[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Structure and Catalytic Activity of Supported Manganese, Copper and Iron Oxides[1]

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The catalytic oxidation of carbon monoxide by air over supported oxides of manganese, iron and copper has been studied. The specific activity shows an increase with decreasing concentration of the supported oxide except for samples of low concentration on which the activity decreases. The results show the influence of increased dispersion of the oxide on the support surface, the increase in activity being due to an increased quantity of exposed catalyst and the decrease at low concentrations probably due to so great a dispersion as to make the reactions stoichiometrically impossible.

In previous papers the susceptibility isotherm method has been applied to the problem of the structure of supported manganese oxides,[2] supported iron oxides[3] and supported copper oxides.[4] In this paper the information obtained about the structure is related to the activity of the materials as catalysts for the oxidation of carbon monoxide by oxygen.

Experimental

The catalytic activity measurements were obtained in a flow system apparatus. Carbon monoxide–air mixtures were passed through the pelleted catalyst contained in a Pyrex tube at 100 cc./min. The temperature of the catalyst was maintained constant to ±1° by a furnace controlled by a Brown potentiometer. Carbon monoxide was prepared by dropping reagent grade formic acid (90%) on hot phosphoric acid (170°). Carbon monoxide–air mixtures were prepared in batches by mixing 1 liter of carbon monoxide with 37.7 liters of air from which the carbon dioxide had been removed with ascarite. The gas mixture was passed through magnesium perchlorate and ascarite before passage over the catalyst. The carbon dioxide in the exit gas was determined by a method described by Reinäcker.[5] This involves bubbling the gas through a suspension of barium carbonate in water. The carbon dioxide in the gas causes the formation of soluble barium bicarbonate the concentration of which was determined by the conductance of the suspension. This was related through the equilibrium expression to the concentration of carbon dioxide in the gas. The conductance was determined to sufficient accuracy with an Industrial Instruments Inc. Conductivity Bridge, Model RC-1B. The temperature of the suspension was held constant with a vapor thermostat using boiling carbon tetrachloride.

The catalysts used were prepared by methods identical with those previously described. In general the method was impregnation with a solution of the nitrate of the metal followed by drying and ignition to form the oxide. The supported manganese oxide samples were ignited at 200° and correspond to the low ignition series previously described.[2] Activity measurements were made on catalysts diluted mechanically with pure alumina. Dilution was to 1.2% manganese for those manganese oxides on alumina of concentration 1.2% and above; and 1.5 g. of the diluted sample was used in the test. The samples containing 0.79%, 0.97% and 1.2% were run at dilutions of 0.79% using 2.28 g. of diluted sample. Iron oxide and copper oxide on alumina were diluted to 0.5% of the metal, and 2.0 g. of the diluted catalyst was used. Catalysts were made into pellets 3 × 3 mm. in size.

Results

Figures 1 and 2 give results of the oxidation of carbon monoxide by oxygen over supported manganese oxide catalysts. These data are plotted as logarithm of the fraction of carbon monoxide oxidized against the reciprocal absolute temperature. The data in Fig. 1 are for the samples diluted to 1.2% manganese, with corrected data for the samples diluted to 0.79% manganese added as dotted lines. Correction for the changed dilution and quantity of catalyst was made by multiplication by the ratio of the activity of the 1.2% sample at the two dilutions. The activation energies for the oxidation over these catalysts are given in Table I.

TABLE I

ACTIVATION ENERGIES OVER LOW-IGNITION MANGANESE OXIDES ON ALUMINA

Weight % manganese	Activation energy, kcal.
0.79/0.79[a]	25.2
.79/0.97	25.2
.79/1.2	25.2
1.2/1.2	24.8
1.2/1.9	25.9
1.2/3.4	24.6
1.2/6.1	24.5
1.2/12.4	25.1
1.2/21.5	24.9

[a] A notation such as 0.79/1.2 means a sample which contained 1.2% manganese diluted with pure alumina to a concentration of 0.79% manganese.

