MANGANESE DIOXIDE IN THE CATALYTIC OXIDATION OF CARBON MONOXIDE[1]

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Introduction

The preparation of active catalysts for the oxidation of carbon monoxide has raised many questions as to the mechanism of the reaction. As method of preparation, choice and manner of incorporation of promoters, physical conditions of the substances, treatment before use, and conditions under which the reaction is carried out seem to be influencing factors, it is necessary to investigate them before any comprehensive theory can be proposed with a measure of assurance.

The discovery and preparation of these oxidation catalysts has been described in an article by Rogers, Piggot, Bahlke and Jennings[2] and also by Scalione and Merrill.[3] Further work done in this Laboratory is described by Lanning[4] and English.[5] Lanning investigated the adsorption isotherms of preparations of manganese dioxide and the catalyst, Hopcalite, composed of manganese dioxide and silver oxide, to obtain an idea of their structure and the effect on adsorption of the method of preparation and treatment of Frémy oxide and the method of incorporation of the promoters. He found that the substances were highly porous, with a large internal surface, the size of the pores approaching molecular dimensions, that water vapor was taken up by physical adsorption and not as hydrate, its poisoning effect being due to a reduction of the active surface, and an alkaline solution did not reduce the surface but very likely changed its character. The Frémy oxide and promoter oxides were found to be oppositely charged, thus helping to give mutual dispersion to a high degree.

English studied the oxygen pressure over these substances at various temperature and found that the dissociation pressures indicated the existence of solid solutions.

Plan of Work

The present investigation was undertaken as a continuation of the study of the mechanism of the reaction, by preparation in different ways of various oxides such as manganese dioxide, silver oxide, cupric oxide, cobaltic oxide, lead dioxide, nickelous oxide, ferric oxide, etc., and the quantitative study of their effects, separately at first and then in mixtures, on the oxidation of carbon monoxide, hydrogen and other convenient, oxidizable substances. As manganese dioxide seemed to be the essential constituent in all previously prepared highly active catalysts studied in this Laboratory it was studied first, with the result that the investigation was given a rather

[2] Rogers, Piggot, Bahlke and Jennings, THIS JOURNAL, 43, 1973 (1921).
[3] Scalione and Merrill, ibid., 43, 1982 (1921).
[4] Lanning, Dissertation, Johns Hopkins University, 1920.
[5] English, ibid., Johns Hopkins University, 1922.

different turn from that outlined, one result being the preparation of catalysts of manganese dioxide alone with equal if not greater activity than former oxide mixtures. They have functioned with 100% efficiency over a wide range of mixtures of carbon monoxide and air at temperatures as low as —20°.

Apparatus and Experimental Conditions

The apparatus and experimental conditions were essentially those described by Rogers, Piggot, Bahlke and Jennings.[2]

Experimental Part

The first experiment was made with a sample of commercial Frémy oxide which had been pressed, screened and dried in an air-oven overnight at 110°. As the results of this experiment determined in large measure the further course of the investigation, they will be given in some detail. The gases were first passed through soda lime and calcium chloride. The data are given in Table I.

TABLE I

EFFECT OF DRYING TEMPERATURE ON CATALYTIC BEHAVIOR OF MANGANESE DIOXIDE

Time of run, 1 hour.   CO, 1 cc. per min.   Air, 100 cc. per min.

Fresh sample.
Time of run, 40 min.

Temp. °C.	Efficiency %	Temp. °C.	Efficiency %	Temp. °C.	Efficiency %
50	61	17	73	0	14.8
20	20	18	54	22	22.8
50	36	125	94	22	9.2
75	49	150	99	22	9.2
100	93	16	98	18	5.5

The temperature was then raised to 150° when considerable moisture came off of the catalyst and condensed in the exit tube. This was swept out with dry air. The temperature was then allowed to fall to that of the room when the efficiency was 95%. The hot zone appeared at the top of the catalyst bed but moved slowly to the bottom with a slight loss of efficiency in the course of 5 to 6 hours. While the gases continued to pass, the temperature was raised to 150° for several hours; the gases were then stopped and the tube cooled to room temperature. When the 1% mixture was then passed through, the hot zone appeared immediately at the top of the bed and practically complete oxidation occurred.

This series of runs brought out a number of points: (1) the poisonous effect of very small amounts of water vapor and perhaps of other adsorbed substances; (2) manganese dioxide as the primary substance in causing the oxidation, as had been previously thought; (3) manganese dioxide when suitably prepared is able to take up oxygen at a sufficiently elevated temperature to restore its activity at a lower temperature.

