[CONTRIBUTION FROM FERTILIZER AND FIXED NITROGEN INVESTIGATIONS, BUREAU OF CHEMISTRY AND SOILS]

THE PREFERENTIAL CATALYTIC OXIDATION OF CARBON MONOXIDE IN THE PRESENCE OF HYDROGEN. II. THE ACTIVITY OF 2-COMPONENT HOPCALITES

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Introduction

Preliminary experiments[1] have shown the possibility of effectively removing the 1–2% of carbon monoxide present in converted water gas of the Haber–Bosch process by preferential catalytic oxidation over hopcalite consisting of 60% MnO_2 and 40% CuO. The present paper presents the results of an extended investigation of various factors influencing the activities of an essentially 2-component commercial hopcalite and of a 2-component laboratory scale preparation for the catalytic oxidation of carbon monoxide.

Apparatus, Materials and Procedure

The apparatus and methods, in general, were those described in Part I.[1] The catalyst was maintained at a constant temperature by means of a vapor-bath with a liquid boiling either at the prevailing atmospheric pressure or under automatically controlled reduced pressure as described elsewhere.[2] The flow of gas through the friction tube flowmeters was automatically controlled to give a constant ratio of air to gas by means of an improved modification of the device described by Oberfell and Mase.[3]

Preparation of the Gases.—Practically all of the experiments were made with actual converted water gas prepared in a moderate scale Haber–Bosch plant at this Laboratory. This consisted in the preparation of water gas from coke and steam, the "conversion" by means of steam of most of the 30% or more of carbon monoxide to carbon dioxide in contact with promoted iron oxide catalyst, the condensation of the excess steam and compression of the resulting "converted water gas" into high pressure cylinders. Air was added in the selective oxidation experiments by means of a flowmeter after expansion of the gas to atmospheric pressure.

In a few experiments pure gases rather than "converted water gas" were used. These gases were prepared as described in Part I.

Catalysts.—Two catalysts were used in the present experiments, a 6–14 mesh essentially 2-component commercial hopcalite (designated "MSA hopcalite" throughout this paper) and a 10–16 mesh 2-component hopcalite prepared at the American University Experiment Station in

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[1] W. E. Kuentzel, THIS JOURNAL, **52**, 437 (1930).

[2] W. E. Kuentzel, *ibid.*, **51**, 3347 (1929).

[3] G. G. Oberfell and R. P. Mase, *J. Ind. Eng. Chem.*, **11**, 294 (1919).

1918 by the Chemical Warfare Service (designated "CWS hopcalite") and preserved in a sealed jar since that time. It is highly probable that this latter catalyst and that used in preferential combustion experiments by Lamb, Scalione and Edgar[4] are identical. The compositions of these catalysts are tabulated in Table I.[5]

TABLE I

COMPOSITION OF MSA AND CWS HOPCALITES ON BASIS OF COMPLETELY DRIED MATERIAL

	Percentages												
	CuO	MnO_2	MnO	MgO	Fe_2O_3	K_2O	Na_2O	H_2O	CO_2	SO_3	SiO_2	Avail. O_2, %	Total %
MSA	12.9	77.5	5.4	1.5	1.0	1.6	...	17.8	0.1	2.0	...	15.7	102.0
CWS	45.0	42.1	3.0	1.0	2.3	0.3	0.8	10.6	4.0	0.1	0.6	12.5	99.2

Methods of Analysis.—The efficiency of carbon monoxide oxidation was determined by following the effluent carbon monoxide content with a continuous conductivity analyzer.[6] In the later experiments a shunted Leeds and Northrup recording potentiometer recorded the conductivity continuously. With these devices the carbon monoxide content of the gases could be determined accurately to 0.002%.

When a complete analysis of the gaseous mixture was required an improved exact gas analysis apparatus was used.[7]

The loss of oxygen from the oxide catalysts was obtained by determining the "available oxygen" before and after the run. The "available oxygen" was determined in the manner described by Almquist and Bray,[8] except that nitrogen was used as a flushing gas instead of carbon dioxide.

