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THE PREFERENTIAL CATALYTIC OXIDATION OF CARBON MONOXIDE IN THE PRESENCE OF HYDROGEN. I. THE ACTIVITY OF TWO WATER GAS CONVERSION CATALYSTS, OF COPPER OXIDE, OF MANGANESE DIOXIDE AND OF A MIXTURE OF THESE OXIDES

BY WARD E. KUENTZEL

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Present practice in the Haber–Bosch process utilizes water gas containing nitrogen, which is mixed with three to four volumes of steam and passed in contact with promoted iron oxide catalysts to yield a 3:1 hydrogen–nitrogen mixture suitable for the synthesis of ammonia after removal of the 1–2% of residual carbon monoxide and the 29–30% of carbon dioxide by scrubbing with cuprous ammonium carbonate or formate solution and water, respectively.

The practicability of a catalytic preferential oxidation process for the removal of carbon monoxide from hydrogen has long been recognized provided the concentration of the carbon monoxide does not exceed 0.5%.[1] Higher concentrations invariably led to reduction of the oxide catalysts by the hydrogen, due to difficulties in heat dissipation.

The necessity of rapid dissipation of the heat of reaction was stressed by Lamb, Scalione and Edgar,[1d] who pointed out the possibility of utilizing hopcalite[2] to oxidize preferentially 0.5% of carbon monoxide in hydrogen by adding air sufficient to give a slight excess of oxygen over that required for complete combustion of the carbon monoxide, saturating the mixture with water vapor at 40° and passing it over hopcalite contained in a small

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[1] (a) Harger and Terrey, Brit. Patent 127,609 (1917); U. S. Patent 1,366,176, Jan. 18, 1921; (b) Rideal and Taylor, British Patent 129,743 (1918); U. S. Patent 1,375,932, April 26, 1921; (c) Rideal, *J. Chem. Soc.*, **115**, 993 (1919); (d) Lamb, Scalione and Edgar, THIS JOURNAL, **44**, 738 (1922); (e) Frazer, Lamb and Merrill, U. S. Patent 1,418,246, May 30, 1922.

[2] Mixtures of finely divided manganese dioxide with various metallic oxides, such as copper, cobalt, silver, etc., have been termed hopcalite. (a) Lamb, Bray and Frazer, *J. Ind. Eng. Chem.*, **12**, 213 (1920); (b) Frazer and Scalione, U. S. Patent 1,345,323, June 29, 1920.

bore copper tube immersed in a liquid-bath. These investigators, as well as others,[3] also showed the importance of water vapor, which seemingly "poisons" the hopcalite toward the oxidation of both hydrogen and carbon monoxide, but more especially toward that of the former. Furthermore, in accord with the results of Lamb and Vail, the water vapor concentration of the gas phase may be greatly increased since their results indicated that the activity of hopcalite was dependent, not upon the water vapor concentration of the gas phase, but upon the actual water content of the catalyzer material and at the same time practically independent of the temperature. It should be possible, therefore, to utilize a large excess of steam in the gas phase at somewhat elevated temperatures in the preferential oxidation process over hopcalite. The use of three or four volumes of steam per volume of gas would then furnish a means of preventing local overheating of the catalyst granules by diluting the reaction mixture and of dissipating the heat of reaction by virtue of the heat capacity of the large volume of steam. The object of the present investigation was to determine experimentally whether under these conditions the higher concentrations of 1–2% or more of carbon monoxide could be efficiently oxidized.

Part I of this paper will refer to preliminary trials of a number of possible catalysts including two catalysts of the water gas conversion type, doubly promoted iron oxide and singly promoted cobalt oxide; two single oxides, copper oxide and manganese dioxide; and two hopcalite mixtures, a 2-component and a 5-component catalyst. Part II will include the more exhaustive tests with a commercially prepared hopcalite of the 2-component type.

Apparatus, Materials and Procedure

The essential features of the apparatus are shown in Fig. 1. By means of the three flowmeters, Q, R and S, mixtures of carbon dioxide and air with a carbon monoxide–hydrogen–nitrogen mixture could be continuously prepared. The gases passed through the indented tube U, which served as a mixing chamber. A continuous flow of steam, generated electrically in the boiler X, met the gas stream at the point G. The mixture of steam and gas could then be passed either through the catalyst tube Y, or through a by-pass depending upon the position of the two stopcocks H and I. The top of the steam generator and the tubes connecting this apparatus with the catalyst tube were heated to above 100° to prevent the condensation of steam. After passage through the condenser J, where the excess steam was condensed and removed through the trap K, the gases could be passed out either (1) to waste through the downward outlet cock L, or (2) partly through the capillary tube M to waste, and partly through the caustic potash scrubber N and soda-lime tube O, for complete removal of carbon dioxide, to the flowmeter P and thence to the carbon monoxide analyzer. The capillary tube M was so proportioned as to cause the proper flow of gas through the analyzer.