The material used in these experiments was the most active preparation of manganese dioxide previously described, and the results indicate that there is some temperature at which the rate of reoxidation is equal to the rate of oxidation of the carbon monoxide under the given conditions, that is some point at which this substance is just completely catalytic.

Inasmuch as impurities seem to play such an important part in the catalytic activity of many substances, it was thought that a purer sample of manganese dioxide might prove completely catalytic at ordinary temperatures. All previously prepared Frémy oxide had been made from potassium permanganate and sulfuric acid. It is difficult to wash sulfates from samples of manganese dioxide made in this way. As nitrates are less strongly adsorbed than sulfates it was thought the decomposition of permanganate in nitric acid might give a better product, and attention was turned in this direction. The idea proved very fruitful and resulted in the preparation of samples by methods which give very active catalytic oxides at temperatures as low as —20°. These methods are as follows.

1. Decomposition of potassium permanganate in concd. nitric acid. Powdered permanganate is poured into concd. nitric acid. Several hours are required for the decomposition of the permanganic acid and the mixture must be well stirred and cooled to prevent explosion. When these precautions are observed the decomposition goes smoothly and the danger is not great. A very black, finely divided, "sandy" product is obtained which can be washed and filtered rather easily. It must be pressed to secure necessary hardness as otherwise it dries to a sandy powder.

2. Retreatment of the commercial Frémy oxide. The moist oxide is treated with concd. nitric acid, diluted, washed, and filtered. It is best to allow the product to stand in contact with the acid solution for several hours and occasionally stir the mixture to keep the particles in suspension. This product dries fairly hard without being pressed, the precipitate being more gelatinous than that described in the preceding method.

3. Oxidation of manganese sulfate with potassium permanganate in nitric acid solution. Powdered permanganate or a concentrated solution is added to the equivalent amount of manganous sulfate in solution in nitric acid. This is a very rapid method of preparation, as precipitation of the dioxide is complete almost immediately. The product is of the same order of fineness as that described in the first method and must be washed, filtered and pressed in the usual way. The final washings are always made with distilled water.

4. Oxidation of manganous hydroxide precipitated from manganous sulfate. The hydroxide is precipitated from the sulfate solution by sodium or ammonium hydroxide and washed thoroughly. It may then be treated in two ways: (a) it may be dissolved in nitric acid and the solution evaporated,

the nitrate decomposing to the dioxide; care must be taken to avoid heating it too strongly as otherwise the product may become very dense and inactive, resembling the natural substance; the dry dioxide is then treated with concd. nitric acid, washed, and dried; (b) manganous hydroxide may be oxidized as far as possible in the air (this occurs most rapidly when the hydroxide is nearly dry) and then treated with concd. nitric acid which converts the brown hydrated oxide into a very black product that is washed and filtered in the usual way; it is unnecessary to press this material.

These samples are perfectly catalytic for the oxidation of carbon monoxide at ordinary temperatures, giving a sharp hot zone 0.5 cm. to 1.0 cm. wide at the top of the catalyst bed, which remains well defined after a continuous 20-hour run. When the drying tubes are removed the catalysts are rather rapidly poisoned by the moist gases and the activity is recovered extremely slowly at room temperature when the train is reconnected. It regains its activity immediately, however, when heated to about 150° in a stream of dry air. In fact, all the catalysts should be dried under these conditions before use. Above —20° pure carbon monoxide is oxidized quantitatively with corresponding reduction of the manganese dioxide to lower oxides of manganese. Using a 1 to 2% mixture of carbon monoxide in air, there is no induction period at the beginning of the reaction and complete oxidation occurs at once even at the low temperatures mentioned. An attempt was made to reduce the catalyst using carbon monoxide diluted with nitrogen, but so little reduction seemed to occur that it was investigated more closely, when it was found that the 2 to 3% of oxygen in the compressed nitrogen was being used up by the carbon monoxide, with little apparent reduction of the oxide occurring.

Adsorption of Carbon Dioxide and Carbon Monoxide

During the first experiment with a sample of preparation No. 1 the carbon dioxide was held back by adsorption so long that it was thought worth while to work out its isotherm at 0°.[6] The data are given in the following table from which the curve has been plotted.

