The Synthesis of Oxygenated Organic Compounds from Methanol and Carbon Monoxide-Hydrogen Mixtures in the Presence of a Mixture of Cobalt Acetate and an Iodide Used as the Catalyst

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The treatment of methanol with carbon monoxide-hydrogen mixtures under the oxo reaction conditions results in the formation of ethanol. This is well known as the homologation of methanol. When cobaltcarbonyl or cobalt salts were used as catalysts in this reaction, small portions of the methanol were converted into ethanol.1) However, Berty found that the yields of ethanol and other oxygenated compounds (acetaldehyde, methyl or ethyl acetate) were increased by adding a small amount of iodine as an additive for the cobalt acetate catalyst.2)

In a preceding paper,3) it was shown that, in a bathwise experimental run using a mixture of cobalt acetate and an iodide (LiI, NaI, KI and CaI_2) as the catalyst, acetic acid was synthesized in a 90% yield from methanol and carbon monoxide in a liquid phase under pressures from 300 to 500 kg./cm^2 and at temperatures from 210 to 240°C. However, when this reaction was carried out in a flow reactor under the same conditions except that the carbon monoxide contained 10% hydrogen, it was found that the amount of hydrogen was strikingly decreased, that this reaction was invariably accompanied by the formation of acetaldehyde and ethanol, and that the extent of methanol conversion into free acetic acid was less than 60%.4) This led us to investigate the homologate of methanol with the same catalyst.

For acetic acid synthesis with a mixture of cobalt acetate and an iodide at the catalyst, it is necessary to add a considerable amount of water,3) while for the formation of ethanol and other oxygenated compounds from methanol and carbon monoxide-hydrogen mixtures with the same catalyst, it in unnecessary to add water to methanol. This is very significant.

From a comparison of the effect of an iodide with that of iodine on the extent of methanol conversion into C_2-oxygenated compounds, we found that an iodide serves as an additive for increasing the yield of ethanol and other oxygenated compounds.

The present work was undertaken in order to study in detail the influence of an iodide

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1) K. H. Ziesecke, *Brenn. Chem.*, **33**, 385 (1952).

2) J. Berty and L. Marko, *Chem. Tech.* (*Berlin*), **8**, 260 (1956).

3) T. Mizoroki, M. Nakayama, Y. Andō and M. Furumi, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **65**, 1049, 1054 (1962).

4) T. Mizoroki, M. Nakayama, Y. Andō and M. Furumi, *Repts. Govt. Chem. Ind. Research Inst. Tokyo* (*Tokyo Kōgyo Shikensho Hōkoku*), **58**, 310 (1963).

as an additive for a cobalt acetate catalyst on the reaction of methanol with carbon monoxide-hydrogen mixtures.

Experimental

Apparatus for Carrying out the Reaction.—In all experiments, the reaction was carried out in a titanium-manganese alloy autoclave (185 or 225 ml.). The complete apparatus used was essentially the same as that described in the preceding paper.[3)]

When a solution of cobalt acetate and an iodide in methanol is heated without the addition of acetic acid, a precipitate is formed. However, in the presence of acetic acid*[1] no precipitate is formed by heating, though the color of the solution changes from pale pink to blue or green. (These observations have been made by heating the solutions in a sealed, thick-walled glass tube.) In the latter case, the reaction between methanol and carbon monoxide-hydrogen takes place without an induction period being exhibited.

The experiments were carried out in the following way. The reaction vessel was heated in a shaking-type electric furnace (60 r. p. m.) after a mixture of methanol and acetic acid containing cobalt acetate and an iodide had been charged. After this solution had been maintained at a reaction temperature (between 160 and 240°C) for about one hour, the synthesis gases were introduced and continuously supplied from the pressure accumulator to keep the pressure (between 250 and 500 kg./cm^2) constant during the reaction. After a predetermined time of reaction, the heating and the addition of gases were stopped, the reaction vessel was allowed to cool to room temperature, and the gases and the liquid product were discharged.

Materials.—The methanol, acetic acid, cobalt acetate and iodides used were obtained from commercial sources. The synthesis gases were mixtures*[2] of hydrogen from water electrolysis and carbon monoxide from formic acid decomposition, materials which had been compressed into the pressure accumulator.