Catalysts.—The copper oxide, manganese dioxide and 5-component hopcalite were well preserved samples which had been prepared by the

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[3] Lamb and Vail, This Journal, **47**, 123 (1925).

Chemical Warfare Service investigators in 1918 during the development of hopcalite. The two water gas catalysts were prepared several years before this investigation by Mr. M. C. Molstad, at this Laboratory. The method of preparation, source and approximate composition of the catalysts are shown in Table I.

Table I

Catalysts

Catalyst	Method of preparation	Source	Approximate composition
No. 50	Pptn.	FNRL	94 parts Fe as Fe_2O_3, 5 parts Al as Al_2O_3, 1 part K as KOH
No. B-5	Pptn.	FNRL	95 parts Co as Co_2O_3, 5 parts Al as Al_2O_3
Copper oxide	Pptn.	CWS	100% CuO
Manganese dioxide	Electrolytic	CWS	100% MnO_2
2-Component hopcalite	Mixture of the CuO and MnO_2	. . .	60% MnO_2, 40% CuO
5-Component hopcalite	Pptn.	CWS	39% MnO_2, 30% CuO, 17% Co_2O_3, 8% Fe_2O_3, 6% Ag_2O

Temperature of the Catalyst.—In some of the tests the catalyst was maintained at a constant temperature by immersion of the catalyst tube in a well-stirred, manually controlled glycerine bath. The catalyst temperature as recorded in the data was taken as that of a mercury thermometer immersed in the bath liquid near the catalyst chamber. The temperature was constant to within 1 or 2°. In other tests a vapor-bath boiling at the prevailing atmospheric pressure was used. The temperature here was constant to within 0.5°. The temperature bath and control device shown in Fig. 1 were used in the work presented in Part II and have been described elsewhere.[4]

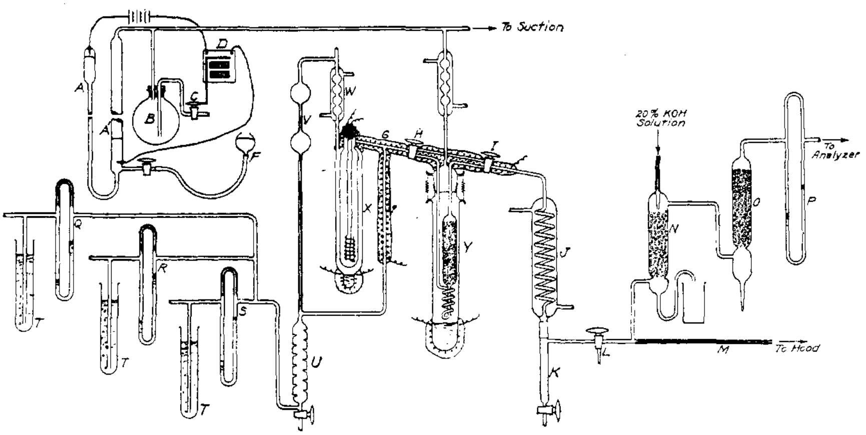

Fig. 1.—Apparatus.

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[4] Kuentzel, This Journal, 51, 3347 (1929).

Preparation of the Gases.—The carbon monoxide was made by the interaction of formic and sulfuric acids and freed from acid and carbon dioxide by bubbling through potassium hydroxide solution. A supply of gas mixture containing 1.6% of carbon monoxide was made by compressing a 3:1 hydrogen–nitrogen mixture[5] to 135 atmospheres' pressure in a cylinder previously filled with the required amount of carbon monoxide. Oxygen or air and carbon dioxide were added to this gas mixture before it entered the catalyst chamber. The air was taken from the laboratory service lines with no purification other than a cotton-wool dust trap. The carbon dioxide was the unpurified commercial product. Tests in which continued high carbon monoxide oxidation efficiencies were obtained proved the absence of catalyst poisons from these materials.

