1915).

[4] W. F. K. Wynne-Jones and H. Eyring, *J. Chem. Phys.*, **3**, 493 (1935).

[5] E. A. Guggenheim and J. Weiss, *Trans. Faraday Soc.*, **34**, 57 (1938).

[6] Symposium on Kinetics, *ibid.*, 3–81 (1938).

[7] H. A. Kramers, *Physica*, **7**, 284–304 (1940); see also S. Chandrasekhar, *Rev. Modern Phys.*, **15**, 1 (1943).

[8] N. F. Mott and H. S. W. Massey, "Theory of Atomic Collisions," Oxford University Press, 1933.