

PAROVAYA I KARBONATNAYA KONVERSIYA METANA

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ABSTRACT

In this work, the reactions of carbonate and steam-carbonate conversion of methane on the catalyst $(Ni_2O_3)_x(Co_2O_3)_y*(ZrO_2)_z*(B_2O_3)_k*Me/Al_2O_3$ were studied. Depending on the temperature, the conversion of methane and carbon dioxide reaches 100%. with an increase in temperature from 700 to 800 °C, the $N_2: SO$ ratio also increases from 1.47 to 4.00. As a result of the research, the following optimal conditions for the vapor-carbonate conversion reaction of methane in the catalyst $Al_2O_3(Ni_2O_3) x * (Co_2O_3) y * (ZrO_2) z * (B_2O_3) k * Me$ were determined: $CH_4 : CO_2 = 1:1$; $P = 0,1 MPa$; $V_0 = 1000 hours^{-1}$, $T = 750^{\circ}C$.*

KEYWORDS: Methane, Carbon Dioxide, Water Vapor, Catalyst, Conversion, Synthesis Gas.

INTRODUCTION

The increase in energy consumption will lead to the rapid depletion of oil, which is the main source for the production of various fuels and oil products, and the need to find alternative raw materials for energy and petrochemical synthesis.

Synthesis-gas production is considered to be the most developed among the various approaches with the subsequent production of synthetic liquid fuels or oxygenates, and in some cases, is already economically viable as long as it does not depend on oil price formation [1-2]. The synthesis gas consists of a mixture of hydrogen and carbon monoxide in various proportions and can be obtained from any carbon-retaining raw material. Synthesis gas serves as a primary raw material for the production of many chemical and petrochemical products (methanol and other oxygenates, products of Fisher-Tropsch synthesis).

It is also used as an environmentally friendly source of heat and energy. Synthetic liquid fuel does not lag behind conventional (ordinary) fuel, and the fuel obtained by the GTL method is superior in its characteristics [3-4]. On an industrial scale, the largest amount of synthesis gas is used in the production of methanol (more than 50%), oxysynthesis products (15%) and acetic acid (10-15%).

Small amounts of CO are used in the manufacture of herbicides and pharmaceuticals. Depending on the raw material used and the method of production, the ratio of components in the synthesis gas varies in a wide range from 1: 1 to 1: 3. This ratio is approximate because it is possible to increase the amount of CO by increasing the temperature during the synthesis process, and by increasing the amount of H_2 by increasing the pressure.

The production of synthesis gas is one of the main tasks on the way of converting natural gas into other hydrocarbons. There are three main ways to obtain synthesis gas [5-6]: steam reforming of methane, partial oxidation of methane and carbon dioxide reforming of methane (UKM). The first two methods are implemented in industry. But UKM is still at the stage of laboratory research, although it is considered quite promising.

Recently, interest has also arisen in the carbon dioxide conversion of other light hydrocarbons (for example, ethane and propane), the implementation of which, together with UKM, allows the conversion of natural and associated gases into synthesis gas without preliminary separation of C₂-C₄ hydrocarbons from them.

Most of the work related to the carbon dioxide reforming of methane and other light hydrocarbons is aimed at either developing new catalysts (for example, intermetallic and carbide) or improving the quality of existing nickel-based catalysts, or developing new methods for performing the conversion of fluidized bed reactors or membrane reactors. The catalyst of the composition (Ni₂O₃)_x*(Co₂O₃)_y*(ZrO₂)_z*(B₂O₃)_k*Me/Al₂O₃, unlike other catalysts, is more resistant to sintering, coking, and the effects of catalytic poisons. This makes them promising for use in the processes of carbon dioxide conversion of light hydrocarbons. In high-temperature pyrolysis of methane, ethylene, acetylene and hydrogen can be formed as the main products. This version of the conversion of methane to ethylene (oxidative condensation of methane) is of great industrial interest, since ethylene is the main starting compound for the production of many petrochemical products [7-11]. The authors of [12-15] found that ethylene is formed by the interaction of methane with oxygen on various oxide catalysts at temperatures from 600 to 750 °C. The main problem of the oxidative condensation of methane is [16-19] that the active sites of the methane condensation catalyst can activate C-H bonds in C₂H₆ and C₂H₄ molecules, which can promote the formation of CO₂ [20-25]. The formation of carbon dioxide leads not only to a decrease in selectivity, but also to an increase in the released heat of this reaction, so heat removal is an important problem [26-28]. In the carbonate conversion of methane to a synthesis gas, the main reaction of the process is strongly endothermic and takes place at a temperature of 700-800 °C, at atmospheric pressure in the presence of a catalyst.