Analytical Procedure. — The main components in the liquid product were determined by the gas-chromatographic procedure. A 2.5 meter glass column with carbo-wax 400 on a Johns-Manville C-22 fire brick was used at the temperature of 80°C with a hydrogen carrier at the gas flow rate of 70 ml. per minute. In this way, dimethyl ether, acetaldehyde, methyl acetate, ethyl acetate, methanol, ethanol, crotonaldehyde and water were quantitatively determined using pyridine as an internal standard. Since formic acid, propionic acid and their esters could not be detected in the liquid product, the amount of free acetic acid was determined by titration with an aqueous potassium hydroxide solution. The amount of each of these components as determined by this method was approximately in agreement with that obtained from the fractional distillation (Podbielniak 3500, Heli-Grid column).

Cobaltous ions and iodide ions were determined by EDTA and Volhard's methods respectively in the usual manner, but cobalt-carbonyl complex compounds in the liquid product were too unstable to be investigated.

Carbon monoxide, carbon dioxide, methane and hydrogen in gases were determined by absorption and combustion methods in the usual manner.

Results

A Comparison with Iodine. — In order to compare the effect on the extent of methanol conversion of an iodide as an additive for a cobalt acetate catalyst with the effect of iodine, the reaction was carried out by the use of sodium iodide and iodine under the same conditions. The volume of synthesis gases supplied during the reaction for maintaining the reaction pressure constant is plotted against the time in Fig. 1, while the conversion values of methanol into C$_2$-oxygenated compounds are presented in Table I.

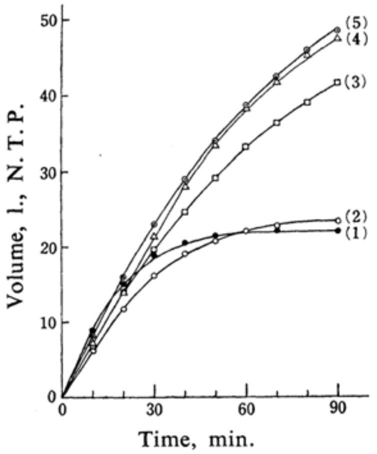

Fig. 1. The effect of iodine or sodium iodide as an additive for a cobalt acetate catalyst when a mixture of MeOH (1.62 mol.), AcOH (0.18 mol.) and $Co(AcO)_2 \cdot 4H_2O$ (9.0 mmol.) is treated for 90 min. under 300 kg./cm^2 and at 200°C. The added amounts of additives are (1) I_2 3.0 mmol., (2) I_2 6.0 mmol., (3) NaI 6.0 mmol., (4) NaI 12.0 mmol. and (5) NaI 18.0 mmol.

When iodine is used as an additive, the gas volume supplied becomes nearly constant after 30∼40 min., the reaction ceases, and, as is shown in Table I, a considerable amount of dimethyl ether is formed. However, when sodium iodide is used instead of iodine, the reaction proceeds smoothly, the extent of methanol conversion to C$_2$-oxygenated compounds is about twice as much as that obtained with the use of iodine, and the amount of

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*[1] The amount of acetic acid in methanol is 5.0 to 10.0 mol. %.

*[2] The amounts of CH$_4$, CO$_2$ and N$_2$ were less than 1.0 vol. %.

TABLE I. MASS BALANCE OF METHANOL

No in Fig. 1	Total AcOH	Total EtOH	Total aldehyde	Residual MeOH	CH_4	CH_3OCH_3	Others	MeOH conversion into C_2
1	11.9	4.3	13.6	40.6	5.5	13.1	10.5	30.3
2	10.0	4.4	11.1	38.2	5.0	21.3	11.0	25.1
3	15.7	25.6	4.8	42.2	5.9	1.9	3.6	46.4
4	16.5	25.3	6.3	37.7	5.6	1.0	7.6	48.1
5	14.6	23.4	8.6	38.4	5.6	1.5	6.7	47.2

Total AcOH = free acetic acid + acetic esters
Total EtOH = ethanol + ethyl acetate
Total aldehyde = acetaldehyde + crotonaldehyde

ethanol in the product is relatively large. From these results, the addition of iodine as an additive for a cobalt acetate catalyst in this reaction is undoubtedly disadvantageous.

The infrared spectra of the high temperature fractions obtained from the fractional distillation of the product showed the presence of *n*-butanol, but its amount was too small to be quantitatively determined. A trace of dimethylacetal, also, was detected.

