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Abstract

Full Text

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CHEMISTRY

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SYNTHESIS OF ETHANOL FROM CARBON DIOXIDE AND HYDROGEN

(Presented by Academician A. V. Topchiev on 12 VII 1957)

The catalytic reduction of carbon dioxide with hydrogen at normal pressure usually leads to the formation of hydrocarbons and carbon monoxide. The principal product formed is methane; the yield of liquid hydrocarbons is 20–40 g per 1 m^3 of the gas mixture $CO_2 : H_2 = 1 : 3$ ([1]-[5]).

Carrying out the synthesis from CO_2 and H_2 under pressure on oxide catalysts leads mainly to the formation of methanol ([6]–[8]). Along with methanol, depending on the process conditions and the composition of the catalysts, a certain amount of higher alcohols is formed (ethanol, propanol, butanol, etc.) ([9], [10]). This gave us grounds to undertake a study aimed at carrying out the directed synthesis of ethanol from CO_2 and H_2. For this purpose, a large number of different catalysts were tested and the influence of various factors (pressure, temperature, composition of the initial gas, etc.) on the synthesis process was studied.

Synthesis was carried out in a high-pressure apparatus, described more than once in our previous works ([11]). When operating under recirculation conditions, the effluent gases were returned to the synthesis by a circulating pump. Fresh gas was fed directly into the reactor.

Before being put into synthesis, the catalysts were subjected to reduction with hydrogen.

Table 1

Influence of various factors on the composition of the products obtained

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Temperature, °C	Pressure, atm	Space velocity, ml/hr	Ratio CO_2 : H_2 in the initial gas mixture	Alcohol content in condensate, wt. %	Fractional composition of alcohols, wt. % up to 72°	Fractional composition of alcohols, wt. % 72–82°	Fractional composition of alcohols, wt. % 82–94°
335	200	300	1 : 3	21.3	60.8	22.3	16.9
350	200	300	1 : 3	16.6	16.9	74.6	8.5
370	200	300	1 : 3	12.2	20.5	45.2	34.3
350	200	300	1 : 3	16.6	16.9	74.6	8.5
350	250	300	1 : 3	12.5	46.6	36.2	17.2
350	300	300	1 : 3	13.7	53.3	30.7	16.0
350	350	300	1 : 3	14.7	59.8	25.6	14.6
350	400	300	1 : 3	10.8	66.6	33.4	0
350	200	300	1 : 1.7	10.8	32.4	50.2	20.4
350	200	300	1 : 3	16.6	16.9	74.6	8.5
350	200	300	1 : 20	6.8	6.7	68.2	25.1

The products obtained in the synthesis were subjected to analysis. The aqueous condensate from the receiver, which was a colorless, slightly turbid liquid with traces of oil, was subjected to fractional distillation on a column with high separating power into fractions of methyl, ethyl, and propyl alcohols. Alcohols —butyl and higher—were present in very small amounts. The effluent gases were passed through a charcoal adsorber, in which hydrocarbons and volatile oxygen-containing products were trapped. After desorption, the reaction products were analyzed.

Various precipitated catalysts prepared on the basis of iron, cobalt, and nickel were tested, as well as fused iron catalysts (of the ammonia-synthesis catalyst type), promoted with various additives (K_2O, Al_2O_3, SiO_2, MnO, etc.).

The most effective proved to be alkaline additives introduced during fusion of the catalyst or by impregnating it with an aqueous solution of alkalis. The fused iron catalysts possessed greater stability and selectivity of action than the precipitated ones. Table 1 gives the results of several experiments showing the influence of temperature, pressure, and composition of the initial gas mixture on the composition of the products obtained.

The condensate obtained in the synthesis from CO_2 and H_2 over one of the samples of fused iron catalysts was subjected to more detailed investigation. During an experiment lasting more than 2500 h, the activity of the catalyst and the composition of the products obtained remained practically unchanged.

The condensate had: d_4^{20} 0.9701, acid number 9.2, ester number 0, carbonyl

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number 2.1.

The alcoholic fraction isolated by distillation (up to 94°) was treated with caustic potash and silver nitrate and, after drying over metallic calcium, was distilled on a high-efficiency rectification column.