The carbonate conversion process is not used as an independent method due to the small cross-ratio of CO: H₂ in the synthesis gas and the high probability of catalyst coking. The disadvantage of the process is the formation of C₂ + hydrocarbons, which requires the purification of the synthesis gas obtained. Nevertheless, the prospects of MKK are associated with the emergence of a new catalyst and the growing interest in the processes of industrial waste CO₂ (greenhouse gas) utilization. By combining the carbonate and vapor conversion of methane, a synthesis gas of the required composition (methane vapor carbonate conversion - MBKK) can be obtained.

For example, in industry, when it is necessary to obtain a synthesis gas with a commodity ratio, it is used in the synthesis of methanol, the main product of which is synthesized gas, 5-7% SO₂ is added to the raw material for steam conversion of methane.

The following reactions occur in the process of MBKK:



All methods of methane synthesis-gas conversion have one thing in common: these are processes involving group VIII metals that occur at high temperatures (750°C and above) under conditions close to equilibrium.

The biggest problem hindering the introduction of MKK into production is the coating of the surface of existing catalysts.

Therefore, active research on more stable and effective catalysts is underway.

Experiment Section

Processes are carried out in a flow reactor at atmospheric pressure without the presence of water vapor (carbonate conversion of methane) and in the presence of (methane vapor carbonate conversion) in a 1:1 ratio of CH₄:CO₂ at a volumetric feed rate of 1000 h⁻¹ (V₀) and a process temperature of 300 to 755°C.

Analysis of the initial and final products of the reaction was carried out on-line using gas chromatography.

(Ni₂O₃)_x*(Co₂O₃)_y*(ZrO₂)_z*(B₂O₃)_k*Me:Al₂O₃ catalysts were synthesized by adding 0 and 4 mas.% Me metal. In order to determine the coke formation of the used catalysts, a thermodynamically reduced reduction was carried out in an H₂ medium with a linear rise in temperature to 750°C.

RESULTS AND THEIR DISCUSSION

In order to increase the amount of hydrogen in the synthesis gas (Ni₂O₃)_x*(Co₂O₃)_y*(ZrO₂)_z*(B₂O₃)_k:Al₂O₃ in the catalyst in the following volume ratio of reagents CH₄:CO₂:H₂O=1:1:0.2, at atmospheric pressure, Attempts were made to carry out the conversion of methane to carbon dioxide at a volumetric rate of 1000 h⁻¹ and a change in temperature in the range of 450–750°C. (Ni₂O₃)_x*(Co₂O₃)_y*(ZrO₂)_z*(B₂O₃)_k: The Al₂O₃ catalyst exhibits very low activity in the vapor-carbonate conversion of methane. In the temperature range of 450-750 °C, the conversion of methane varies from 0.5 to 5.9%, and the conversion rate of carbon dioxide from -2.5 to 4.9%. The synthesis gas is the only product and is formed at a temperature of ≥ 700 °C. At T < 700 °C, the formation of CO, which is a synthesis-gas component, does not occur. Depending on the temperature, the H₂: CO interaction ratio is 0.9–1.2 (Table 1).

TABLE 1 THE EFFECT OF TEMPERATURE ON THE ACTIVITY OF THE CATALYST CONTAINING (Ni₂O₃)_x*(CO₂O₃)_y*(ZRO₂)_z*(B₂O₃)_k/AL₂O₃ (CH₄:CO₂:H₂O=1:1:0.2; P=1ATM; V₀ = 1000HOUR⁻¹)

t, °C	Conversion rate, %		H ₂ :CO
	X(CH ₄)	X(CO ₂)	
700	3,3	3,9	1,2
750	5,9	4,9	1,2
750	3,2	2,5	1,9

Thus, the study of the effect of water vapor on the polymetallic (Ni₂O₃)_x*(Co₂O₃)_y*(ZrO₂)_z*(B₂O₃)_k:Al₂O₃ catalyst showed the negative effect of water.