Figure 3 is a plot of the activity of these catalysts as a function of manganese concentration. The fraction of carbon monoxide oxidized at 225° is used as the measure of activity. Data for the 0.79 and 0.97% samples have been corrected for differences in quantity and dilution.

Figure 4 shows the results of the oxidation over iron oxide supported on alumina. In Fig. 5 the activities (fraction of carbon monoxide oxidized at 275°) of these catalysts are presented as a function of their original iron concentrations. Table II shows the activation energies of the oxidation over the supported iron oxide catalysts

TABLE II

ACTIVATION ENERGIES OVER IRON OXIDE ON ALUMINA

Weight % iron	Activation energy, kcal.
0.5/0.5	30.0
.5/1.05	30.2
.5/2.0	29.6
.5/3.8	30.5
.5/7.1	29.2

In Fig. 6 are given the results of the oxidation on copper oxide on alumina catalysts, and in Fig. 7

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(1) This is the twelfth paper from this Laboratory on the susceptibility isotherm. The eleventh, by Mooi and Selwood, appeared in THIS JOURNAL, **74**, 1750 (1952). Inquiries concerning this paper should be addressed to P. W. Selwood.

(2) P. W. Selwood, T. E. Moore, M. Ellis and K. Wethington, *ibid.*, **71**, 693 (1949).

(3) P. W. Selwood, M. Ellis and K. Wethington, *ibid.*, **71**, 2181 (1949).

(4) P. W. Selwood and N. Dallas, *ibid.*, **70**, 2145 (1948).

(5) G. Reinäcker, *Z. anorg. Chem.*, **258**, 280 (1949).

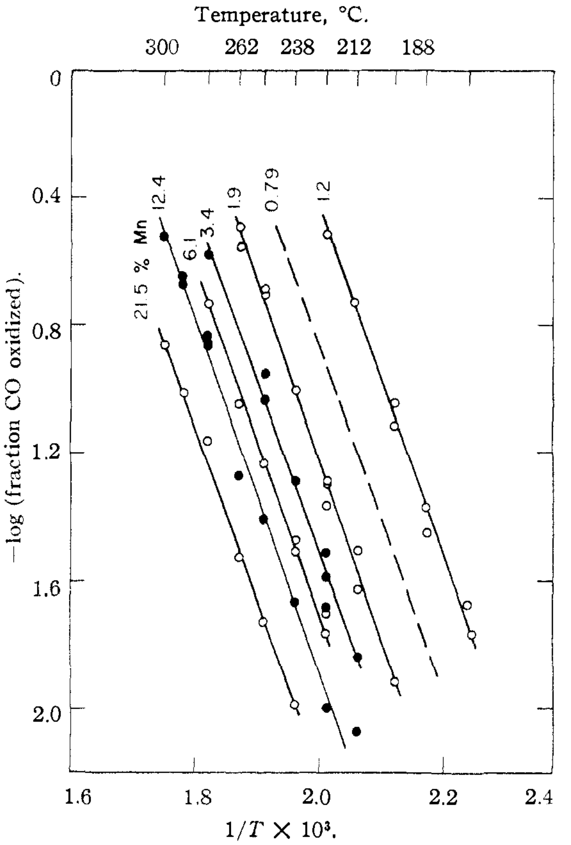

Fig. 1.—Activity of manganese oxides on "γ"-alumina as catalysts for the oxidation of carbon monoxide; log fraction CO oxidized against reciprocal temperature is given for various undiluted sample concentrations as shown.