Procedure.—Each experiment consisted in passing a 3:1 by volume steam–gas mixture at 720 dry gas space velocity over one of the catalysts at a fixed temperature and analyzing the effluent gases. Samples were taken, after condensation of the excess steam at the downward outlet stopcock L (Fig. 1), directly into an improved Orsat type of gas analysis apparatus equipped with a long 100-cc. compensated buret and analyzed in the usual way.

In order to obtain more accurate data, the continuous carbon monoxide analyzer described by White[6] was used in the final experiments. When the continuous analyzer was operating, a constant flow of gas through this instrument provided analytical data as often as desired.

Experimental Results

Experiments with Water Gas Conversion Catalysts.—The results of experiments in which two precipitated water gas conversion catalysts, No. 50 and No. B-5, were tested as preferential oxidation catalysts indicated that these catalysts were of little or no value as selective oxidation agents. Practically identical results were obtained with gas containing no oxygen and with gas containing oxygen 100% in excess of that required for complete oxidation of the carbon monoxide present. In the case of the iron oxide catalyst, No. 50, a separate test in which the steam–gas ratio was varied from 0 to 8 resulted in the establishment of the water gas equilibrium regardless of oxygen content up to 100% in excess. When the steam content was decreased or cut off entirely in the case of the cobalt oxide catalyst, No. B-5, however, the carbon monoxide was converted to methane. These catalysts, therefore, are in the presence of an excess of steam predominantly water gas conversion catalysts. The addition of air to the final stages of a water gas converter operating at a lower temperature would have little or no effect upon the carbon monoxide content of the effluent gases.

Experiments with Copper Oxide.—The results of a few typical tests with a copper oxide catalyst are shown in Table II.

A preliminary test indicated that only about 50% of the influent carbon monoxide could be oxidized at temperatures up to 174°. From 185 to 225° the results were characterized by excessive reduction of the oxide

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[5] Prepared in a moderate scale plant similar to that described by Ernst, Reed and Edwards, *Ind. Eng. Chem.*, **17**, 775 (1925).

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

TABLE II

ACTIVITY OF COPPER OXIDE CATALYST

S. V. 720. Steam–gas ratio, 3:1. Influent gas compn.: CO_2, 27.5%; CO, 1.1%; O_2, 1.1%; CH_4, 0.3%; H_2, 47.6%; N_2, 22.6%

Cat. temp., °C.	Time[a]	Effluent gas				Percentage efficiency of oxidation of		Oxygen removed from cat. mg./min.
		CO, %	O_2, %	H_2, %	N_2, %	CO	H_2	
185	8 min.	0.2	0.3	46.2	24.2	82.2	9.3	3.2
185	23 min.	.1	.3	47.1	23.5	95.4	4.9	1.6
185	5.75 hrs.	.3	.3	47.9	23.4	72.4	2.7	0.4
200	3.25 hrs.	.3	.3	47.4	23.4	72.4	3.8	.9
200	5.5 hrs.	.3	.2	47.3	23.4	72.4	4.1	.9
216	5 min.	.2	.3	45.9	23.8	82.0	8.7	3.0
216	2.5 hrs.	.3	.4	46.8	23.5	72.6	5.7	1.8
225	45 min.	.3	.2	47.1	23.6	72.7	5.5	1.3
185	1.25 hrs.	.7	.2	47.3	23.3	34.5	3.6	0.2

[a] The accumulated time of testing at each temperature is indicated in this column

catalyst, as shown by the last column of Table II, in which the mg. of oxygen removed from the catalyst have been tabulated. This was true especially during the first few minutes of the test at each succeeding higher temperature. High carbon monoxide and hydrogen oxidation efficiencies were usually obtained during this initial period of excessive reduction. When the amount of reduction decreased, the efficiency of carbon monoxide and hydrogen oxidation also diminished. This behavior indicated that during the first part of the test at a given temperature the catalyst was so active that both carbon monoxide and hydrogen were oxidized, not only catalytically by means of the free oxygen but also chemically at the expense of the oxygen content of the catalyzer itself. This loss of oxygen on the part of the catalyst resulted in lower activity toward both carbon monoxide and hydrogen oxidation, but more especially toward the oxidation of the latter.

Operation at the lower temperature of 185° after high temperature treatment at 225° resulted in decreased efficiencies. This was probably due to the excessive reduction occurring at the higher temperatures. Copper oxide, therefore, although catalytically active in the oxidation of carbon monoxide is partially reduced by carbon monoxide and hydrogen to such an extent that its activity is markedly impaired. Its use as a preferential oxidation catalyst for the removal of over 1% of carbon monoxide from hydrogen in the presence of carbon dioxide and a large excess of steam is not recommended.