TABLE II

ADSORPTION OF CARBON DIOXIDE BY MANGANESE DIOXIDE AT ZERO DEGREES

| x/m = cc. of CO_2 per g. of oxide	Pressure Mm. of mercury	x/m = cc. of CO_2 per g. of oxide	Pressure Mm. of mercury	x/m = cc. of CO_2 per g. of oxide	Pressure Mm. of mercury
0.39	0.6	12.09	44.36	26.30	223.88
3.42	5.27	16.74	86.53	32.54	369.58
6.41	13.13	21.78	149.93	38.77	538.46

The sample had been dried at 180° for 3 hours in a stream of air over phosphorus pentoxide and then evacuated for $3^1/_2$ hours at 30°.

[6] This work was done by Mr. Preston with the apparatus which is used in this laboratory for measuring adsorption.

Several of Lanning's curves are reproduced for the sake of comparison.

These data show an unusually high adsorption of carbon dioxide by this particular sample, the curve lying entirely above that of silica gel even at the higher pressures. At lower pressures the amount taken up is twice that absorbed by silica gel or previous preparations of the sample or mixed oxides. This was rather surprising, as the sample was so "sandy" and non-gel-like in structure when precipitated. It thus shows a very large internal surface.

As it seemed likely that these catalysts were specific adsorbents for carbon monoxide, several attempts were made to test this experimentally.
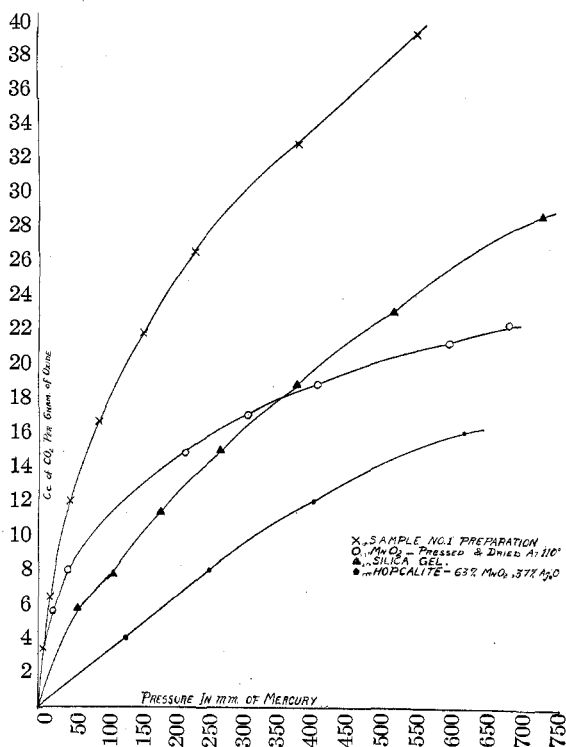
Runs were first made to obtain an approximate idea of the rate of desorption of adsorbed carbon monoxide. Carbon dioxide was dried by calcium chloride and phosphorus pentoxide and then passed through a 3g. sample of the catalyst at $-21°$ for 10 minutes at atmospheric pressure and at a rate of 30 cc. per minute. Then the train was closed at the exit end of the catalyst tube and left open to the carbon dioxide tank for 30 minutes. The train was then swept out with air at the rate of 30 cc. per minute until the atmosphere over the catalyst had been changed about twice, when bulbs containing 0.2034 N barium hydroxide solution were connected

with the apparatus and the amount neutralized was determined at various intervals.

<div align="center">TABLE III</div>

<div align="center">RATE OF DESORPTION OF CARBON DIOXIDE FROM MANGANESE DIOXIDE</div>

Temp., °C.	−15	−15	16	16	16–100
Time, min.	15	15	15	15	30
Ba(OH)₂ neut. cc.	10.9	1.8[a]	2.0	0.7	0.9[b]

[a] Only a trace was then coming over, so the temperature was allowed to rise.

[b] Only the slightest trace was then retained.