Results of the distillation:

		g	%
Taken		371.4	
Beginning of boiling	62°		
Fraction	62.5–65.0	40.2	10.8
Fraction	65.0–77.0	7.8	2.1
Fraction	77.0–79.0	279.6	76.3
Fraction	79.0–96.5	6.3	1.7
Fraction	96.5–98.0	20.8	5.6
Residue		13.4	3.6
Losses		3.3	0.9

The fractions of methyl, ethyl, and propyl alcohols obtained were distilled again, with collection of fractions boiling within ranges of 0.2–0.3°,

Table 2

Results of the investigation of the alcohols

Alcohol	d_4^{20} found	d_4^{20} literature data	Boiling point, °C found	Boiling point, °C literature data	n_D^{20} found	n_D^{20} literature data	Hydroxyl number found	Hydroxyl number calc.	m.p. of phenylurethane, °C found	m.p. of phenylurethane, °C literature data
Methanol	0.7947	0.7942	64.3	64.56	1.3286	1.32857	1733	1751	47–48*	47
Ethanol	0.7899	0.7893	78.2	78.33	1.36125	1.36127	1215	1218	51–52*	52
n-Propanol	0.8055	0.8044	97.5	97.22	1.3848	1.38543	926	934	50.3–51.3*	51

* When determining the melting temperature of samples of mixtures of the phenylurethanes obtained and the phenylurethanes of the corresponding alcohols, no depression was observed.

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corresponding respectively to methanol, ethanol, and propanol. The results of the study of these alcohols are given in Table 2.

The results presented show that the alcohols obtained in the catalytic reduction of carbon dioxide consist mainly of ethyl alcohol.

Along with the alcohols, acids were isolated in an amount of about 1%, calculated on the condensate. The study showed that the bulk of the acids (more than 90%) is represented by acetic acid. For the isolated acid, the silver content in the silver salt was determined as 64.7%; for acetic acid it should be 64.64%.

Next, the product desorbed from activated carbon was subjected to study (see Tables 3, 4).

The liquid desorption product, which we shall conventionally call gasolene, had d_4^{20} 0.7052, n_D^{20} 1.3933, iodine number 103.9. Analysis of the gaseous desorption product was carried out by low-temperature fractionation (Table 4).

Table 3

Distillation of gasolene (72.0 g taken for distillation)

Boiling range, °C	d_4^{20}	n_D^{20}	Iodine number	Yield, g	Yield, %
Up to 90	0.6785	1.3810	124.8	38.31	53.2
90–122	0.7407	1.3971	80.8	21.27	29.5
122–150	0.7703	1.4075	65.1	8.25	11.5
150–200	0.7662	1.4150	55.9	1.51	2.1
Residue and losses	–	–	–	2.66	3.7

In the course of the investigations, some data were obtained on the chemistry of the catalytic reduction of carbon dioxide under pressure. An essential feature of this process is its stepwise character. The interaction of carbon dioxide with hydrogen in the initial stage leads to the formation of carbon monoxide in concentrations not exceeding the equilibrium concentrations of the water-gas reaction.

Table 4

Results of low-temperature distillation

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Empirical formula of the chemical compound	Content, vol. %	Content, wt. %
H_2	3.0	0.2
CH_4	11.6	4.8
C_2H_4	1.1	0.8
C_2H_6	24.3	19.0
C_3H_6	5.7	6.2
C_3H_8	39.4	45.2
iso-C_4H_8	0.1	0.2
n-C_4H_8	1.8	2.6
iso-C_4H_{10}	1.3	2.0
n-C_4H_{10}	7.8	11.7
Residue	3.9	7.3
	100	100

Table 5

Effect of space velocity on the alcohol content in the condensate (temperature 335°, pressure 200 atm, initial gas $CO_2 : H_2 = 1 : 3$)

In a once-through system	In a once-through system	Under recirculation conditions	Under recirculation conditions
Space velocity, $l/l \cdot h$	Alcohol content in condensate, wt. %	Space velocity, $l/l \cdot h$	Alcohol content in condensate, wt. %
300	21.3	600	20.5
600	16.8	3,400	19.4
7,200	9.6	8,000	18.1
30,400	7.2	20,800	16.6
70,500	5.0	57,200	12.3
145,000	3.2	109,000	6.4
197,000	1.4	142,000	5.8

