

312. *Catalytic Syntheses with Carbon Monoxide and Hydrogen under Pressure.*

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THE synthesis of ethyl alcohol from carbon monoxide and hydrogen under pressure in presence of catalysts containing cobalt has already been demonstrated in this laboratory (Morgan, Taylor, and Hedley, *J. Soc. Chem. Ind.*, 1928, **47**, 117T; Morgan and Taylor, *Proc. Roy. Soc.*, 1931, *A*, **131**, 533), and since the process necessarily involves a first step in the synthesis of higher alcohols, further investigations have been made into the conditions under which ethyl alcohol is produced. An addition of a small quantity of cobalt oxide had a marked effect on the catalytic properties of a mixture of copper and manganese oxides, so it was thought that the composition of the product might be controlled by the amount and form in which cobalt was added to this catalyst. The optimum result was obtained with 0.05 g.-equiv. of cobalt oxide added to 1 g.-equiv. each of copper and manganese oxides, 12% of the carbon monoxide reacting being converted into ethyl alcohol and 47% hydrogenated to methane (Morgan and Taylor, *loc. cit.*).

To 1 g.-equiv. of each of the same two catalysts, 0.1 g.-equiv. of cobalt phosphate, borate, sulphide, or selenide was added in order to moderate the hydrogenating action; considerable methane was still produced, but the catalyst containing cobalt sulphide gave the highest conversion of carbon monoxide into ethyl alcohol so far attained. With the borate, alcohols were produced as follows: methyl 18, ethyl 15, higher alcohols 15%, and the corresponding amounts with the phosphate and sulphide were 16, 13, 6%, and 16, 21, 11%, respectively. Catalyst containing cobalt selenide was almost inactive. Since cobalt sulphide gave the best conversion into ethyl alcohol, sulphides of iron, molybdenum, and nickel were tested in its place, but the first two were less efficient for the purpose and the last was inactive.

A series of experiments in which the proportions of copper oxide, manganese oxide, and cobalt sulphide were varied showed that the mixture containing 1 g.-equiv. each of oxides and 0.1 g.-equiv. of the sulphide was the optimum for ethyl alcohol production. This catalyst was tested under various conditions of temperature, pressure, and rate of circulation, and although these factors did not have any marked effect on the proportion of ethyl alcohol in the products, yet the optimum yield was obtained at 400° under 200 atm. pressure, with a rate of circulation of approximately 200,000 vols. (at N.T.P.) per hour per unit volume of catalyst. Under these conditions, the carbon distribution among the products was: methyl alcohol 17, ethyl alcohol 22, higher alcohols 11, and methane 47%.

In order to determine the composition of the higher alcohols, fractions boiling above 83°, from a number of experiments with catalysts containing copper oxide, manganese oxide, and cobalt sulphide, were combined, and the dried alcohols separated by distillation into fractions containing *n*-propyl, -butyl, -amyl, -hexyl, and -heptyl, also *isobutyl* and β -methylbutyl alcohols; over 90% of these alcohols had straight chains, and the two highest alcohols were identified for the first time in products obtained synthetically in this laboratory.

Weights of the constituent alcohols per kg. of crude product are tabulated below, to which have been added, for comparison, figures obtained with a manganese-chromium-rubidium oxide (RbIK) and a zinc-manganese-potassium-cobalt oxide catalyst (C. 16)

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(Morgan, Hardy, and Procter, *J. Soc. Chem. Ind.*, 1932, **51**, 11; Morgan and Taylor, *loc. cit.*). The data for the copper-manganese oxide-cobalt sulphide catalyst (D. 15) were obtained with product which had been hydrogenated, and aldehydes and acids had been removed from the other two products before distillation of the alcohols.

Wt. of alcohol (g.) per kg. of crude product.

Alcohol.	Catalyst.			Alcohol.	Catalyst.		
	D. 15.	RbIK.	C. 16.		D. 15.	RbIK.	C. 16.
Methyl	220	420	198	<i>n</i> -Amyl	6	—	1
Ethyl	200	12	86	β -Methylamyl	—	6½	—
<i>n</i> -Propyl.....	50	43	17	<i>n</i> -Hexyl	2	—	—
<i>iso</i> Butyl	3	69	11	<i>n</i> -Heptyl	< 1	—	—
<i>n</i> -Butyl	16	—	4	Residue.....	1	89	1½
β -Methylbutyl	2	8	1½				

It is noteworthy that catalyst D. 15, which contained cobalt but no alkali, produced alcohols higher than C₂, the majority of which had straight chains, and that RbIK, which contained alkali but no cobalt, gave higher alcohols, a large proportion of which had branched chains, whilst C. 16, which included both alkali and cobalt, gave a mixture of straight- and branched-chain alcohols.

It may be assumed that the higher alcohols are produced through the intermediate formation of aldehydes, which unite to give aldols; these lose water to form unsaturated aldehydes, which are hydrogenated to saturated aldehydes, and these, in turn, either condense to form aldols with still more carbon atoms or by hydrogenation produce the corresponding alcohols.

The active hydrogen in aldol condensation is usually provided by an α -carbon atom (Lieben, *Monatsh.*, 1901, **22**, 289), so that aldehydes with more than two carbon atoms will produce aldols with α -substituted chains, and in order to obtain hydroxy-aldehydes with straight chains it is necessary to postulate the presence of acetaldehyde. It must be noted, however, that in the condensation of propaldehyde with acetaldehyde, Schmalzhofer (*Monatsh.*, 1900, **21**, 671) found that the former aldehyde gave the active hydrogen. Coupling may not therefore be confined to an α -carbon atom, in which event synthesis of alcohols with a cobalt catalyst may have proceeded through formaldolisation, but whatever the actual mechanism involved, it is evident that the constitution of synthetic alcohols is dependent on the catalyst employed, and that cobalt has a marked directive action in the production of alcohols with straight chains.