Lithium iodide, sodium iodide, potassium iodide and calcium iodide were used as additives, there was little difference between their effects on the reaction rates and the extent of methanol conversion into C_2-oxygenated compounds. The results obtained with the use of lithium iodide or sodium iodide will be described later.

The Effect of Pressure, the Composition of Synthesis Gases and Temperature.—The effect of reaction pressure on the extent of methanol conversion was examined by using the synthesis gases of 1-CO : 1-H_2. The results are presented in Fig. 2, in which the conversion values of methanol into aldehyde (acetaldehyde + crotonaldehyde), acetic acid[*3] (acetic esters + free acetic acid) and ethanol (ethanol + ethyl acetate) are plotted against the pressure; the volume % of carbon monoxide and hydrogen in the discharged gases after reaction is plotted in the upper part.

The increase in pressure results in an increase in the extent of methanol conversion, but it has little more effect on the ratios of the yield of ethanol, acetaldehyde or acetic acid than that of the other. The amount of hydrogen in the discharged gases is much less than that in synthesis gases in every case. The loss of methanol by the formation of methane and dimethyl ether is less than 5%.

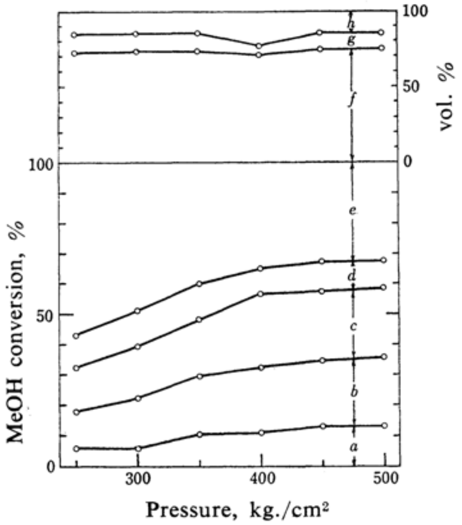

Fig. 2. The effect of pressure when a mixture of MeOH (1.425 mol.), AcOH (0.075 mol.), $Co(AcO)_2 \cdot 4H_2O$ (6.0 mmol.) and LiI (9.0 mmol.) is treated for 90 min. at 200°C.
a : total aldehyde, b : total acetic acid, c : total ethanol, d : methane + dimethyl ether + others, e : residual methanol, f : carbon monoxide, g : hydrogen and h : methane + carbon dioxide + nitrogen.

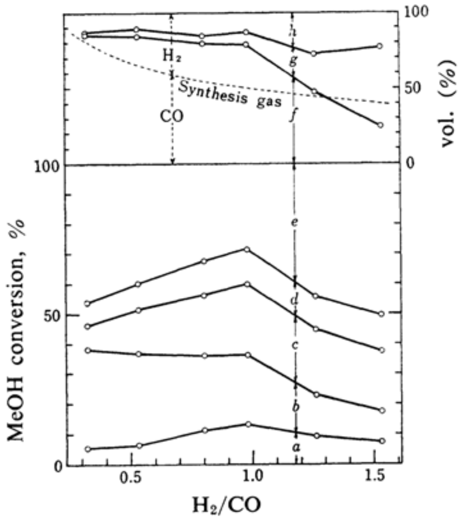

Fig. 3. The effect of the composition of synthesis gases when a mixture of MeOH (1.425 mol.), AcOH (0.075 mol.), $Co(AcO)_2 \cdot 4H_2O$ (6.0 mmol.) and LiI (9.0 mmol.) is treated for 90 min. under 400 kg./cm² and at 200°C.

[*3] The amount of acetic acid previously charged in the autoclave was excluded and acetic acid was confirmed not to be hydrogenated under these conditions.

TABLE II. CONVERSION VALUES OF METHANOL OBTAINED AT SUITABLE CATALYST CONCENTRATIONS

The amounts, respectively, of MeOH and AcOH are 1.35 and 0.15 mol., the temperature 200°C and the reaction time 90 min.