From this catalyst carbon dioxide is, therefore, desorbed much more readily and completely than from Hopcalite as found by Lamb, Scalione and Edgar.[7] In Hopcalite it is most likely held chemically to some extent by the more strongly basic oxide promoters. Adsorption of carbon monoxide was tried at —20°, —15°, 0° and 20° with practically identical results. The procedure was as follows. Carbon monoxide diluted with nitrogen freed from oxygen by bubbling through alkaline pyrogallol was passed slowly over the catalyst. The amount of nitrogen was gradually cut down until pure carbon monoxide was being passed, when the train was closed off at the exit of the catalyst tube and left open to the carbon monoxide tank for one hour. Then the train was swept out slowly with oxygen-free nitrogen until the tube was filled with nitrogen when the rest of the train was connected. Nitrogen was passed first at the temperature of the experiment until desorption was complete and finally with the catalyst at 100°. In all cases carbon dioxide appeared in the barium hydroxide tube at about the same rate as in the previous desorption run with carbon dioxide. It was hoped that any carbon monoxide adsorbed would be desorbed as such and thus appear in the second barium hydroxide tube. The same results were obtained by the use of moist as with dry nitrogen during the desorption. After the catalyst has been reduced sufficiently, the carbon dioxide comes off more slowly and at a higher temperature, indicating probably the formation of unstable carbonates by the lower oxides of manganese. No monoxide appeared in the second barium hydroxide tube, showing that oxidation of the carbon monoxide had occurred before desorption from the catalyst. This will be discussed later.

Effect of Carbon Dioxide on the Catalysis

Several runs were made with mixtures of carbon monoxide, carbon dioxide and air to test for a possible poisoning effect of the carbon dioxide. These tests were made with a 3g. sample of preparation No. 3. Some of the typical data are given in the following table, which is self explanatory. Analyses were made at 30-minute intervals when equilibrium appeared to have been reached, as the results could be checked rather closely.

[7] Lamb, Scalione and Edgar, THIS JOURNAL, **44**, 744 (1922).

TABLE IV

EFFECT OF VARYING PARTIAL PRESSURES OF CARBON DIOXIDE ON THE CATALYTIC OXI-
DATION OF CARBON MONOXIDE

Temp. °C.	CO Cc./min.	CO_2 Cc./min.	Air Cc./min.	Remarks
0	1	1	100	100% oxidation
0	1	100	100	100% oxidation
0	1	100	50	100% oxidation
−15	1	25	100	100% oxidation
−15	1	35	100	Trace of CO passed
−15	2	35	100	Several % of CO passed
−20	1.2	60	60	80% oxidation[a]
−20	1.2	60	100	50% oxidation

[a] At this point the CO_2 was shut off and the air-CO mixture was passed for 5 min-
utes. At the end of this time 100% oxidation was occurring. CO_2 was again turned on.

Analytical Data

Analyses of samples for adsorbed alkali and available oxygen are given
below, results being the average of several determinations on the various
preparations described above.

TABLE V

ANALYSIS OF SAMPLES OF MANGANESE DIOXIDE MADE BY METHODS DESCRIBED ABOVE

Sample	Mn: O	K_2O %	Remarks
1	$MnO_{1.853}$	0.64	Samples dried in current of air over P_2O_5 at 180° for several hours
2	$MnO_{1.908}$	..	Sample dried in an oven at 120°
3	$MnO_{1.986}$	..	Wet sample
3	$MnO_{1.868}$	0.27	Sample dried as No. 1 above
5	$MnO_{1.947}$	1.75	Sample Hopcalite, 60% MnO_2 − 40% CuO, dried in oven at 120°

Available oxygen was determined by the Bunsen method; this was found
to be more rapid and satisfactory than the oxalic acid method. Total
manganese was determined by means of sodium bismuthate, and potassium
by precipitation with chloroplatinic acid.

Experiments with Hydrogen

In these experiments the water formed was collected in a weighed bulb
of phosphorus pentoxide just after the catalyst tube. The total amount
of hydrogen passed was obtained from the flowmeter readings. Inasmuch
as the catalyst holds back water, especially at low temperatures, this
method of procedure would not be so very satisfactory except for the fact
that only slight oxidation appears to occur below 100–150°. Pure
hydrogen does not reduce manganese dioxide at room temperature, judging
from the absence of a heat effect. At 100°, 1 to 2% oxidation occurs and
at 200° about 40 to 50%. Reduction of manganese dioxide by hydrogen
begins at a higher temperature than in the case of Hopcalite, which con-

tains as high as 40% of the more easily reducible cupric oxide. This should make the manganese dioxide catalysts somewhat better for the removal of carbon monoxide from mixtures of this gas with hydrogen than Hopcalite under properly controlled conditions. Several qualitative tests have verified this.

Preparation of Cupric Oxide

Cupric hydroxide was precipitated from cupric nitrate solution with sodium hydroxide, and the precipitate washed thoroughly, pressed and dried. A sample of this oxidized 1 to 2% of a 1.0% mixture of carbon monoxide and air at room temperature but was not catalytic under these conditions.