Conditions of Operation.—Certain conditions of operation were chosen as standard, such as a dry gas space velocity of 1000 with 10 cc. apparent volume of catalyst; a 3:1 volume mixture of steam and gas; and an oxygen concentration approximately equal to that of the carbon monoxide. Preliminary tests with MSA hopcalite in which the effect of slight variations in these operating conditions were determined indicated that variations in space velocity of 760 to 1500 resulted only in slightly lower efficiencies at the higher space velocity with no appreciable effect on the subsequent activity at the lower space velocities. Variations in oxygen content ranging from 100 to 145% in excess of that required for complete combustion of the carbon monoxide had only a slight effect, the higher concentration always yielding only a slightly higher efficiency. Although a change in the quantity of admixed steam from 3:1 to 4:1 by volume resulted in efficiencies lower than those obtained with the standard

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[4] A. B. Lamb, C. C. Scalione and G. Edgar, THIS JOURNAL, **44**, 738 (1922).

[5] The writer is indebted to Miss K. S. Love and Miss E. Z. Kibbe for analyses of the catalytic material other than water and available oxygen.

[6] E. C. White, THIS JOURNAL, **50**, 2148 (1928).

[7] W. E. Kuentzel, *ibid.*, **51**, 2759 (1929).

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

mixture of 3 :1, no permanent injury followed the use of the higher steam concentrations, but a definite decrease in efficiency usually resulted from treatment with steam in the volume ratio of 2:1. The flow of steam could be controlled accurately to within ±1%, which precluded the possibility of any appreciable influence of the latter condition.

Experimental Results

Influence of Temperature and Continued Usage on the Activity of MSA Hopcalite.—The results of a study of the effect of temperature and continued usage upon the activity of MSA hopcalite are shown in Fig. 1.

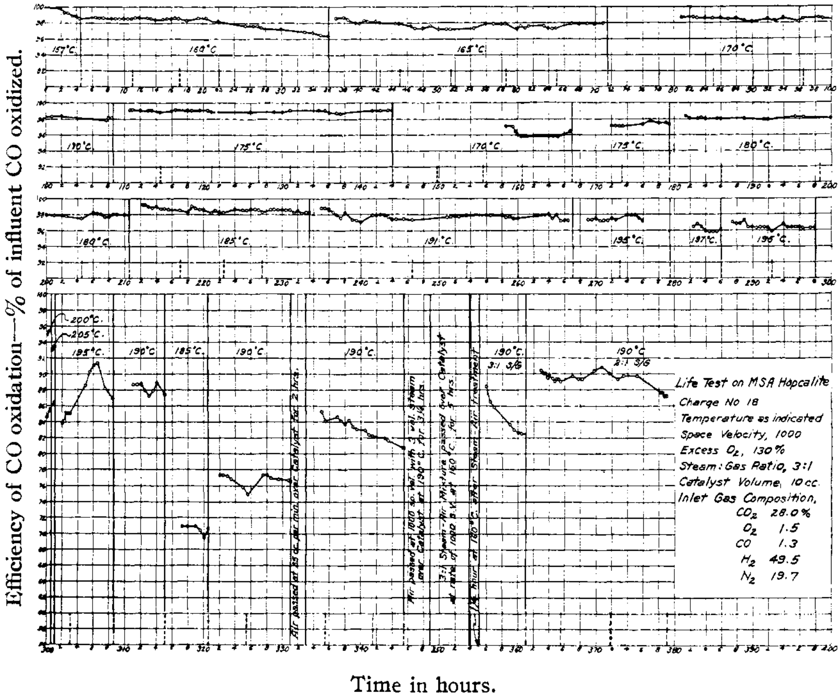

Fig. 1.

The activity was studied at progressively higher temperatures, starting at the lowest feasible temperature. These data were all obtained with a single charge of catalyst during 379 hours of actual testing. (The short vertical broken lines either along the curve or axis of abscissas indicate that the test was discontinued overnight at these points.)

A study of these data indicates that from 97 to 99% of the carbon monoxide may be oxidized in the presence of three volumes of steam to one of gas containing approximately 1.3% carbon monoxide, 1.5% oxygen, 49.5% hydrogen, 28.0% carbon dioxide and 19.7% nitrogen in the temperature range of 160 to 195°.

Attempts to restore the activity after it had been greatly decreased by high-temperature operation through the agency of re-oxidation by means of both dry air and air mixed with steam at 190 and at 160° were only partly successful. The activity at 190° was improved, but the activity at 160° was still very low after these air treatments, as shown by the single point at 56% efficiency at the 355th hour. Decreasing the quantity of steam to a 2:1 volume ratio also only slightly improved the efficiencies.