Synthesis gases CO : H_2	Catalyst Concn., mol. ratio $Co(AcO)_2\cdot4H_2O$: NaI	Press. kg./cm²	Total AcOH %	Total EtOH %	Total aldehyde %	CH_4 and CH_3OCH_3 %	Others %	MeOH conversion into C_2 %
1 : 1	0.1 : 2.0	300	16.5	3.0	20.6	3.7	6.9	40.1
1 : 1	0.1 : 2.0	400	20.0	5.3	28.3	3.8	6.3	54.5
1 : 1	0.1 : 2.0	500	21.9	10.1	24.9	3.5	11.4	55.9
1 : 1.26	0.27 : 0.73	400	16.8	20.6	13.3	2.8	8.0	50.8
1 : 1.26	0.27 : 0.73	500	17.8	23.8	14.3	3.3	8.8	55.9
1 : 1.57	0.45 : 0.55	350	10.6	22.3	8.8	3.5	10.3	41.7
1 : 1.57	0.45 : 0.55	400	11.1	26.3	10.1	4.5	8.6	47.7
1 : 1.57	0.45 : 0.55	450	10.0	28.2	14.3	5.5	8.7	52.5

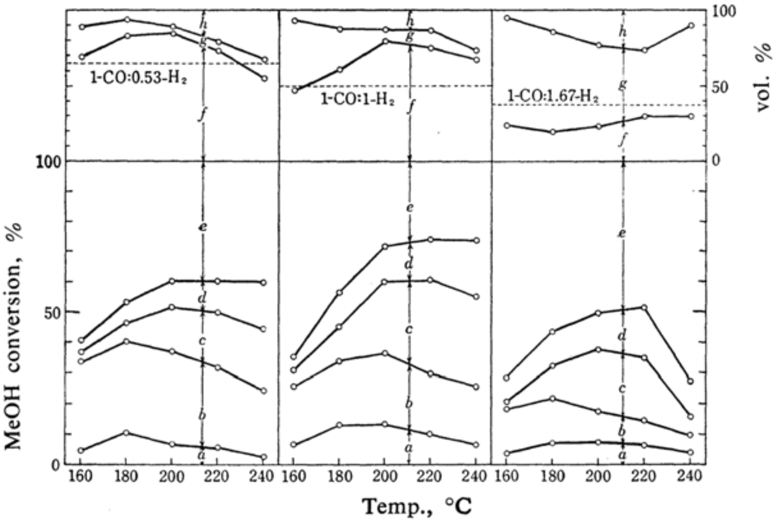

Fig. 4. The effect of temperature when a mixture of MeOH (1.425 mol.), AcOH (0.075 mol.), $Co(AcO)_2\cdot4H_2O$ (6.0 mmol.) and LiI (9.0 mmol.) is treated for 90 min. under 400 kg./cm².

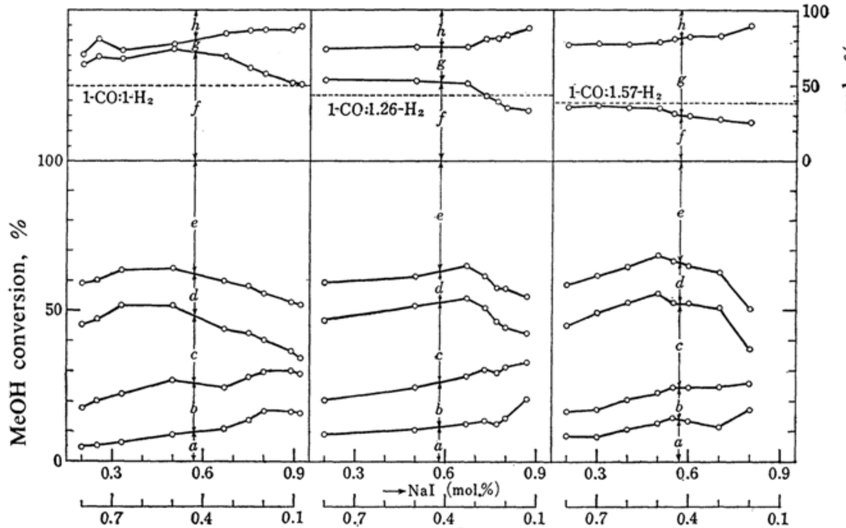

Fig. 5. Effect of the catalyst concentration at 200°C and the reaction time 90 min.

The effect of the composition of synthesis gases is represented in Fig. 3. Since the reaction was carried out at a constant pressure of 400 kg./cm^2, independently of the composition of synthesis gases, the partial pressures of hydrogen and carbon monoxide were different from each other. The evident formation of ethanol is expected to be favored in the presence of a large amount of hydrogen in this reaction, while the yield of ethanol does not increase as much as expected.

