OXIDATION OF METHANE TO CARBON MONOXIDE AND HYDROGEN.

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Attention has recently been called to the methane-oxygen reaction as a source of hydrogen-carbon monoxide mixtures. Patart(1) obtained a suitable mixture for the catalytic synthesis of methanol by incomplete combustion of methane. The methane, mixed with half its volume of oxygen was injected into coke maintained at 1000°. Brownlee and Uhlinger(2) employed a method of obtaining carbon monoxide, hydrogen and nitrogen from the products of combustion of internal combustion engines. This method of incomplete combustion of methane was proposed in many patents, often combined with the process using the reaction between methane and steam, but few information has been made on the scientific works with regard to the oxidation of methane to carbon monoxide and hydrogen.

The present work was undertaken to investigate the reaction at atmospheric pressure with the view of obtaining the efficient catalysts to accelerate the reaction or to cause it to take place at lower temperatures. The experiments were carried out by a flow method at 800—1000°, with and without catalysts, using methaner-air and methane-oxygen mixtures. It was found that nickel and cobalt were efficient catalysts and their activity was promoted by the addition of various oxides. The most efficient catalysts of those studied were nickel-thoria and nickel-silica. In the presence of those catalysts, the reaction proceeds at 850—900° almost quantitatively as shown in the following equation

$$2\,CH_4 + O_2 = 2\,CO + 4\,H_2$$

Without a catalyst, the analysis of the effluent gas reveals that the greater part of methane was unchanged at 1000°.

Experimental.

Methane was obtained from a cylinder of natural gas from the Kashiwazaki Province and gas mixtures containing 2 volumes of methane and 5 volumes of air, and 2 volumes of methane and 1 volume of oxygen, were used. The oxygen was obtained from cylinder of that gas. The gases were allowed to pass at the rate of 15 *l*. per hour over a catalyst which was placed centrally in the porcelain reaction tube in the gas furnace. The temperature was measured by means of a platinum and platinum-rhodium thermo-couple. The off gas was collected and analyzed. Analysis was carried out with an usual method, and hydrogen and methane were determined by oxidation with copper oxide at 300° and 550° respectively. Confining fluid was water.

In the experiments 3—5 gr. of oxides were carried on 5 gr. of small grains of pumice which gave a layer of a catalyst of 14 cm., when packed into a reaction tube. The temperature was raised to 800—1000° and gases were allowed to pass over the catalyst. During the reaction, easily reducible oxides in catalysts were reduced and converted to metals. In the case of nickel catalyst, experiments were carried on also with the catalyst which

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(1) Brit. Pat., 247,176.

(2) U. S. Pat., 1,107,581.

was reduced at 400° with hydrogen before the commencement of the reaction. The catalyste were prepared by the following methods:—

Nickel oxide—Ignition of nickel nitrate.
Cobalt oxide—Ignition of cobalt nitrate.
Iron oxide—Ignition of iron oxalate.

The mixed catalysts were prepared by the ignition of nickel or cobalt nitrate with nitrates of other metals. (in the case of mangan and magnesium the formates were used.) Nickel-silica and cobalt-silica catalysts were prepared by the ignition of the nitrates with anhydrous silicic acid.

The results obtained are given in Tables 1, 2 and 3. As may be seen from Table 1, when the mixture of methane and air is used, without a catalyst, hydrogen appears at 800° only in 4% in effluent gas and at 1000° in 12%. The use of nickel and cobalt catalysts greatly accelerates the reaction and lowers the reaction temperatures. Iron catalyst is not suitable because it favours the production of carbon dioxide. It is clear from the

Table 1.

Methane-air mixture, rate of flow 15 *l.* per hr. with catalysts, 30 *l.* per hr. without a catalyst.

Catalysts	Original gas	CO_2	Heavy hydrocarbons	O_2	CO	H_2	CH_4	N_2
	Temp.	0	0	14.3	0	0	28.6	57.1
Without catalysts	800°	1.1	1.1	1.4	9.1	4.2	19.0	64.2
	900°	.7	.9	0	10.7	8.1	16.2	63.2
	1000°	.9	1.1	0	10.8	12.4	14.2	60.6
Ni (reduced at 400°)	900°	4.1	0	.3	10.5	20.7	13.6	50.8
	1000°	2.4	0	0	14.4	30.7	8.	44.4
Ni	900°	2.4	0	.3	14.3	33.1	6.9	43.0
	1000°	.9	0	.8	18.7	38.9	2.4	38.3
Co	900°	3.0	0	.1	16.8	36.2	4.9	39.0
	1000°	.5	0		18.5	38.4	3.1	39.5
Fe	900°	8.1	.3	.5	2.2	2.2	23.3	63.4
	1000°	6.6	.1	.5	5.0	11.0	18.4	58.4

Table 2.

Methane-air mixture, rate of flow 15 *l.* per hr.