Factors Contributing to a Decrease in Efficiency of the Catalyst.—Although a high efficiency of carbon monoxide oxidation was maintained in the above tests for a considerable period of time, there is evidence that the catalyst continually decreased in activity, as indicated by the necessity of increasing the temperature in order to maintain the high efficiency, as well as by the rather rapid decrease in efficiency after high temperature operation.

Several factors which might contribute to a decrease in the efficiency of the catalyst readily suggest themselves, such as (1) reduction of the catalyst by carbon monoxide, (2) reduction of the catalyst by hydrogen, (3) loss of available oxygen through thermal dissociation of the oxides composing the catalyst, (4) insufficient dissipation of heat of reaction and (5) the possible presence of catalyst poisons. Experiments to test the part played by these various factors were accordingly carried out.

Influence of Carbon Monoxide and Hydrogen Concentration on Catalyst Reduction.—Three experiments were made at 156° in which carbon monoxide concentrations of 1.3, 0.5 and 0% were used. The results of the first two are plotted in Fig. 2, Curves 17 and 28, respectively. In the former the gas concentrations were the same as those used in the long-time test (Fig. 1), while in the latter the converted water gas entering the catalyst chamber consisted of 0.5% carbon monoxide, 0.5% oxygen, 31.2% carbon dioxide, 50.8% hydrogen and 17.0% nitrogen.

Analysis of the catalyst charges used in these two tests showed that No. 17 had lost 33.5% of the total available oxygen content of the original material during thirty-six hours of testing, whereas No. 28 lost 27.8% of its total available oxygen in twenty-five hours of testing. When due corrections are applied for the relative lengths of the runs and cognizance is taken of the fact that most of the reduction occurred in the early part of each run, it will be seen that a slightly greater loss of available oxygen occurred with the higher concentration of carbon monoxide.

The slightly greater efficiency with 1.3% carbon monoxide as compared to 0.5% may be explained by the plausible assumption that the greater heat of reaction in the former served to heat the catalyst granules to a slightly higher temperature than that existing in the latter.

The third experiment, in which the concentration of carbon monoxide was zero, was also carried out at 156°. The gas mixture prepared from pure hydrogen-nitrogen mixture, carbon dioxide and air which together with three volumes of steam entered the catalyst chamber, contained 32.0% carbon dioxide, 1.0% oxygen, 50.2% hydrogen and 16.8% nitrogen.

The activity of the catalyst was followed by determining the oxygen consumed rather than the actual decrease in hydrogen content. Samples of both influent and effluent gases were taken from time to time and analyzed for oxygen in the bulbed exact gas analysis apparatus. These analyses were then plotted against time and the quantities of oxygen entering and leaving the catalyst chamber determined by taking the areas under the smoothed curves. Upon completion of the test the loss in available oxygen was determined by analysis of the catalyst. The total hydrogen oxidized was then the sum of the hydrogen equivalents of the free and combined oxygen consumed.

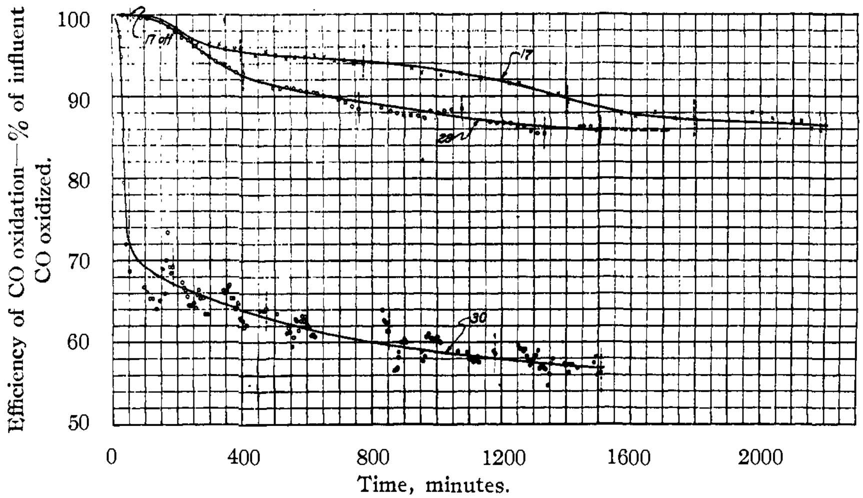

Fig. 2.—Comparison of oxidation of 0.5 and 1.3% carbon monoxide in converted water gas and effect of substituting nitrogen for steam. Curve 17—oxidation of 1.3% CO at 156°, 3:1 steam-gas mixture in glass catalyst chamber; Curve 28—oxidation of 0.5% CO at 156°, 3:1 steam-gas mixture in glass catalyst chamber; Curve 30—oxidation of 0.5% CO at 156°, 3:1 nitrogen-gas mixture in glass catalyst chamber.