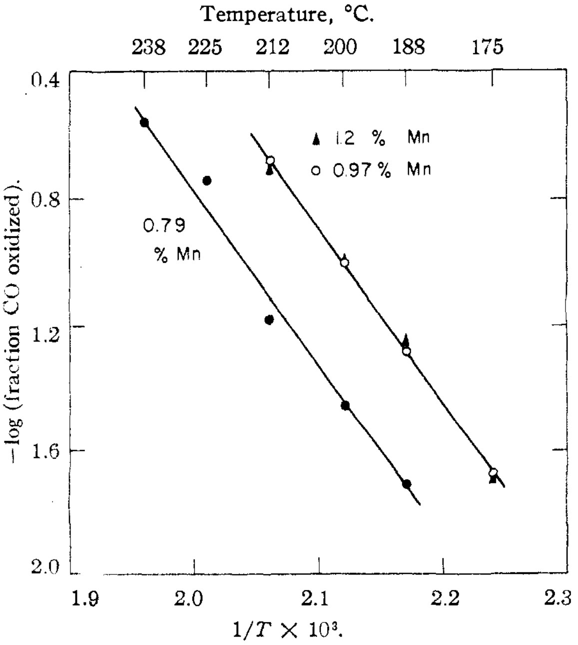

Fig. 2.—Comparison of activity in low manganese concentration range.

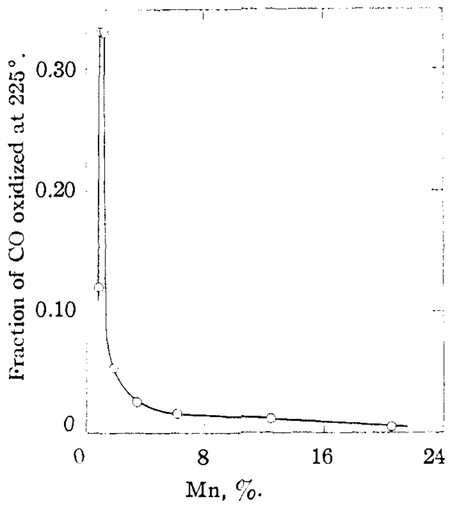

Fig. 3.—Fraction carbon monoxide oxidized at 225° as a function of undiluted manganese concentration.

are the activities (fraction of carbon monoxide oxidized at 212°) of these catalysts as a function of the original copper concentration. The activation energies of the oxidation on these catalysts is given in Table III.

TABLE III

ACTIVATION ENERGIES OVER COPPER OXIDE ON ALUMINA

Weight % copper	Activation energy, kcal.
0.5/1.42	26.1
.5/2.92	27.2
.5/4.29	27.1
.5/7.29	27.5
.5/9.72	25.9
.5/11.6	26.1
.5/13.5	25.9
.5/20.3	27.2

Discussion

The results of the catalytic oxidation of carbon monoxide on the supported oxides follow the same general pattern for all three series. With decreasing concentration of the active oxide, the specific activity first increases then drops. The position of the maximum varies with the different oxides, coming at about 1% metal for the case of the supported manganese and iron oxides, but at about 7% with the supported copper oxide. Differences between these supported oxides have also appeared in the susceptibility isotherms. Iron oxide and manganese oxide were shown to have an isotherm in which the susceptibility shows a great increase at low concentrations. The susceptibility isotherm for the supported copper oxide, however, shows the increase in susceptibility at about 10% copper and levels off at lower concentrations.

The increase in the activity of the catalysts as the supported oxide decreases is undoubtedly associated with an increased dispersion of the catalytic material on the support surface. An increased dispersion has been shown to be the cause of the increased susceptibility for these samples. This causes more oxide to be on the surface where it can act as a catalyst, and less to be used to support other oxide. The sharp increases in magnetic susceptibility come roughly at the same concentrations as the sharp increases in catalytic activity. Although the relation between susceptibility and