Several experiments were made similar to those described for manganese dioxide to test for possible adsorption of carbon monoxide. Pure monoxide at the rate of 15 cc. per minute was passed over the catalyst for about 30 minutes at —20°, the train was swept out very thoroughly with nitrogen, and finally the barium hydroxide bulbs were connected. From an 8g. sample, between 0.8 and 4.0 cc. of carbon monoxide, calculated from the barium hydroxide neutralized, was desorbed and appeared in the second barium hydroxide tube. It was not expected that duplicate experiments on the same sample would agree closely, as the condition of the catalyst would be changed by its previous treatment. The carbon monoxide came off slowly at the low temperatures while no dioxide appeared in the first tube until nearly room temperature was reached. Then the adsorbed carbon dioxide came off until the final temperature of heating at 200°. From 8 to 20 cc. of dioxide was desorbed in this way from the 8g. sample during the different runs, showing that appreciable oxidation had occurred at the low temperatures, as was also shown by the appearance of carbon dioxide in the first tube during the time carbon monoxide was passing through the cupric oxide. Very likely, some carbon monoxide is oxidized in the process of desorption, so that the measured amount does not give the total monoxide held as such. Carbon dioxide is desorbed much less readily from this oxide than from the samples of manganese dioxide.

Discussion of Results

There are several points of interest which the present investigation has contributed in connection with the particular reaction studied, both to a knowledge of this reaction and the subject in general. From the results, it is clearly shown that manganese dioxide in Hopcalite mixtures is the initial cause of the oxidation, certainly at the lower temperatures. The active preparations are able to oxidize carbon monoxide extremely rapidly, either catalytically or at the expense of their own oxygen. The analytical data show that these active samples have a very low potash content, less than 0.5 to 1.0% of K_2O, while the partially active sample initially tried

contained very likely 3% or more, as has been shown by other investigators (English).[5]   These samples were otherwise quite alike as to physical structure.   The commercial sample after partial reduction was able to take up enough oxygen at an elevated temperature to restore its activity for a time.   When it was more completely freed from potash it was able to take up oxygen fast enough to become completely catalytic at lower temperatures.   This points to a mechanism of alternate reduction and oxidation of the catalyst.   The efficiency is quite evidently dependent on the nature of the active surface as well as on its extent.   A sample of preparation No. 4, for example, which had been ignited too strongly, on evaporation became quite dense, resembling the natural product and was entirely inactive, although alkali free.   This meant a packing and possibly a total change of structure of the material and a reduction and probably alteration of the nature of the surface but without destruction of the porous structure.   The "promoted," Hopcalite, sample is active, although it still may contain 1.74% of K_2O.   To state with certainty the effect of the cupric oxide on the mixture it would be necessary to have data on a sample of manganese dioxide containing this amount of alkali.   If the alkali is all associated with the manganese dioxide, as the Hopcalite is 60% of manganese dioxide, the latter actually contains 2.90% of K_2O. As a sample of manganese dioxide containing this much impurity would hardly be completely catalytic alone it seems that the cupric oxide does show promoter action.   It is still possible that it cuts down the adsorbed alkali or affects the way it is held so that its poisonous effect is annulled. On the other hand, both cupric and manganous ions are catalysts in other oxidation processes.   These adsorbed ions may, therefore, act as oxygen carrier to the carbon monoxide.   The activity seems to be intimately connected with the ability and rapidity with which the substance can take up oxygen, which may be caused by the rapid shifting of electrons in manganese atoms, so the poison or promoter may affect the stray field or the atomic or molecular configuration of the catalyst itself.

Attention is next called to the manganese-oxygen ratios in the samples. Here as in the previous investigations the loss of oxygen by manganese dioxide is noticed even at room temperatures and in a wet sample, indicating a dissociation pressure of oxygen in the pure manganese dioxide greater than the partial pressure of the oxygen in the atmosphere.   English[5] finds that these oxides behave as solid solutions, the oxygen pressure varying with the composition of the mixture; this is similar to the conclusions of Sosman and Hostetter[8] in the case of the oxides of iron.   The action of promoters and poisons may be due to their presence as constituents of such solutions.   The fact that the mixtures lose oxygen at room temperature shows that they have a dissociation pressure greater than the oxy-

[8] Sosman and Hostetter, THIS JOURNAL, **38**, 807 (1916).

gen in the air, and the activity because of this is greatly increased by the fineness of division of the particles. The molecules are at a point where electron changes occur with great rapidity and oxygen evaporates and condenses as readily as molecules do in the case of a liquid at its boiling point.