A loss of 24% of the total available oxygen content of the catalyst resulted from twenty-five hours of operation, as compared to losses of 27.8 and 33.5% with hydrogen plus 0.5 and 1.3% carbon monoxide, respectively. The efficiency of hydrogen oxidation was calculated to be 1.1%.

Further evidence that the presence of hydrogen contributed to the reduction of the catalyst is shown by a comparison of the above tests utilizing carbon monoxide-free gas with tests carried out with hydrogen-free gas containing 0.5% carbon monoxide. Two tests, the results of which are plotted in Fig. 3 (Curves 31 and 32), were made at 156° with a gas mixture prepared from carbon monoxide, carbon dioxide, nitrogen and air. The mixture entering the catalyst chamber, together with three volumes of steam, contained 0.5% carbon monoxide, 0.7% oxygen, 29.1% carbon dioxide and 69.7% nitrogen. In Run 31 an accidental lowering of the temperature to 140° produced a temporary lowering of efficiency. In the duplicate test (No. 32) a very gradual decline in efficiency from 100 to 98% resulted in twenty-five hours of testing. Analysis of the catalyst charges showed losses of 18.4 and 20.3% of the total available oxygen content of the original material, respectively, compared to a loss of 24.0% with gas containing 50% hydrogen but no carbon monoxide.

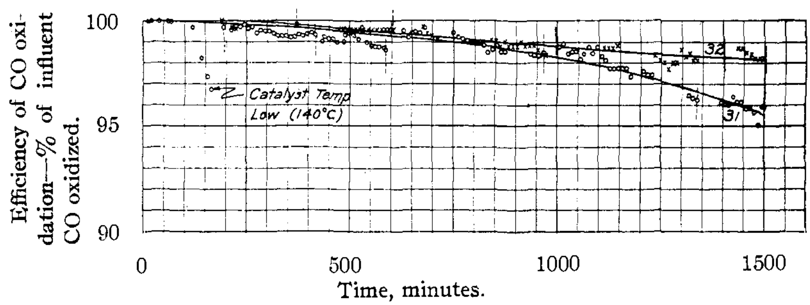

Fig. 3.—Oxidation of carbon monoxide alone. Curves 31 and 32—MSA hopcalite at 153°, 3:1 steam-gas mixture in glass catalyst chamber.

Loss of Available Oxygen by Thermal Dissociation.—In order to ascertain what fraction of the above-mentioned oxygen losses might be caused by thermal decomposition, a separate test was made. This test consisted in determining the loss in weight, other than water, of a fresh sample of the material after having been swept with dry nitrogen at 156° for 20.25 hours. This value when extrapolated to twenty-five hours, showed that the maximum loss in available oxygen would have been 8.2% due to thermal dissociation alone. The greater part of the oxygen loss in the presence of reducing gases was therefore probably due to reduction of the catalyst.

Influence of the Heat Conductivity of the Catalyst Tube on the Efficiency of the Catalyst.—Lamb, Scalione and Edgar[4] successfully oxidized 0.5% of carbon monoxide in slightly moist gas containing hydrogen over hopcalite by utilizing a copper catalyst tube to dissipate the heat of reaction. It was considered of interest to duplicate their experiments in both glass and copper catalyst chambers.

A gas mixture containing 0.5% carbon monoxide, 0.5% oxygen, 74.8% hydrogen and 24.2% nitrogen was saturated with water vapor at 40 ± 0.1° and passed over catalyst samples at a space velocity of 6000 and a temperature of 102°. The results of tests with CWS and MSA hopcalites in glass catalyst tubes are plotted in Fig. 4, Curves 35 and 36, respectively. In both instances high initial efficiencies of about 94% which rapidly decreased with time to 70 and 48%, respectively, were obtained.