Experiments with Manganese Dioxide.—The results obtained with a sample of electrolytic manganese dioxide are shown in Table III.

With this particular sample the carbon monoxide oxidation efficiency was markedly low at 167° and reached a value of only 91% at the high temperature of 250°. Even then it fell off to 77% after only a short time of testing. At these temperatures the catalyst was appreciably reduced, as shown by the loss of oxygen in the last column of Table III. This particular catalyst is therefore of little value as a selective oxidation agent under the conditions of steam and gas compositions here encountered.

TABLE III

ACTIVITY OF MANGANESE DIOXIDE CATALYST

S. V. 720. Steam–gas ratio, 3:1. Influent gas compn.: CO_2, 27.5%; CO, 1.1%; O_2, 1.1%; CH_4, 0.3%; H_2, 47.6%; N_2, 22.6%

Cat. temp., °C.	Time[a]	Effluent gas				Efficiency of oxidation of		Oxygen removed from cat., mg./min.
		CO, %	O_2, %	H_2, %	N_2, %	CO	H_2	
167	5 min.	0.6	1.1	47.7	23.6	45.3	4.1	2.1
190	1.5 hrs.	.3	0.9	47.2	23.4	72.4	4.1	1.9
200	15 min.	.3	.8	46.9	23.3	72.5	4.3	1.9
215	3.75 hrs.	.3	.5	47.2	23.4	72.5	4.5	1.5
221	25 min.	.2	.3	47.6	23.5	81.7	3.9	0.9
230	35 min.	.3	.2	47.7	23.5	77.1	3.5	0.7
250	10 min.	.1	.2	46.6	24.2	91.1	8.6	2.8
250	1.25 hrs.	.3	.2	47.3	23.7	77.3	5.5	1.5
200	30 min.	.6	.7	47.9	23.3	49.2	2.4	0.8
220	1.75 hrs.	.3	.5	47.8	23.3	72.3	2.6	0.7
230	35 min.	.3	.3	47.8	23.4	77.8	5.0	1.3

[a] The accumulated time of testing at each temperature is indicated in this column.

Experiments with a 2-Component Hopcalite.—A 2-component hopcalite catalyst was prepared by weighing out unused portions of the two previously tested oxides in the proportions of 60% of manganese dioxide to 40% of copper oxide and mixing them in a finely ground wet paste. Most of the water was then filtered off, the mixture kneaded and finally pressed under hydraulic pressure of about 2000 pounds per square inch. The resulting product was dried at 50°, crushed and screened to 6–10 mesh and then finally dried at 190°. The results of tests on this material are shown in Table IV.

TABLE IV

EFFECT OF MIXING MANGANESE DIOXIDE AND COPPER OXIDE IN THE PROPORTION OF 60:40 BY WEIGHT

S.V. 720. Steam–gas ratio, 3:1. Influent gas compn.: CO_2, 27.5%; CO, 1.1%; O_2, 1.1%; CH_4, 0.3%; H_2, 47.6%; N_2, 22.6%

Cat. temp., °C.	Time[a]	Effluent gas				Efficiency of oxidation of		Oxygen removed from cat., mg./min.
		CO, %	O_2, %	H_2, %	N_2, %	CO	H_2	
150	5 min.	0.1	1.3	46.3	23.9	91.0	8.2	4.4
150	9.5 hrs.	.2	0.7	48.2	23.0	81.3	0.7	0.3
163	2.5 hrs.	.1	.6	47.9	23.0	95.3	1.2	.5
150	3 hrs.	.2	.6	48.5	23.3	81.5	1.1	.4
163	2 hrs.	.1	.5	48.3	23.2	90.7	1.1	.3

[a] The accumulated time of testing at each temperature is indicated in this column.

The effect of simply mixing the two constituent catalysts was very marked. Over 90% of the influent carbon monoxide was oxidized at a temperature of only 150° during the first hour of operation, and after nine and one-half hours over 81% efficiency was still obtained. At 163° an efficiency of 95% was obtained for two and one-half hours. Operation at 150° after this gave over 81% oxidation. Such efficiencies were obtained only when the temperature ranged around 185° in the case of copper oxide alone, and over 200° in the case of manganese dioxide alone. This behavior of oxide mixtures is in accord with the observations of Almquist and Bray[7] and Bray and Doss[8] who studied the so-called "mixture effect" with these oxides. The reduction of the catalyst was quite appreciable during the initial stages of the test at 150°, but became negligible with continued operation.