The effect of the temperature was examined at the pressure of 400 kg./cm^2 in the use of the synthesis gases of 1-CO : 0.53-H_2, 1-CO : 1-H_2 and 1-C : 1.67-H_2. The experimental results made at temperatures from 160 to 240°C are summarized in Fig. 4. At an elevated temperature, the amount of hydrogen reacting with methanol is more than that of carbon monoxide and the yield of ethanol consequently increases, although at a low temperature, the yield of acetaldehyde is relatively large. However, the increase in temperature beyond 220°C must be avoided, because then the amounts of methane, C_3- and higher oxygenated compounds increase and the methanol conversion decreases. A similar behavior with regard to temperature is observed in the synthesis of aldehydes and alcohols by oxo reactions.[5)]

The Influence of the Catalyst Concentration. —For the purpose of obtaining more detailed information on the effect of the catalyst concentration, the variation of the values of the conversion of methanol into C_2-oxygenated compounds was examined by the use of a mixture of methanol (1.62 mol.) and acetic acid (0.18 mol.) over the range of the ratios of cobalt acetate to sodium iodide from 0.1 to 4.0, in which the sum of their concentrations was kept constant (1.0 mol. %). The reaction pressures were 300, 400 and 450 kg./cm^2 with the synthesis gases of 1-CO : 1-H_2, 1-CO : 1.26-H_2 and 1-CO : 1.57-H_2 respectively. The results are summarized in Fig. 5. The yield of ethanol evidently increases with an increase in the ratio of cobalt acetate to sodium iodide, while the yield of acetaldehyde increases with a decrease in it. It is very interesting to note that the composition of the discharged gases becomes approximately equal to that of synthesis gases at a certain ratio of an iodide to cobalt acetate. Such ratios of I^-/Co^{2+} were more than 10, 3 to 4 and 1 to 1.5 with the H_2/CO ratios of synthesis gases of 1.0, 1.3 and 1.6 respectively.

The experimental results made at the suitable catalyst concentration for each synthesis gas considered from the results of Fig. 5 are represented in Table II. They show that the extent of methanol conversion into ethanol and acetaldehyde considerably depends on the catalyst concentration.

Discussion

The possible reactions leading to the formation of acetaldehyde, ethanol and acetic acid can be represented by the following equations. However, the ease of the formation of these compounds considerably depends on the catalyst concentration, as has already been described.

		$-\Delta F^\circ_{(25^\circ C)}$[6)] kcal./mol.	$-\Delta F^\circ_{(200^\circ C)}$[*4] kcal./mol.
$CH_3OH+CO+H_2$ $=CH_3CHO+H_2O$	(1)	16.1	9.8
$CH_3OH+CO+2H_2$ $=C_2H_5OH+H_2O$	(2)	25.9	11.0
$CH_3OH+CO=CH_3COOH$	(3)	21.3	11.8
$CH_3CHO+H_2=C_2H_5OH$	(4)	9.8	1.2

On the basis of the experimental results, we can postulate that, in the reaction of methanol with carbon monoxide-hydrogen mixtures, methanol is converted in the first place to acetaldehyde, that subsequently this is hydrogenated to ethanol or dimerized to other oxygenated compounds (2·acetaldehyde → ethyl acetate, 2·acetaldehyde → crotonaldehyde → n-butanol), and that the rates of the formation of methylacetate, acetic acid, C_3- and higher compounds are small, partly because the amounts of free acetic acid, C_3- and higher compounds present in the product are small and partly because the amount of hydrogen reacting with methanol is always larger than that of carbon monoxide.

It is well known that cobaltous salts react with carbon monoxide under high pressures to form dicobalt octacarbonyl, which undergoes a homomolecular disproportionation in methanol and which forms cobalt hydrocarbonyl in the presence of hydrogen[5)]. However, only with these cobalt carbonyl catalysts, a small part of the methanol used is converted into C_2-oxygenated compounds under the oxo condition[1,5)], although aldehydes are hydrogenated to alcohols or dimerized[7,8)].

On the other hand, cobaltous halides form green or blue tetrahedral complex anions[9)],

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[5)] P. H. Emett, "Catalysis," Vol. V, Reinhold Press, New York, (1957), p. 73.

[*4] Calculated by $d\ln K_p/dt = \Delta H^\circ_{(25^\circ C)}/RT^2$.