EXPERIMENTAL.

Preparation of Catalysts.—Solutions of manganese and copper nitrates, mixed in the required proportion, were evaporated to dryness, and the residue gently roasted until no more nitrous fumes were evolved, whereupon the mass was cooled and ground to a fine powder; cobalt sulphide, prepared by the action of freshly made ammonium hydrogen sulphide solution on a solution of cobalt nitrate, was added while still moist to the powdered oxides. The resulting paste, after extrusion through a die into a vermiform mass, was dried at 130° and broken into granules. Cobalt phosphate, borate, and selenide were precipitated in analogous manner from the nitrate, and the catalyst prepared by a similar process. Ferrous sulphide was also prepared by precipitation and added in the wet condition to the mixed oxides, but molybdenum sulphide was made by passage of hydrogen sulphide over heated molybdic acid.

Gas Mixture and Circulatory Plant.—Carbon monoxide (1 vol.) and hydrogen (2 vols.) were mixed, and compressed into a high-pressure storage vessel. Commercial hydrogen was employed, and carbon monoxide was prepared by the action of sulphuric acid on formic acid. The gas mixture was passed at the requisite pressure (175—250 atm.) over catalyst heated to 380—435° in the usual form of high-pressure circulatory plant (Morgan and Taylor, *loc. cit.*). The space occupied by catalyst was in each case 70 c.c., and the rate of circulation 80—160 l. of compressed gas per hour.

Examination of Synthetic Products.—The liquid product was treated with hydrogen under pressure in the presence of a nickel-kieselguhr catalyst (Covert, Connor, and Adkins, *J. Amer. Chem. Soc.*, 1932, **54**, 1651). The resulting mixture of alcohols was distilled up to 95°, and a

Dufton column 3 ft. long was then used to fractionate the distillate, which was collected in a "methyl fraction" (b. p. < 72°), an "ethyl fraction" (b. p. 72—82°), and a residue of higher alcohols. Carbon contents were determined by ultimate analysis at each stage of the examination.

Examination of higher alcohols. From the combined higher alcohols (see p. 1429), water was removed as a ternary water-carbon tetrachloride-alcohol azeotrope by distillation with carbon tetrachloride in an apparatus designed for the purpose (*J. Soc. Chem. Ind.*, 1934, 53, 193r). The dried alcohols were then fractionally distilled, and an electrically heated Dufton column was employed for temperatures above 100°. The yields over various ranges were as follows:

Temp.	Wt., g.	Temp.	Wt., g.	Temp.	Wt., g.	Temp.	Wt., g.
88—104°	186·5	123—127°	2·6	138—143°	6·5	155—158°	3·6
104—112	12·8	127—131	2·1	143—147	0·5	158—161	2·2
112·6—115	6·7	131—133	4·4	147—149	2·0	161—163	0·9
115—118	45·5	133—136	4·7	149—153	0·8	163—167	0·7
118—123	7·5	136—138	8·8	153—155	0·7	167—176	1·2

The compositions of the various fractions were determined in the usual manner by preparation of derivatives and mixed m. p. determinations with authentic specimens. Propyl, isobutyl, and *n*-butyl alcohols were identified by preparation of the 3-nitrophthalates, and *n*-amyl, *n*-hexyl, and *n*-heptyl alcohols through the *p*-xenylcarbamates. The fraction of b. p. 131—133°, which was expected to contain β -methylbutyl alcohol, gave a *p*-xenylcarbamate, m. p. 78—82°, which was depressed by admixture with an authentic derivative of that alcohol (m. p. 82—83°) to 74—75°, and also by that of isoamyl alcohol to 77—80°, but a mixed m. p. 83·5—88° resulted with *n*-amyl *p*-xenylcarbamate (m. p. 97—102°). The fraction of b. p. 155—158° gave *n*-heptyl *p*-xenylcarbamate, m. p. 96—98°, mixed m. p. 101·5—104° with an authentic specimen of m. p. 106—107° (Found: C, 77·3; H, 8·8. Calc. for C₂₆H₂₅O₂N: C, 77·1; H, 8·1%).

Examination of intermediate fractions failed to yield any evidence for the presence of 6- or 7-carbon β -substituted alcohols such as were found in products from a manganese-chromium-rubidium oxide catalyst (Morgan, Hardy, and Procter, *loc. cit.*), and it was concluded that the original mixture consisted substantially of all the normal alcohols up to C₇ together with isobutyl and β -methylbutyl alcohol.

The fraction of b. p. 131—133° was allocated to *n*-amyl alcohol, and those of b. p. 143—153° and 161—167° were omitted owing to uncertain composition, otherwise Young's "middle point" method ("Distillation Principles and Processes," 1922, Chap. 16, p. 170) was applied to the distillation data and led to the following apportionment of alcohols: propyl, 186·5 g.; isobutyl, 12·7 g.; *n*-butyl, 59·7 g.; β -methylbutyl, 4·7 g.; *n*-amyl, 24·4 g.; *n*-hexyl, 6·5 g.; *n*-heptyl, 1·2 g. (total weight, 301 g.).

Valuable assistance was rendered by Mr. A. J. Bunce in the quantitative examination of these alcohols. The author thanks Professor G. T. Morgan, Director of Chemical Research, for his interest and advice and for permission to publish these results.

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[Received, July 13th, 1934.]