An exact duplication of the conditions of Lamb, Scalione and Edgar with a copper catalyst chamber of the same general dimensions except that the copper tube preheater was somewhat shorter, gave, with new charges of the same catalysts, the results shown in Curves 37 and 38 of Fig. 4. The CWS catalyst now gave 100% oxidation for several hours and as high as 98% after twenty-five hours. The test was continued without interruption for sixty hours with a final efficiency of over 96%. The MSA hopcalite likewise gave a high initial oxidation efficiency, but its activity declined, rapidly at first and then more gradually to a final value of 75%. The superior activity of the CWS catalyst is quite apparent.

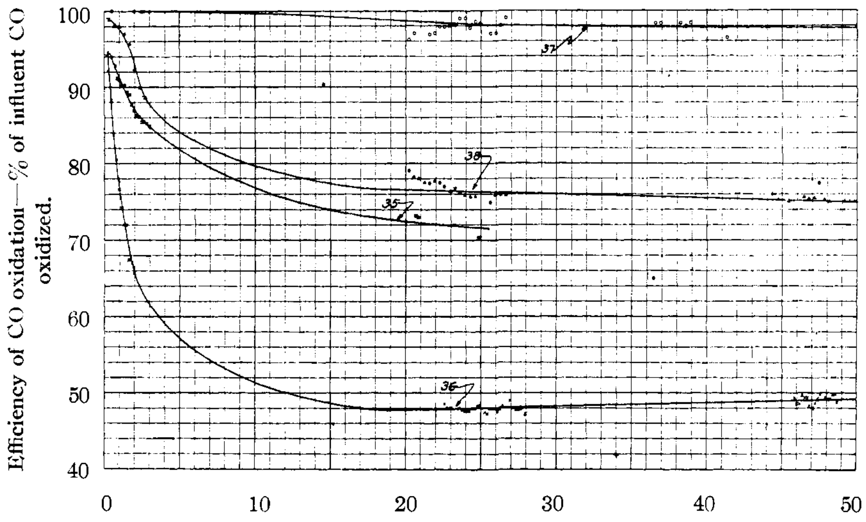

Fig. 4.—The effect of using a copper catalyst chamber. Curves 35 and 36—CWS and MSA catalysts at 102°, gas saturated with H_2O vapor at 40° in glass catalyst chamber, respectively; Curves 37 and 38—CWS and MSA catalysts at 102°, gas saturated with H_2O vapor at 40° in copper catalyst chamber, respectively.

These tests indicate, as Lamb, Scalione and Edgar have pointed out, the extreme importance of rapid and efficient dissipation of the heat of reaction. The inefficiency of the catalysts in glass as compared with copper catalyst chambers can be considered as due to the inability of the glass to conduct away rapidly the heat of reaction.

Influence of an Excess of Steam on the Efficiency of the Catalyst.—The large excess of steam used in previous tests in glass catalyst chambers probably served (1) to dissipate the reaction heat and (2) to exert a specific inhibition to oxidation of hydrogen[9] and to reduction of the catalyst by hydrogen.[10] The necessity of using a copper catalyst chamber with slightly moist gases for dissipation of the heat of reaction and the excellent results obtained in glass with an excess of steam indicate that the steam actually served as a dissipator of heat. This was further proved by an experiment in which both steam and a copper catalyst chamber were used.