The carbon monoxide formed is the main source of formation of oxygen-containing compounds and hydrocarbons. As the concentration of water vapor in the reaction mixture increases, the equilibrium concentration of carbon monoxide decreases, and the synthesis practically ceases when the carbon monoxide concentration reaches about 2%. When the synthesis is carried out in a once-through system, such a state occurs at a degree of conversion of the initial gas of about 50%. At high space velocities and, consequently, short contact times, the main product of the reduction of carbon dioxide is carbon monoxide. For

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For illustration, we give data on the effect of the space velocity on the formation of carbon monoxide (temperature 350°, pressure 200 atm, feed gas $CO_2 : H_2 = 1 : 3$):

Space velocity, l/l · h	Fraction of CO_2 converted into carbon monoxide, % of the CO_2 entering the reaction
6 600	20.2
8 200	33.2
17 200	40.0
81 000	53.0
148 000	65.0
246 000	94.5

The data presented show that carrying out the synthesis from CO_2 and H_2 in a flow system at high space velocities is associated with the formation of considerable amounts of carbon monoxide.

Carrying out this synthesis under conditions of recirculation of the exit gases makes it possible, even at space velocities up to 20 000 l/l · h, to suppress to a considerable extent the reaction of carbon monoxide formation. Table 5 gives some data on the composition of the products obtained in carrying out the synthesis from CO_2 and H_2 in a flow system and under conditions of recirculation of the exit gases.

The investigation carried out made it possible to draw up an approximate material balance of the principal synthesis products.

The yield per 1 m^3 of gas used ($CO_2 : H_2 = 1 : 3$) was (in grams):

Product	Yield, g	Product	Yield, g
Alcohols	92	Carbon monoxide	31
Hydrocarbons	81	Other oxygen-containing compounds	10
Water	345		

It is worth mentioning the fact that the yield of acids (mainly acetic acid) increases as the contact time decreases. Changing the space velocity from 6000 to 25000 l/l · h decreased the alcohols/acids ratio by more than 20 times. This circumstance may be regarded as evidence in favor of the view that the principal final product—ethyl alcohol—is formed by reduction of acetic acid.

As a result of the investigations carried out, catalysts and synthesis conditions were found that ensure the production of ethyl alcohol in high yield (about 90 g per 1 m^3 of gas used, $CO_2 : H_2 = 1 : 3$). The best results were achieved when this process was carried out under conditions of gas recirculation at a space

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velocity of 10 000–20 000 l/l · h, a temperature of 325–350°, and a pressure of 200 atm.

The newly developed synthesis of ethyl alcohol from carbon dioxide and hydrogen is of considerable interest and represents a step forward in the development of the still few methods for processing carbon dioxide into valuable chemical products.

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CITED LITERATURE

1. P. Sabatier, J. Senderens, C. R., **134**, 514, 689 (1902).
2. J. Dew, R. White, C. Sliepcevich, Ind. and Eng. Chem., **47**, 140 (1955).
3. H. Küster, Brennstoff Chem., **17**, 203, 221 (1936).
4. W. Russel, G. Moller, J. Am. Chem. Soc., **72**, 2446 (1950).
5. R. Stowe, W. Russel, J. Am. Chem. Soc., **76**, 319 (1954).
6. H. Tropsch, Brennstoff Chem., **9**, 1 (1928).
7. Sh. Kudo, J. Am. Chem. Soc., Japan, Ind. Chem. Sect., **55**, 287 (1952).
8. B. N. Dolgov, M. N. Karpinskii, *Chemistry of Solid Fuel*, **4**, 69 (1933).
9. E. M. Bocharova, B. N. Dolgov, K. I. Kan-Kogan, Yu. N. Petrova, *Chemistry of Solid Fuel*, **8**, 1107 (1937).
10. Japanese patents No. 154318, 21 XII 1942; No. 162927, 15 III 1944; Chem. Abstr., **41**, 5142 (1947); **44**, 1525 (1950).
11. A. N. Bashkirov, Yu. B. Kagan, S. M. Loktev, N. G. Morozov, *Trans. Inst. Petroleum, Academy of Sciences of the USSR*, **10**, 153 (1957).

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