[6)] "Selected Values of Chemical Thermodynamics Properties," Part 1, N. B. S. (1961).

[7)] I. Wender, R. Levine and M. Orchin, *J. Am. Chem. Soc.*, 72, 4375 (1950).

[8)] R. W. Gaetz and M. Orchin, *J. Org. Chem.*, 27, 3698 (1962).

[9)] D. P. Graddon, "An Introduction to Co-ordination Chemistry," Pergamon Press., London, (1961).

such as $CoCl_4^{2-}$, $CoBr_4^{2-}$ and CoI_4^{2-} in an organic solvent[10-12] (nitromethane, *N*, *N*-dimethylformamide or acetone). The same complex ions have been considered to be formed from cobalt acetate and litium or sodium iodide in glacial acetic acid.[13,14] In the experimental section, it was mentioned that cobalt acetate in methanol containing an iodide and acetic acid forms, at an elevated temperature, a greenish compound, which is presumably tetrahedral.

From these facts and experimental results, we can expect the catalytic action of cobalt acetate and an iodide in the reaction of methanol with carbon monoxide-hydrogen mixtures to be as follows: a part of the cobalt acetate forms a complex compound of the $[CoX_4(CO)H]^{2-}$ ($X=I^-$ or CH_3COO^-) type, which is similar in electronic configuration to cobalt hydrocarbonyl $HCo(CO)_4$, hydropentacyano cobaltate anion[15] $[Co(CN)_5H]^{3-}$, carbonyl ferrocyanic anion $[Fe(CN)_5CO]^{3-}$, etc. (Hieber[16] reported that solid cobaltous iodide reacted with pure carbon monoxide to form a dark brown crystalline carbonyl apparently represented by CoI_2CO, in which the cobaltous ion was probably surrounded by more than two iodide ions.) With this complex compound, a methanol reacts with a carbon monoxide and a hydrogen to form an acetaldehyde. The other part of the cobalt acetate froms cobalt hydrocarbonyl, with which the acetaldehyde produced is hydrogenated to ethanol or dimerized to ethyl acetate and other things. When a relatively large amount of an iodide is added, most of cobalt acetate forms $[CoX_4(CO)H]^{2-}$ according to the above expectation and the yield of acetaldehyde therefore increases, while in the presence of a large amount of cobalt acetate, a considerable amount of cobalt hydrocarbonyl is formed simultaneously and the yield of ethanol, therefore, apparently increase.

Summary

The reaction of methanol with carbon monoxide-hydrogen mixtures has been carried out in the presence of a mixture of cobalt acetate and an iodide as catalyst. The extent of methanol conversion into C_2-oxygenated compounds (acetaldehyde, ethanol and acetic esters) was 40 to 60% when the catalyst concentration ($Co(CH_3COO)_2 \cdot 4H_2O +$ an iodide) range was form 1.0 to 20 mol%; the temperature range was from 180 to 220°C; the pressure range was from 300 to 500 kg./cm^2 (the H_2/CO values in synthesis gases were 1.0 to 1.5), and the reaction time was 90 min. The amount of free acetic acid, C_3- and higher oxygenated compounds in the liquid product was small. The use of iodine instead of an iodide as an additive for the cobalt acetate catalyst is disadvantageous for this reaction. From the detailed investigation of the influence of the catalyst concentration on the extent of the conversion of methanol into C_2-oxygenated compounds, it has been shown that the formation of acetaldehyde is favored in the presence of a relatively large amount of an iodide and that an increase in cobalt acetate results in an increase in the yield of ethanol. It has been postulated that, under these conditions, methanol reacted with carbon monoxide and hydrogen to form acetaldehyde, which subsequently was hydrogenated to ethanol or dimerized to other oxygenated compounds.

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[10] N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, **1959**, 3397, 3512.

[11] S. Buffagni and T. M. Dum, ibid., **1961** 5105.

[12] D. A. Fine, *J. Am. Chem. Soc.*, **84**, 1139 (1962).

[13] P. J. Proll and L. H. Sutellife, *J. Phys. Chem.*, **65**, 445, 1993 (1961).

[14] T. Mizoroki, Y. Andō and M. Furumi, Presented at the 16th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1963.

[15] B. DeVries, *J. Catalysis*, **1**, 489 (1962).

[16] W. Hieber, *Z. anorg. u. allgem. Chem.*, **243**, 145 (1939).