The probable cause of this is the oxidation of the metal Co and Ni with water, which is determined by the method of electron microscopy, leading to the formation of inactive Co and Ni hydroxides in this reaction.

It was also found that graphite was formed on the surface of the $(\text{Ni}_2\text{O}_3)_x \cdot (\text{Co}_2\text{O}_3)_y \cdot (\text{ZrO}_2)_z \cdot \text{Al}_2\text{O}_3$ catalyst used in the carbonate conversion of methane. Vapor carbonate conversion of methane $(\text{Ni}_2\text{O}_3)_x \cdot (\text{Co}_2\text{O}_3)_y \cdot (\text{ZrO}_2)_z \cdot (\text{B}_2\text{O}_3)_k \cdot \text{Me}/\text{Al}_2\text{O}_3$ was carried out on the catalyst by adding 20 volumes of % water vapor to the initial $\text{CH}_4:\text{CO}_2=1:1$ mixture.

Figure 1 shows the temperature dependence of methane and carbon dioxide conversion.

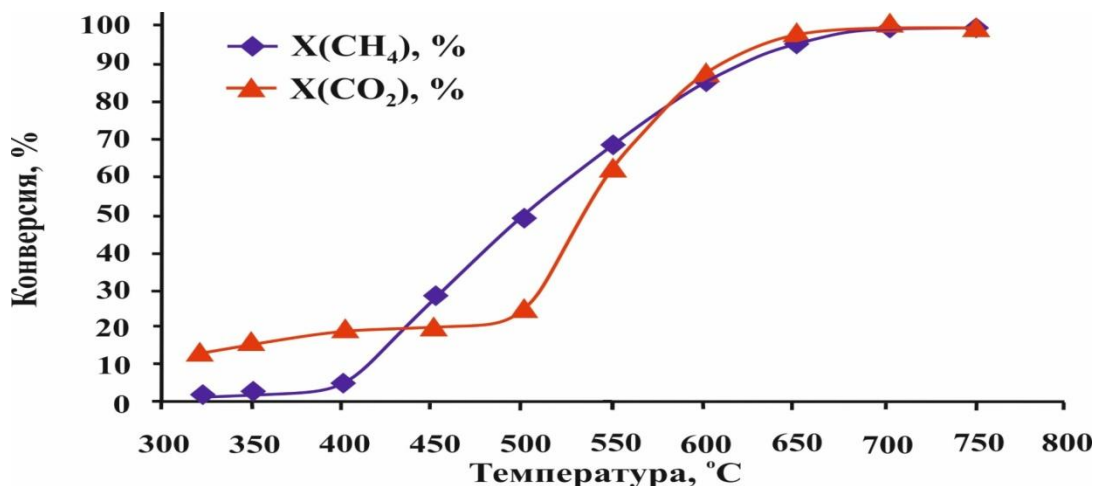


Figure 1. $(\text{Ni}_2\text{O}_3)_x \cdot (\text{Co}_2\text{O}_3)_y \cdot (\text{ZrO}_2)_z \cdot (\text{B}_2\text{O}_3)_k \cdot \text{Me}/\text{Al}_2\text{O}_3$ The effect of temperature on the conversion rate of CH_4 and CO_2 in the vapor carbonate conversion of methane in the catalyst ($\text{CH}_4:\text{CO}_2=1:1$; $P=0.1\text{MPa}$; $V_0=1000\text{ hours}^{-1}$)

Methane and carbon dioxide conversion rates increase from 1.6 and 13% to 100%, respectively, with an increase in temperature from 700 to 800 °C.

Depending on the temperature, the synthesis gas formed has a mutual ratio of

$\text{H}_2:\text{CO}=1.47-4.00$ (Table 1).

Comparison of methane carbonate and vapor carbonate conversion processes in $(\text{Ni}_2\text{O}_3)_x \cdot (\text{Co}_2\text{O}_3)_y \cdot (\text{ZrO}_2)_z \cdot (\text{B}_2\text{O}_3)_k \cdot \text{Me}/\text{Al}_2\text{O}_3$ catalysts shows that water vapor has a positive effect on the production of hydrogen and carbon monoxide from CH_4-CO_2 . The full conversion temperature of the raw material in the MBKK process is 55 °C lower compared to the MKK, and the $\text{H}_2:\text{CO}$ interaction ratio is higher (1.03 and 1.47 in the KK and BKK, respectively).