Effect of High Temperature and Continued Usage upon the Activity of 2-Component Hopcalite.—The same charge of hopcalite already tested at 150 and 163° was used in determining the effect of higher temperatures. The results are given in Table V.

TABLE V

EFFECT OF TEMPERATURE ON ACTIVITY OF HOPCALITE II

S.V. 720. Steam–gas ratio, 3:1. Influent gas compn.: CO_2, 27.5%; O_2, 1.1%; CO, 1.1%; H_2, 47.5%; CH_4, 0.3%; N_2, 22.5%

Temp., °C.	Time,[a] hours	Effluent CO, %	Efficiency of oxidation of CO	Temp., °C.	Time of operation at temp. noted, hours	Effluent CO, %	Efficiency of oxidation of CO
165	3	0.078	95.0	175	1.75	0.096	93.9
175	1.5	.037	97.6	185	2	..	..
165	3	.071	95.5	190	0.5	.069	95.6
175	0.5	.051	96.8	185	0.5	.098	93.8
175	2	.050	96.8	175	0.5	.138	91.2
190	1	.021	98.7	220	1.25	.149	90.5
190	2.75	.023	98.6	220	2	.157	90.0
190	4	.050	96.8	175	0.5	.406	73.8
165	0.5	.17	89.2				

[a] The accumulated time of testing at each temperature is indicated in this column.

A study of these results, obtained with the continuous analyzer, shows that in the range 165 to 190° efficiencies of over 95% may readily be attained, but the high temperature of 220° had a marked deteriorating effect upon the activity of the catalyst. The oxides composing the catalyst were no doubt considerably reduced by this high temperature treatment.

A test was next made in which a fresh charge was maintained constantly at 175° during the passage of gas–steam mixture over it. The test was intermittent in that the catalyst was allowed to cool down to room tem-

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[7] Almquist and Bray, THIS JOURNAL, **45**, 2305 (1923).

[8] Bray and Doss, *ibid.*, **48**, 2060 (1926).

perature overnight, but otherwise conditions were constant throughout the entire run of thirty-seven hours. An initial efficiency of nearly 99% decreased during the first fourteen hours to 96% and remained constant at this value thereafter.

Experiments with a 5-Component Hopcalite.—A few preliminary experiments were made at the beginning of this investigation with a 5-component hopcalite. At the temperature of 218° the catalyst charge was completely reduced with incandescence when the steam–gas mixture containing 1.6% carbon monoxide in 3:1 hydrogen–nitrogen mixture to which 1.6% oxygen had been added was passed over it at the high space velocity of 6000. Further tests at 720 space velocity upon fresh charges of this catalyst with 28% carbon dioxide added to the influent gases yielded practically complete oxidation of carbon monoxide initially at temperatures ranging from 162 to 200°, but only about 50% efficiency upon continued testing. No attempt was made to determine the cause or causes of its failure. It is of interest, however, to indicate that under conditions at which the 2-component catalyst gave excellent results, the 5-component catalyst was decidedly inferior.

The author wishes to express his deep appreciation to Dr. J. A. Almquist, at whose suggestion this problem was undertaken, for his kind advice and encouragement.

Summary

A study has been made of the preferential oxidation of carbon monoxide by oxygen in the presence of hydrogen and carbon dioxide and a large excess of steam in contact with the catalysts (a) promoted iron oxide, (b) promoted cobalt oxide, (c) copper oxide, (d) manganese dioxide, (e) a 5-component hopcalite and (f) a 2-component hopcalite.

Only the last named catalyst showed any promise as a preferential oxidation agent under these conditions. An efficiency of over 96% was obtained with it for a period of thirty-seven hours. The promoted iron oxide and cobalt oxide catalysts were predominantly water gas conversion catalysts and the presence of oxygen in the gas mixture apparently had no effect upon the final result, which was governed entirely by the water gas reaction, $CO + H_2O \rightleftharpoons CO_2 + H_2$. The copper oxide, the manganese dioxide and the 5-component hopcalite, although catalytically active in the preferential oxidation of carbon monoxide, suffered serious reduction with consequent loss in activity.

WASHINGTON, D. C.