Methanol from Hydrogen and Carbon Monoxide

III—Further Work on Dimethyl Ether[1]

Ralph L. Brown[2] and A. E. Galloway

PITTSBURGH EXPERIMENT STATION, U. S. BUREAU OF MINES, PITTSBURGH, PA.

A copper–chromium oxide catalyst in contact with a 2:1 hydrogen–carbon monoxide mixture has been found to yield, in addition to methanol, large quantities of dimethyl ether. The catalyst contained copper and chromium in the mol ratio 3:1 and was precipitated from the nitrates with sodium hydroxide. The conversions of carbon monoxide at 180 atmospheres, expressed in mol per cent, to methanol and to methyl ether were, respectively: at 265° C., 7 and 4; at 285° C., 14 and 6; at 305° C., 24 and 22; at 340° C., 17 and 20; and at 355° C., 11.5 and 13.5. The region of maximal conversion was 315° to 320° C., and the conversions were of the order of 30 mol per cent, that to ether being the larger.

A RECENT report (*4*) on the conversion of hydrogen and carbon monoxide into methanol by the use of normal zinc chromate as catalyst showed methyl ether to be a by-product of the reaction. It was not possible to say definitely that the reaction

$$2CH_3OH = CH_3OCH_3 + HOH \qquad (1)$$

resulted from the activity of the reduced normal zinc chromate itself, for prepared by the method of Gröger (*6*) that catalyst could have contained small amounts of free chromium oxide, which is known to be a strongly dehydrating catalyst. Also, free zinc oxide might have existed in slight amount, and this has been found by Adkins and Perkins (*1*) to induce the formation of ether from methanol to a slight degree. Continuing their interest in the conversion of carbon monoxide and hydrogen into ether the present writers selected a copper–chromium oxide mixture for their next study. It was considered that the chromium oxide of the reduced catalyst might, in addition to serving as a promoter, function effectively as a dehydrating catalyst toward the methanol formed from carbon monoxide and hydrogen. The extensive studies of Audibert and Raineau (*2*), in which many binary and ternary mixtures were employed as methanol catalysts, had by this time become available. They carried no information as to the formation of products other than methanol in any case. The simple binary mixture of copper and chromium oxide was not mentioned. The results obtained with this catalyst, therefore, form the basis of the present paper.

Apparatus and Gas

The apparatus and the preparation of the gas employed has been described in an earlier paper (*3*). The gas was a 2:1 mixture of hydrogen and carbon monoxide, containing an average of 11 per cent of inerts (mainly nitrogen containing about 10 per cent carbon dioxide and traces of hydrocarbons) in the initial and make-up gas. The inerts in the residual gas, and hence the average reactant pressure, varied in the several experiments, notwithstanding the fact that the total gas pressure in the system was maintained at 200 atmospheres at all times. These variations have been recorded and are taken into account in the tabulated results given later.

Catalyst and Preparation

The catalyst was a mixture of reduced copper and chromium oxides, in which the atomic ratio of Cu to Cr was 3 to 1. Two hundred and fifty cubic centimeters (177 grams) of this catalyst were employed. Its method of preparation follows:

A boiling solution of copper and chromium nitrates in the atomic ratio of 3 Cu to 1 Cr was added slowly and with efficient stirring to a boiling solution of sodium hydroxide containing 6 per cent in excess of that calculated to precipitate the metals. The precipitate was washed by vigorous mechanical stirring in large volumes of hot water. Eleven successive washings were given the precipitate. The wash water from the several final washings persisted in giving a very feeble test with phenolphthalein for hydroxyl ions. The moist precipitate was extruded to yield threads (2 mm. diameter), which were air-dried first at room temperature, broken into uniform lengths, and dried at 105° C. The precipitate was reduced at 200–240° C. over a period of about 15 hours with a slow stream of a mixture of 19 parts of carbon monoxide and 1 part hydrogen. The proportion of hydrogen was increased as the reduction neared completion and the tendency for rapid temperature increase became small. The mixed oxides lost on reduction 21 per cent of their weight.

Procedure

The experimental procedure consisted primarily in measuring, under a constantly maintained gas pressure of 200 atmospheres and at selected temperatures, the hourly production of liquid products and determining their composition and the change in composition of the gas during the experiment. The methyl ether, by reason of its widely different boiling point, was easily separated. This crude ether was subjected to the examination outlined in the previous paper, and the crude methanol was fractionally distilled as shown in Figure 1. From the data collected and the known characteristics of the apparatus, the temperature, and other readings, the results have been reduced to a comparable basis.

Results and Discussion

Runs were made at five reaction temperatures between 265° and 355° C. The total gas pressure was maintained at 200 atmospheres and a space velocity of 3000 was employed in each run. The results of these experiments have been calculated and summarized in Table I.

The average reactant pressures (column 3) are the products of the total gas pressure, 200 atmospheres, and the average percentage of $CO + H_2$ in the gas during that particular run. In columns referring to methanol pure CH_3OH is meant. The values of column 13 were approximated from the values of column 9 by multiplying the latter by the ratio of the

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[2] Present address, Atmospheric Nitrogen Corp., Syracuse, N. Y.