TABLE 2 $(Ni_2O_3)_x*(CO_2O_3)_y*(ZrO_2)_z*(B_2O_3)_k$ *THE EFFECT OF WATER ON THE REFORMATION OF METHANE IN THE CATALYST Me/Al_2O_3 ($CH_4:CO_2=1:1$; $P=0.1MPa$; $V=1000 HOURS^{-1}$)

Processes	V_{H_2O} volume, %;	t, °C	X_{CH_4} , %	X_{CO_2} , %	$H_2:C$ ratio	Difference between MKK and MBKK process indicators (Δ)			
						$\Delta H_2:CO$	ΔX_{CH_4}	ΔX_{CO_2}	Δt , °C
MKK	0	755	100	100	1,03	+0,44	0	0	-55
MBKK	20	700	100	100	1,47				

In order to study the effect of the amount of metal Me on the process of carbonate conversion of methane, its large amount is 4% by mass. catalyst was synthesized with. Carbonate conversion of methane was carried out in the catalyst $(Ni_2O_3)_x*(Co_2O_3)_y*(ZrO_2)_z*(B_2O_3)_k*Me/Al_2O_3$ in the temperature range 300-750 °C. The effect of temperature on gas conversion is illustrated in Figure 2. The conversion of CH_4 and CO_2 increases with increasing temperature. This means that the conversion rate of methane increases from 10.5 to 100%, and that of carbon dioxide - from 7.9 to 100% - in this temperature range.

In the temperature range of 450-750 °C, the yield of both hydrogen and carbon monoxide increases from 0.025 to 0.151 $\mu mol: g_{kat}\cdot c$ and from 0.030 to 0.141 $\mu mol: g_{kat}\cdot c$, respectively. Vapor carbonate conversion of methane was carried out by adding 20% by volume of water vapor. Methane and carbon dioxide conversion rates range from 1.1 and 0.3 to 100%, respectively, in the temperature range of 300–710 °C (Figure 3). The increase in temperature is accompanied by an increase in the yield of synthesis gas. In the temperature range of 450–710 °C, the yields of hydrogen and carbon monoxide increase from 0.022 and 0.006 to 0.173 and 0.121 μmol , respectively: $g_{kat}\cdot s$. At 710 °C, the $H_2:CO$ ratio is 1.43 (Table 3).

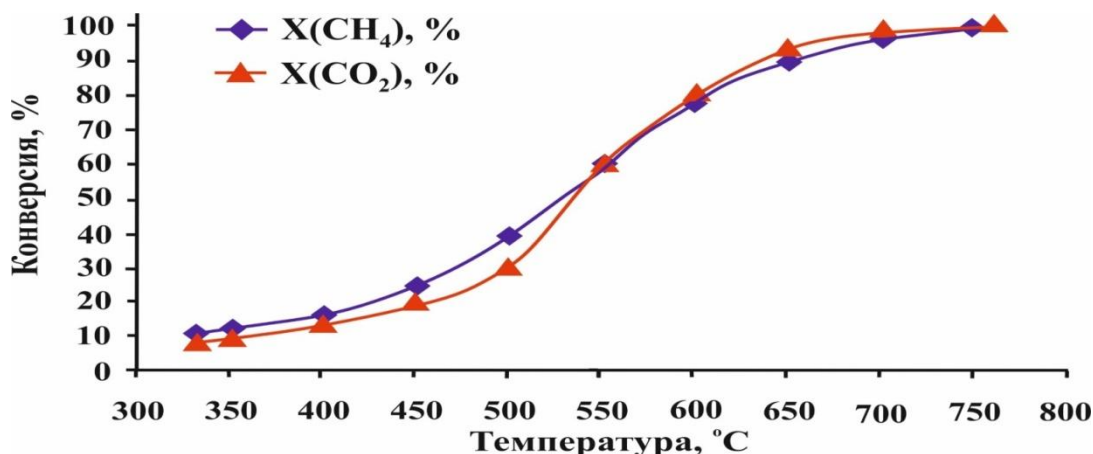


Figure 2. $(Ni_2O_3)_x*(CO_2O_3)_y*(ZrO_2)_z*(B_2O_3)_k$ *The effect of temperature on the conversion rate of CH_4 and CO_2 in the carbonate conversion of methane in the catalyst Me/Al_2O_3 ($CH_4:CO_2= 1:1$; $P=0.1 MPa$; $V_0=1000 hours^{-1}$)