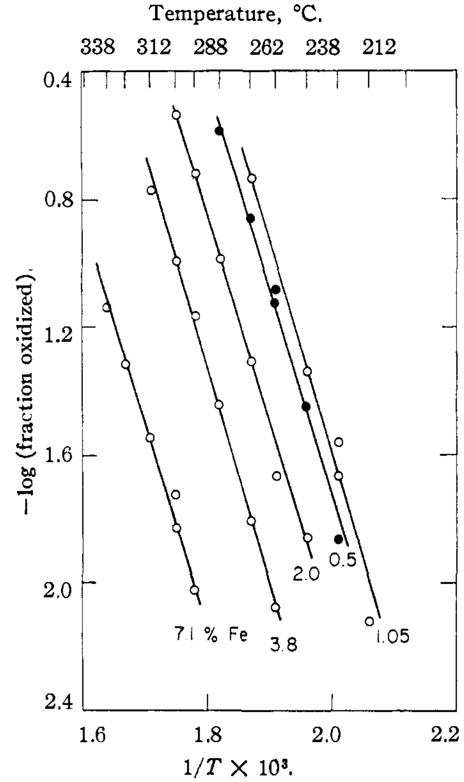

Fig. 4.—Log fraction carbon monoxide oxidized against reciprocal temperature for supported iron oxide. Undiluted concentrations of iron are shown.

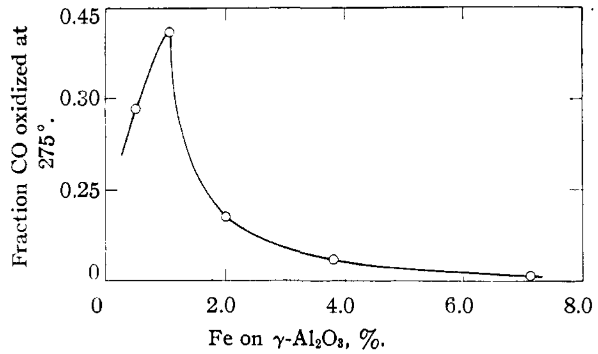

Fig. 5.—Fraction carbon monoxide oxidized at 275° as a function of undiluted iron concentration.

catalytic activity in this concentration range is not a direct proportionality, the similarity of the curves is an indication that they depend on the same structural characteristic.

A possible explanation for the decrease in activity at low original metal concentrations might be made on the basis of a loss of catalyst from the surface through solid solution formation with the alumina. Solid solution formation at the ignition temperatures does not seem likely, but, since the high area alumina is a defect structure, it might be possible that a certain amount of the catalyst oxide could be taken into the alumina structure at the defects. To test this, proton relaxation times were obtained on three samples of the manganese oxide on alumina with the lowest manganese concentrations. These were determined by methods previously described.[6,7] The data were kindly supplied by Mr. R. L. Conger of the Northwestern University Physics Department, and are shown in Table IV.

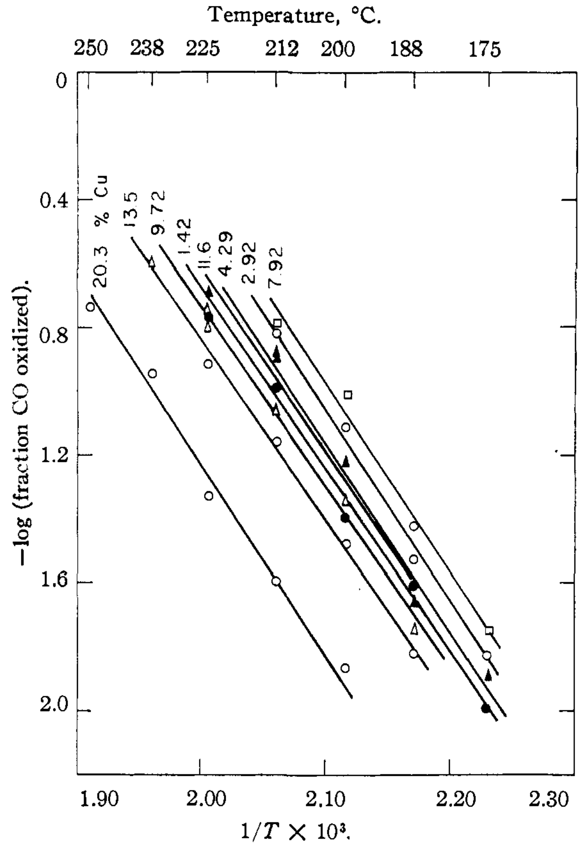

Fig. 6.—Log fraction carbon monoxide oxidized against reciprocal temperature for supported copper oxide. Undiluted concentrations of copper are shown.