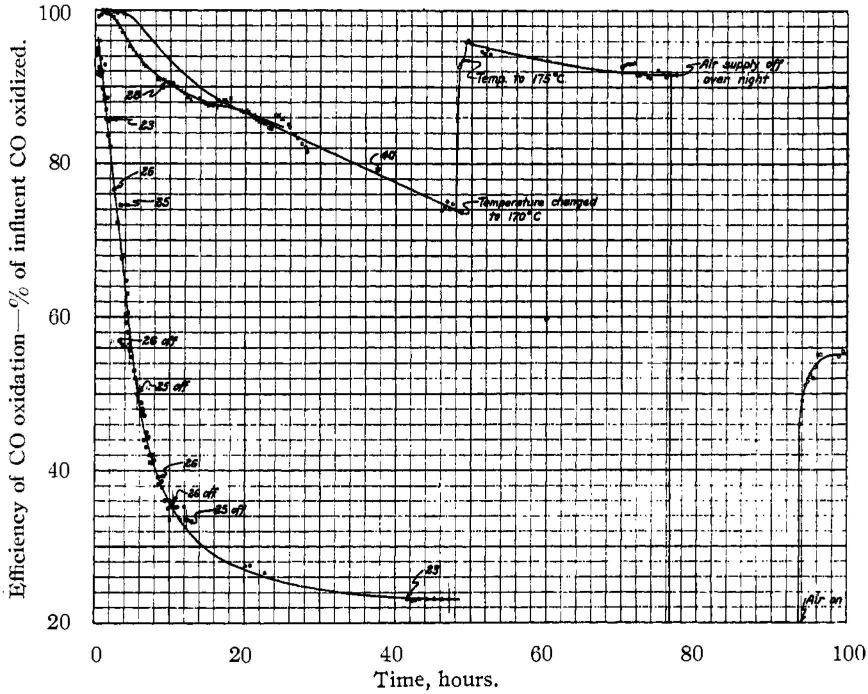

Fig. 5.—Effect of steam in copper catalyst chamber and tests with purified and unpurified gases. Curve 28—MSA hopcalite at 156°, 3:1 steam–gas mixture in glass catalyst chamber; Curves 23 and 25—tests at 130° with unpurified converted water gas; Curve 26—test at 130° with converted water gas purified by hot copper and chromic-sulfuric acid; Curve 40—MSA hopcalite at 156°, 3:1 steam–gas mixture in copper catalyst chamber.

The results of a "steam-in-copper" test are plotted together with a "steam-in-glass" experiment in Curves 40 and 28, Fig. 5. Both curves show decreasing efficiencies with time; those in the glass tube fell only slightly more rapidly during the initial stages than those in the copper, but both were practically coincident after about twenty hours. It may therefore be concluded that the excess of steam eliminated overheating of the catalyst sufficiently well to make a copper catalyst tube of no added benefit.

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[9] A. B. Lamb and W. E. Vail, This Journal, **47**, 123 (1925).

[10] R. N. Pease and H. S. Taylor, *ibid.*, **43**, 2179 (1921).

Experiment No. 40 was continued for 100 hours' duration in all at temperatures up to 175°. While the catalyst was operating at an efficiency of 92% after seventy-six hours, the air supply to the catalyst was accidentally cut off overnight while gas and steam containing no oxygen passed over the catalyst for a period of about fifteen hours. When the air supply was again admitted, the efficiency was only 55%. Reduction of the catalyst occurred in the absence of oxygen. Thus it would appear that not only steam, but free oxygen as well, is essential to the prevention of the reduction of the catalyst.

The specificity of water vapor in inhibiting reduction of the catalyst was confirmed by an experiment in which nitrogen was substituted for steam. The heat capacity and consequently the heat dissipating ability of nitrogen at 156° is roughly of the same order of magnitude as that of steam, the latter being only about one-fifth greater. Nevertheless, as can be seen by comparing Curve 30, Fig. 2, obtained with nitrogen, and Curve 28, Fig. 2, obtained with steam, the steam acts specifically to maintain the catalytic activity. Subsequent analysis revealed that the catalyst charge had lost 64.5% of its total available oxygen in the nitrogen experiment whereas only 27.8% loss was incurred in the steam experiment. The inhibition of reduction by the excess steam is thus quite apparent.

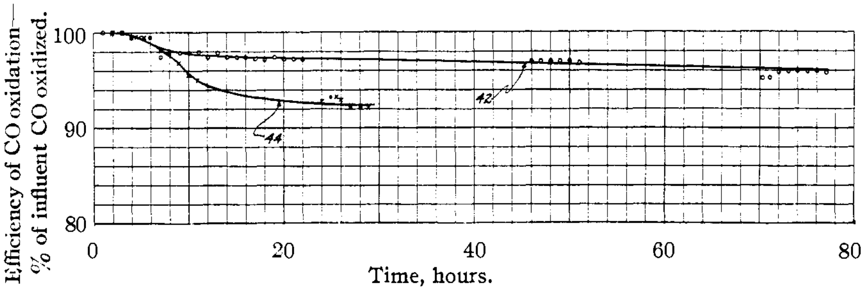

Fig. 6.—Comparison of activities of MSA and CWS hopcalite in presence of steam in glass catalyst chambers. Curve 42—CWS hopcalite at 156°, 3:1 steam-gas mixture; Curve 44—MSA hopcalite at 175°, 3:1 steam-gas mixture.