TABLE 3. $(Ni_2O_3)_x*(CO_2O_3)_y*(ZrO_2)_z*(B_2O_3)_k*Me/Al_2O_3$ TEMPERATURE DEPENDENCE OF THE SYNTHESIS-GAS COMPOSITION IN THE PROCESSES OF CARBONATE AND VAPOR CARBONATE CONVERSION OF METHANE IN THE CATALYST ($CH_4:CO_2=1:1$; $P=0,1$ MPA; $V_0=1000$ HOURS⁻¹)

Process	t, °C	Products, mkmol: g _{kat} ·°C		H ₂ :CO relative
		H ₂	CO	
MKK	450	0,025	0,030	0,83
	500	0,050	0,055	0,90
	650	0,133	0,127	1,05
	700	0,145	0,136	1,07
	750	0,151	0,141	1,07
MBKK	450	0,022	0,006	3,66
	500	0,071	0,030	2,36
	650	0,160	0,110	1,45
	700	0,172	0,120	1,43
	710	0,173	0,121	1,43

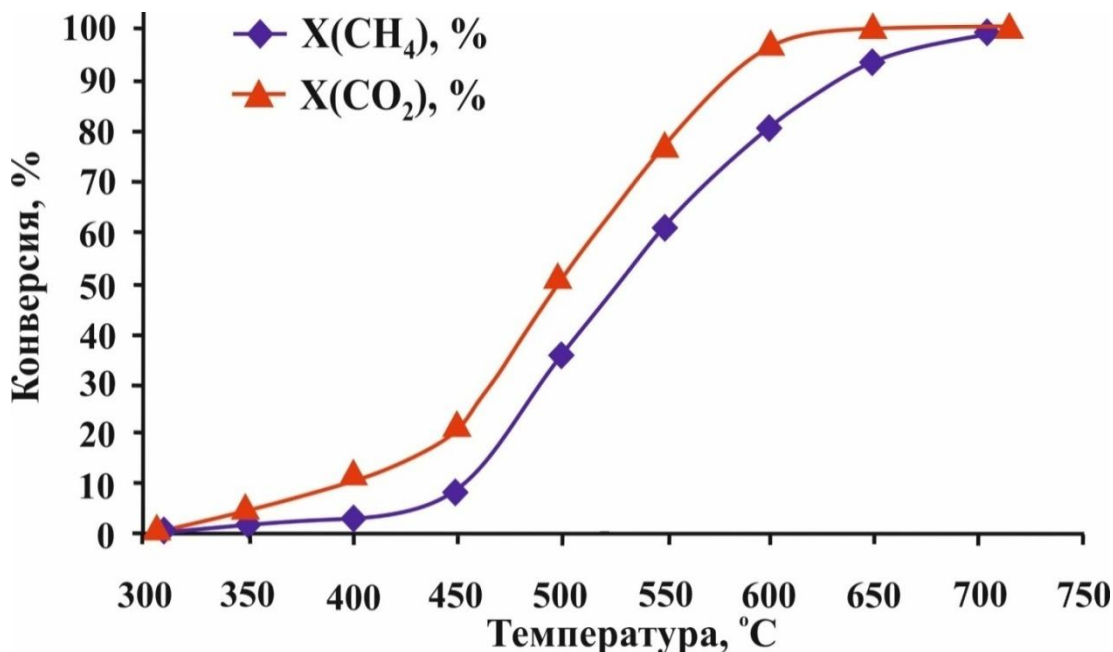


Figure 3. $(Ni_2O_3)_x*(CO_2O_3)_y*(ZrO_2)_z*(B_2O_3)_k*Me$: The effect of temperature on the conversion rate of CH_4 and CO_2 in the vapor carbonate conversion of methane in the Al_2O_3 catalyst ($CH_4:CO_2=1:1$; $P=0,1$ MPA; $V_0=1000$ hours⁻¹)

$(Ni_2O_3)_x*(CO_2O_3)_y*(ZrO_2)_z*(B_2O_3)_k*Me$: Comparative data on the carbonate and vapor carbonate conversion of methane in the Al_2O_3 catalyst are given in Table 4.