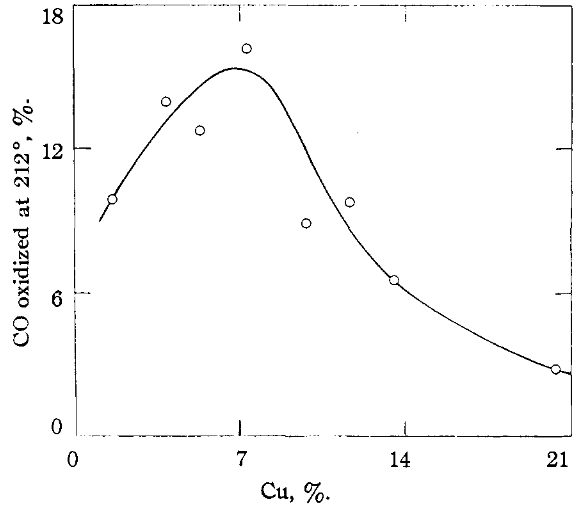

Fig. 7.—Fraction carbon monoxide oxidized at 212° as a function of undiluted copper concentration.

The relaxation times show a very definite trend toward lower values with lower manganese concentrations. This indicates clearly that the man-

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[6] R. B. Spooner and P. W. Selwood, THIS JOURNAL, 71, 2184 (1949).

[7] P. W. Selwood and F. K. Schroyer, *Discussions Faraday Soc.*, No. 8, 337 (1950).

TABLE IV

SOME PROTON RELAXATION TIMES FOR SUPPORTED MANGANESE OXIDES

Manganese, %	Relaxation times, millisecs.
0.79/0.79	1.83
.79/0.97	3.66
.79/1.2	6.33

ganese oxide remains on the surface, and dispersion increases out to the lowest concentrations used in these studies.

The decrease in activity at very low concentrations is probably caused by a dispersion of the catalyst oxide in particles so small that they can no longer take part in the reaction. Mechanisms for the carbon monoxide oxidation on various oxides used in hopcalite mixtures have been discussed by Benton,[8] Bray,[9] Frazer[10] and Schwab.[11] The mechanism indicated by all of this work is simultaneous reduction of the surface by carbon monoxide and reoxidation by molecular oxygen. For example, the manganese dioxide catalyst can be reduced to manganese sesquioxide with carbon monoxide and sesquioxide reoxidized with oxygen. For the reaction $2Mn_2O_3 + O_2 \rightarrow 4MnO_2$ to proceed, it is difficult to see how atomically dispersed manganese ions could be effective. Patches containing less than perhaps four manganese ions would remain reduced and be inactive as catalysts.

The constant activation energies for the reaction within each catalyst series seems difficult to reconcile with the above mechanism. Previously published work[1] on the hydrogen peroxide decomposition on manganese oxide catalysts similar to those used in this study showed that the activation energy of the reaction can be changed by 3 or 4 kcal. by the stabilization of one valence state by the support. It would seem that a change of that magnitude should be easily detected in these experiments, and should be expected if the above mechanism is involved. It is possible that this difference in activation energy between members of each series is not found because the rate controlling step in the reaction is not the oxidation or the reduction of the active oxide. But if the measured activation energy actually relates to the oxidation or reduction of the manganese (or other ion), we can only conclude that valence stabilization is less important for the oxidation of carbon monoxide than it seems to be for the catalytic decomposition of hydrogen peroxide.