Water being a highly unsaturated substance with a strong field is readily adsorbed and is, therefore, a poison for many catalytic reactions. Carbon monoxide is often thought of as an unsaturated compound, but it has a weak stray field and molecules of stable configuration, as evidenced by its low boiling point and other physical properties. Yet in the catalysis of the reactions, $2H_2 + O \rightleftharpoons 2H_2O$ and $N_2 + 3H_2 \rightleftharpoons 2NH_3$, carbon monoxide is a poison because it is rather strongly adsorbed, although in the latter case the poison effect may be due to the formation of water by the reduction of the carbon monoxide by hydrogen. It reduces most metallic oxides at a lower temperature than hydrogen and in the case of manganese dioxide this difference in temperatures of reduction seems to be especially large. It is known that manganese dioxide catalyzes the reaction, $O_2 \rightleftharpoons O + O$, which fact together with the reasons outlined previously would account for the increased activity of the oxygen. The low temperature of oxidation of carbon monoxide as compared with that for the oxidation of hydrogen points, however, to the activation of the carbon monoxide as an important factor. Taylor and Burns[9] point out the importance of specific adsorption in the case of metallic catalysts. They say,

"Some metals, which show specific adsorption for carbon monoxide hold it very tightly. Maximum catalytic activity does not occur at temperatures at which maximum adsorption is shown. Free evaporation of reactants and resultants is necessary. It seems likely that any substance which can distort or disarrange the stable configuration of the molecule or arrangement of outer shell electrons will greatly increase reactivity."

The rapidity of oxidation of carbon monoxide (the time of contact is of the order of 0.01 second, comparable to that in the oxidation of ammonia) shows that the monoxide is not held very tightly as such. If it were, it would be its own poison. Failure to effect desorption of carbon monoxide as such from manganese dioxide points to a rapid rearrangement and reaction. That carbon monoxide may be adsorbed is shown by the experiments with the less active cupric oxide. The course of the reaction would be, then, adsorption and simultaneous oxidation of carbon monoxide by the catalyst; desorption of the carbon dioxide or its adsorption by capillary condensation in case the catalyst were not already saturated; and finally reoxidation of the catalyst. The carbon dioxide is inert and chemically inactive and therefore does not poison the catalyst except by mechanically covering the surface and preventing contact of the reactant with the catalyst surface.

⁹ Taylor and Burns, THIS JOURNAL, **43**, 1273 (1921).

The range through which molecular forces may act is variously put at 1 to 1500 $\mu\mu$. Assuming it to be near the larger limit it might not be necessary to postulate actual contact of the gas molecules and catalyst surface. The field of force might be strong enough at some distance to bring the gases into a reactive condition. Adsorbed poisons would modify or annul this stray field. The effect of temperature in altering the distance through which these molecular forces may exert themselves might conceivably have considerable influence on the temperature coefficients of chemical reactions.

Since this work was completed, two articles have appeared by Benton,[10] one on "Adsorption of Gases by Oxide Catalysts," and the other on "Adsorption and Catalysis in Carbon Monoxide Oxidations." This author proposes a mechanism for the reaction practically identical with that arrived at as a result of this investigation. This would indicate that oxidation of the carbon monoxide was caused by the oxygen of the catalyst, and that subsequently oxygen was taken up by the catalyst.

He described his manganese as a product of "high purity' and low density. Such a sample should have been very active according to the results recorded in the present investigation, but his results show that this was not the case and it still contained, very likely, several per cent. of impurities. The experience of the present writers has been that each preparation must be treated as a special case without assuming too much from previous work done on other preparations, unless accurate analytical data are available for comparison.

Summary

1. Methods for the preparation of active samples of manganese dioxide for the catalytic oxidation of carbon monoxide have been described.

2. Analytical results show that the amount of impurities, such as adsorbed alkali, plays an important part in the activity of these catalysts.

3. Experiments show a considerable temperature interval between the points required to oxidize hydrogen and carbon monoxide by these samples of active manganese dioxide.

4. A dynamic method for measuring the adsorption of carbon monoxide by manganese dioxide shows that it is desorbed from the catalyst as carbon dioxide.

5. A mechanism for the reaction is proposed and discussed.

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[10] Benton, THIS JOURNAL, 45, 887 (1923).