Catalyst Poisons.—The absence of catalyst poisons in the converted water gas used in these tests was definitely proved by a series of tests with MSA hopcalite at the low temperature of 130° in which both purified and unpurified gases gave identical results. Purification was by means of hot reduced copper and chromic–sulfuric acid scrubbing. Comparison of the data for Tests 23 and 25, Fig. 5, obtained with unpurified gases and those shown in Test 26 with purified gases reveals no evidence of poisoning by the unpurified gases. The duplicability of results with different charges of the same catalyst is also illustrated by the results of these tests.

Activity of CWS Hopcalite in the Presence of Steam.—The effect of using the very active CWS catalyst in the presence of steam remained to be determined. A glass catalyst chamber was used. The conditions of the test were 156°, 3:1 steam–gas mixture, 1000-space velocity, composition of influent gas: 0.57% carbon monoxide, 0.6% oxygen, 74.1% hydrogen and 24.7% nitrogen. The data are plotted in Fig. 6, Curve 42. The efficiency remained over 96% during the entire test of seventy-seven hours.

A test with MSA hopcalite utilizing the same gas and other conditions as in the above experiment with CWS catalyst with the exception of a higher temperature of 175° is also plotted in Fig. 6, Curve 44. The efficiency after twenty-nine hours was 92%. The superiority of the CWS catalyst is here again quite evident.

Discussion

The Function of Steam.—Although previous investigators found that it was impossible to oxidize carbon monoxide in excess of 0.5% in the presence of hydrogen with moderate amounts of water vapor, it has here been demonstrated that in the presence of a large excess of steam it is possible to burn as high as 1.6%. With proper steam concentrations and temperature adjustment higher concentrations of 2–4% of carbon monoxide undoubtedly can also be handled. The functions of the steam are two-fold: (1) to dissipate rapidly the heat of reaction, thus preventing local overheating of the catalyst granules and (2) to specifically inhibit reduction of the catalyst and oxidation of hydrogen. The use of steam should permit the use of large catalyst beds and catalyst chambers built of poor heat-conducting materials.

The Decline in Activity.—The gradual decline in activity at the low temperature of 156° in the presence of three volumes of steam per volume of gas with 0.5–1.3% of carbon monoxide (Curves 28 and 17, Fig. 2) in converted water gas may have been due either (1) to the presence of catalyst poisons or (2) to a change in structure of the catalyst with decrease of active catalytic surface, most probably incurred through loss of oxygen.

The first of these possibilities is rendered improbable by the poisoning experiments cited above. The probable correctness of the second hypothesis is shown by the fact that, as can be seen in Table II, the activities decrease with increased loss of oxygen.

Table II

Variation of Activity with Oxygen Lost from Catalyst

Run number	32	28	17	30
% of total avail. oxygen lost	20.3	27.8	33.5	64.5
Efficiency of CO oxidation, %	98	89	86	57

It should be noted that no appreciable portion of the total carbon monoxide consumed in the 379-hour test run could have been furnished by the available oxygen in the catalyst. Calculation shows that the total available oxygen of the catalyst is equivalent to only 4% of the total carbon monoxide consumed.

In conclusion the author wishes to express his deep appreciation to Doctors E. C. White and P. H. Emmett for their kindly suggestions in the course of this work.

Summary

1. A study of the activity of a commercial hopcalite as a preferential carbon monoxide oxidation catalyst has shown that from 97 to 99% of the influent carbon monoxide may be oxidized catalytically by free oxygen in the temperature range of 160–195° from converted water gas of the composition: 1.3% carbon monoxide, 1.5% oxygen, 28.0% carbon dioxide, 49.0% hydrogen and 20.2% nitrogen, in the presence of three volumes of steam per volume of gas at 1000 dry gas space velocity.

2. A further study indicated that the catalyst always suffered a loss in available oxygen both through thermal dissociation and reduction by hydrogen and carbon monoxide. A decrease in the catalytic activity resulted from this loss of available oxygen.

3. The importance of rapid and efficient dissipation of the heat of reaction has been shown by tests with slightly moist gases in which very inefficient oxidations were obtained with hopcalite in poorly conducting glass catalyst containers while continued high efficiencies were obtained with a copper catalyst chamber.

4. The steam has the two-fold function of dissipator of reaction heat and inhibitor of reduction of the catalyst by hydrogen. The use of catalyst chambers constructed of good heat-conducting material would be of no added benefit in the presence of an excess of steam.

5. A comparison of the activities of commercial hopcalite and a laboratory scale preparation by the Chemical Warfare Service showed the former to be the less active.

WASHINGTON, D. C.