Catalysts	Temp.	CO_2	Heavy hydrocarbons	O_2	CO	H_2	CH_4	N_2
	Original gas	0	0	14.3	0	0	28.6	57.1
Ni–ZnO	900°	1.9	0	0	17.3	39.2	2.3	39.3
0.1*	1000°	2.6	0	0	15.6	38.2	3.9	39.7
Ni–BeO	900°	2.6	0	0	15.9	35.6	3.2	42.7
0.1	1000°	1.1	0	0	18.2	40.9	2.0	37.8
Ni–MnO	900°	1.7	0	0	17.9	38.1	2.4	39.9
0.1	1000°	1.0	0	0	17.9	38.5	2.9	39.7
Ni–Cr_2O_3	900°	0.8	0	0	19.3	37.9	1.5	40.5
0.05	1000°	0.4	0	0	19.5	39.6	1.3	39.2
Ni–Al_2O_3	900°	1.3	0	0.1	18.6	38.0	1.3	40.7
0.2	000°	0.3	0	0	19.2	40.4	1.8	38.3
Ni–MgO	900°	2.4	0	0	18.2	37.4	1.2	40.8
0.1	1000°	0.5	0	0	19.3	41.0	1.4	37.7
Ni–CeO_2	900°	1.0	0	0.2	18.8	38.3	1.4	40.3
0.1	1000°	0.9	0	0.1	18.8	41.3	1.2	37.7
Ni–ThO_2	900°	0.2	0	0.2	19.1	38.1	2.1	40.3
0.1	1000°	0	0	0.2	19.4	40.5	1.6	38.3
Ni–ThO_2	850°	0.3	0	0	19.1	39.0	1.4	39.2
0.1	900°	0	0	0.1	19.5	39.9	1.3	39.2
Ni–SiO_2	850°	2 2	0	0.4	16.6	36.0	1.6	43.1
0.01	900°	0.4	0	0	19.0	39.5	1.4	39.7
Ni–SiO_2	850°	0.5	0	0.1	19.1	38.8	1.3	40.2
0.05	900°	0.1	0	0.2	19.3	39.4	1.4	39.6
Ni–SiO_2	850°	0.6	0	0	19.1	38.9	2.3	39.4
0.1	900°	0.3	0	0.5	19.6	39.3	2.1	39.2
Ni–SiO_2	850°	1.3	0	0	18.8	39.0	1.8	38.1
0.2	900°	0.4	0	0.2	19.2	40.2	1.7	38.3
Ni–SiO_2	850°	1.1	0	0	18.4	40 4	1.3	38.9
1.0	900°	0.2	0	0.3	19.1	40.3	1.4	38.7
Co–ThO_2	850°	2.4	0	0.1	17.4	40.1	1.2	38.8
0.1	900°	3.0	0	0	16.6	42.6	1.5	36.3
Co–SiO_2	850°	1.1	0	0	17.9	38.0	2.5	40.5
0.1	900°	0.8	0	0.5	19.1	38.1	1.6	39.9

* The figure indicates gram molecule of the oxide added to 1 gram atom of Ni or Co.

Table 2.—(*Concluded*)

Catalysts	Original gas / Temp.	CO$_2$	Heavy hydrocarbons	O$_2$	CO	H$_2$	CH$_4$	N$_2$
		0	0	14.3	0	0	28.6	57.1
Ni–ThO$_2$–CeO$_2$ 0.1 0.1	900°	0.9	0	0	19.2	40.0	1.0	38.9
	1000°	0.5	0	0	19.5	41.8	1.0	37.2
Ni–ThO$_2$–CeO$_2$ 0.1 0.01	900°	0.6	0	0.1	19.5	39.1	1.3	39.4
	1000°	0.2	0	0.2	19.8	40.2	1.2	38.4
Ni–ThO$_2$–Al$_2$O$_3$ 0.1 0.1	900°	1.8	0	0	17.9	38.9	1.2	40.2
	1000°	0.7	0	0	19.3	40.2	1.0	38.8
Ni–SiO$_2$–ThO$_2$ 0.1 0.02	850°	0.2	0	0.2	18.3	38.9	2.7	39.7
	900°	0.2	0	0.1	19.6	40.2	0.9	39.0
Ni–SiO$_2$–MgO 0.1 0.02	850°	0.3	0	1.1	19.5	36.5	2.8	39.8
	900°	0	0	0.2	19.5	38.3	1.4	40.6

Table 3.

Methane-oxygen mixture, rate of flow 15 *l.* per hr.

Catalysts	Original gas / Temp.	CO$_2$	Heavy hydrocarbons	O$_2$	CO	H$_2$	CH$_4$	N$_2$
		0	0.4	30.8	0	0	61.6	7.2
Ni–ThO$_2$ 0.1	850°	0.3	0	0.1	29.2	62.7	2.8	4.9
	900°	0	0	0.4	29.0	64.0	2.3	4.3
	Original gas / Temp.	0	0.4	32.5	0	0	61.2	6.9
	850°	0.7	0	0.1	30.8	59.3	3.5	5.1
	900°	0.4	0	0	30.6	61.4	3.1	4.5

results in Table 2 the addition of other oxides increases the catalytic activity of nickel and cobalt. The most efficient catalysts are nickel-thoria and nickel-silica. As shown in Table 3, when the mixture of methane and oxygen is used, the similar results are obtained with nickel-thoria catalyst.

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