It should be pointed out that work in this Laboratory and elsewhere has now accumulated a substantial group of reactions and catalyst systems for which a minimum catalytic particle size, or "domain," is necessary. The maximum of specific activity found at low promoter concentrations is reminiscent and confirmatory of Griffith's[12] results on promoted molybdena and similar systems.

Acknowledgment.—It is a pleasure to acknowledge receipt of the Sinclair Refining Company Fellowship, which was held by the junior author. Part of the work was done under contract with the Signal Corps Engineering Laboratories.

EVANSTON, ILLINOIS

[8] A. F. Benton, THIS JOURNAL, **45**, 887, 900 (1923).

[9] J. A. Almquist and W. C. Bray, *ibid.*, **45**, 2305 (1923).

[10] W. A. Whitsell and J. C. W. Frazer, *ibid.*, **45**, 2841 (1923); E. C. Pitzer and J. C. W. Frazer, *J. Phys. Chem.*, **45**, 761 (1941).

[11] G. M. Schwab and G. Drikos, *Z. physik. Chem.*, **A185**, 405 (1940).

[12] R. H. Griffith, *Trans. Faraday Soc.*, **33**, 407 (1937).

[CONTRIBUTION FROM THE DEPARTMENT OF INORGANIC AND ANALYTICAL CHEMISTRY OF THE HEBREW UNIVERSITY AND THE LABORATORIES OF THE SCIENTIFIC DEPARTMENT, MINISTRY OF DEFENCE]

Thermal Decomposition of Potassium Chlorate and Chlorate–Chloride Mixtures[1]

BY A. GLASNER AND L. WEIDENFELD

The continuous evolution of oxygen from pure potassium chlorate and from potassium chlorate–chloride mixtures was measured gasometrically, at temperatures ranging from 400 to 575°, and in each case the composition of the residue was determined. The activity of potassium chloride depends on the history of each specimen; certain specimens accelerate the evolution of oxygen, while others, due to their assumed ability to absorb "active" oxygen, favor the formation of perchlorate. Also in ternary mixtures of chlorate–chloride–perchlorate an induced formation of perchlorate has been observed. These phenomena explain the establishment of an equilibrium made evident by almost complete cessation of the evolution of oxygen, especially at lower temperatures. The conflicting results reported by previous workers were compared with our results and were found to conform with the use of different specimens of potassium chloride.

The thermal decomposition of potassium chlorate has been studied by Serullas[2] and others.[3-5] Farmer and Firth[3] found that potassium chloride accelerated the reaction so that in shorter time intervals, as compared with pure chlorate, equal amounts of perchlorate were produced, but the amount of oxygen evolved increased whereas the data of Otto and Fry[4] indicate the effect of potassium chloride to be just the opposite. When Hofmann and Marin[5] heated pure potassium chlorate, they obtained a 72% by weight conversion to perchlorate.

The object of this work was to clarify the mechanism of these complex reactions and elucidate whether or not an equilibrium exists between oxygen and the oxygenated halogenides. Experimental: $KClO_3$ Kahlbaum p.A. and Baker Analyzed $KClO_3$ and KCl were used.

Experimental

The apparatus consisted of a Pyrex reaction vessel and a gasometer (Fig. 1). The lower part of the apparatus fitted

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[1] For material supplementary to this article order Document 3490 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.00 for photocopies (6 × 8 inches) readable without optical aid.

[2] Serullas, *Ann. chim. phys.*, [2] **45**, 270 (1830); **46**, 325 (1831).

[3] W. Farmer and J. B. Firth, *J. Chem. Soc.*, **125**, I, 82 (1924).

[4] C. E. Otto and H. S. Fry, THIS JOURNAL, **46**, 272 (1924).

[5] K. A. Hofmann and P. H. Marin, *Sitzber. preuss. Akad. Wiss. Phys.-math. Klasse*, 448 (1932).