Table I—Methanol and Ether Production with a Copper-Chromium Oxide Catalyst

Run	Av. Reaction Temperature	Av. Reactant Pressure	CO Content of Gas: Initial	CO Content of Gas: Residual	CO Content of Gas: Av.	Methanol Produced		Conversion CO to CH₃OH	Methyl Ether		Conversion CO to Ether	Approx. Conversion of CO at 180 Atm. Reactant Pressure: To CH₃OH	To Ether
	° C.	Atm.	%	%	Mols	Mols per hour	Mols per pass	Mol % per pass	Mols per hour	Mols per pass	Mol % per pass[a]	Mol % per pass	
A	265.5	179	30.0	26.3	4.50	0.76	0.322	7.15	0.16+	0.068	3.1	7.2	3.1
B	285.5	166	30.1	25.1	4.40	1.32	0.563	12.75	0.28	0.119	5.4	14.3	6.1
C	305+	158	30.3	20.0	4.00	1.85	0.790	19.8	0.87	0.370	18.5	23.8	22.3
D	337	159	29.9	18.0	3.79	1.37	0.584	15.4	0.87	0.370	18.5	18.4−	22.0
E	353	153	29.9	16.1	3.56	0.80	0.341	9.6	0.48	0.205	11.4+	12.1	14.5

[a] Two mols of CO are required for each mol of ether.

theoretical conversion for 180 atmospheres to that for the reactant pressure of that particular run. This puts them on a uniform basis and permits the representation of the conversions given in Figure 2.

The values of column 14 were calculated from those of column 12 on the basis of the assumption that the ratio of methanol to dimethyl ether would be the same at 180 atmospheres as that found at the reactant pressures of the several runs. This seems to be a reasonable assumption in view of the absence of volume change in Reaction 1 and the constancy of temperature and time of contact that would exist in runs at two such pressures.

As stated above, the ether was examined as given in the previous paper. The expected properties for the ether were found; for example, the molecular weights of two samples were determined as 46.139 and 46.162, which is close to the theoretical value of 46.046.

The source of the ether is undoubtedly largely by Reaction 1. There is, of course, the thermodynamic possibility of the formation of methyl formate, as, for example, by

$$CH_3OH + CO = H.COOCH_3 \qquad (2)$$

or $$2CH_3OH = 2H_2 + 2HCHO = HCOOCH_3 + H_2 \qquad (3)$$

and its subsequent decomposition according to the reaction

$$2HCOOCH_3 = CO_2 + CH_3OCH_3 + H_2CO \text{ (or } H_2 + CO) \qquad (4)$$

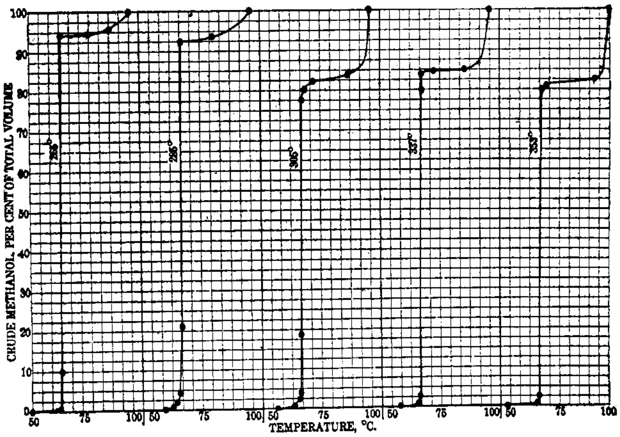

Figure 1—Methanol Distillation Curves; Catalyst, Copper-Chromium Oxide

In view of the small quantity of carbon dioxide found and the practically equivalent quantity of hydrocarbons—methane containing a little ethane—together with the amounts of water found in the crude methanol, not more than a slight amount of the ether obtained could have been produced by any other reaction than by Reaction 1.

In Figure 2 the conversion of carbon monoxide to methanol and ether as arrived at in columns 13 and 14 of Table I is plotted in mol per cent against temperature. Obviously, in view of the form these curves take, more points between 300° and 340° C. would be of advantage in drawing more exactly the maximal portions of the two curves. The formation of methanol begins under 260° C. and rises in a typical way for an activity curve up to about 318–320° C. and falls away rather rapidly. Since these data were taken (summer of 1928) the paper of Frolich (*5*) and his co-workers has appeared in which it is reported that the presence of traces of sodium hydroxide or sodium nitrate in copper catalysts promotes them, and also causes them to lose their activity above the melting points of those materials (318° and 316° C., respectively). The methanol curve in Figure 2 shows such a break and presumably it is to be so explained, since it is evident that the production of the methyl ether likewise goes through a similar maximum. In the present writers' experiments, as shown also in Figure 2, the ether formation begins below the lowest temperature (265° C.) and increases moderately with temperature at first and then rapidly between about 290° and 310° C., where it enters a maximal region and then falls away similarly to the decrease of methanol formation, upon which it is obviously dependent.

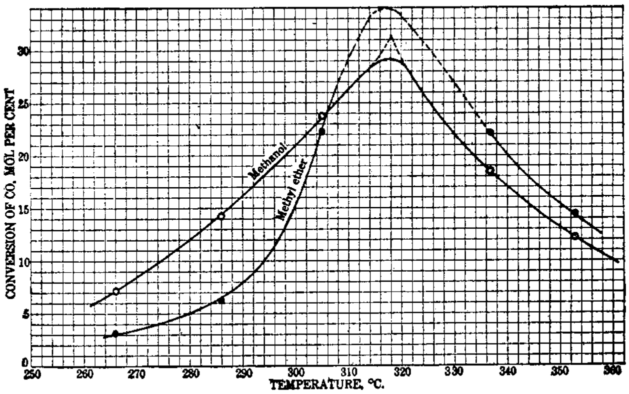

Figure 2—Conversion of Carbon Monoxide to Methanol and Methyl Ether in Mol Per Cent

($CO:H_2 = 1:2$; Reactant pressure, 180 atmospheres)

Figure 1 shows the fractionation curves of the crude methanol obtained from the primary distillation at the time of the separation of the methyl ether. The methanol as determined by fractionation was closely checked by the amounts indicated by the specific gravity determinations. The quantities of water found were slightly smaller than the theoretical values calculated from the ether obtained. The differences were due to the water left in the pieces of apparatus during the distillation and fractionation.

Literature Cited

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