In the carbonate conversion of methane, the complete conversion of carbon dioxide and methane occurs at 750 °C, the synthesis-gas content being $H_2:CO= 1.07$. In the vapor carbonate conversion

of methane, the conversion rate of CH_4 and CO_2 is achieved at $\sim 100\%$ at temperatures well below 750°C , resulting in a much higher ratio of synthesis gas, $\text{H}_2:\text{CO}=1.43$.

Similarly, the optimized ranges of $\text{CH}_4:\text{CO}_2:\text{H}_2\text{O}$ molar ratios for the process of steam-carbon dioxide conversion at different temperatures in the pressure range of 1-5 atm were selected, presented in Table 4. For each region, the molar ratios of $\text{CH}_4:\text{CO}_2:\text{H}_2\text{O}$ were found, at which the content of impurities in the synthesis gas reaches its minimum values at a given temperature and pressure.

TABLE 4 OPTIMIZED RANGES OF MOLAR RATIOS $\text{CH}_4:\text{CO}_2:\text{H}_2\text{O}$ FOR THE PROCESS OF STEAM-CARBON DIOXIDE CONVERSION OF METHANE.

T, °C	p, atm	$\text{CH}_4:\text{CO}_2:\text{H}_2\text{O}$
750	1	1:0.28–0.45:0.75–1.13
	5	1:0.42–0.53:1.05–1.3
850	1	1:0.27–0.37:0.75–1.04
	5	1:0.25–0.4:0.8–1.18
1000	1	1:0.27–0.33:0.7–0.91
	5	1:0.26–0.36:0.8–1.05

The obtained optimized molar ratios for the process of steam-carbon dioxide conversion of methane and the corresponding parameters of the synthesis gas are shown in Table 5.

TABLE 5 OPTIMIZED MOLAR RATIOS OF $\text{CH}_4:\text{CO}_2:\text{H}_2\text{O}$ FOR THE PROCESS OF STEAM-CARBON DIOXIDE CONVERSION OF METHANE AND THE CORRESPONDING PARAMETERS OF SYNTHESIS GAS

T, °C	p, atm	$\text{CH}_4:\text{CO}_2:\text{H}_2\text{O}$	$\text{CO}_2, \%$	$\text{CH}_4, \%$	$\text{H}_2:\text{CO}$	$\Delta H, \text{kcal/mol}$
750	1	1:0.31:0.83	1.68	1.46	2.18	52.81
	5	1:0.42:1.03	6.08	5.85	2.19	44.22
850	1	1:0.27:0.78	0.46	0.53	2.18	54.93
	5	1:0.32:0.91	2.16	2.17	2.18	51.41
1000	1	1:0.26:0.76	0.15	0.2	2.18	55.58
	5	1:0.28:0.84	0.84	0.82	2.19	54.21

The calculation of the optimized molar ratios was carried out by the Gibbs energy minimization method. Experiments confirming the correctness of thermodynamic calculations were carried out at a pressure of 5 atm. The choice of this pressure is due to the fact that at a pressure of 5 atm over the entire temperature range, the calculated content of methane and carbon dioxide in the resulting synthesis gas is less than 7%.

In addition, with increasing pressure, the experiment becomes much more complicated, since the equipment used requires higher mechanical characteristics, and the likelihood of uncontrolled coke formation in the lower layers of the catalytic layer, where the endothermic reaction proceeds most intensively, also increases.

CONCLUSION

Thus, the vapor-carbonate and carbonate conversion reaction of methane $(\text{Ni}_2\text{O}_3)_x \cdot (\text{Co}_2\text{O}_3)_y \cdot (\text{ZrO}_2)_z \cdot (\text{B}_2\text{O}_3)_k \cdot \text{Me}/\text{Al}_2\text{O}_3$ was studied in the presence of a catalyst.

The study concluded that the complete conversion of carbon dioxide and methane in the carbonate conversion of methane occurs at 750 °C, with the synthesis-gas content being $\text{H}_2:\text{CO}=1.07$.

In the vapor carbonate conversion of methane, the conversion rate of CH_4 and CO_2 is achieved at ~ 100% at temperatures well below 750 °C, resulting in a much higher ratio of synthesis gas, $\text{H}_2:\text{CO} = 1.43$.

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