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OF THE REPUBLIC OF KAZAKHSTAN

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PARTIAL OXIDATION OF METHANE TO SYNTHESIS GAS IN THE PRESENCE OF Mg-Mn-Co-Al CATALYSTS

Abstract. The results of studies of the partial oxidation of methane to synthesis gas on Mg-Mn-Co-Al catalysts prepared by solution combustion synthesis are presented in this paper. The tests were carried out in the temperature range 300-600°C at a different ratio of catalyst components by varying of reaction conditions. At present, the partial oxidation of methane to synthesis gas is an alternative process among traditional methods. It was found that 12.5% Mg - 12.5% Co - 12.5% Mn - 12.5% Al / 50% CO(NH₂)₂ and 41% Mg - 3% Co - 3% Mn - 3% Al / 50% CO(NH₂)₂ catalysts prepared at 300°C are the most optimal for selective production of synthesis gas from methane at 900°C and W = 2500 h⁻¹. It was shown that hydrogen yields are 65% and 67%, and CO yields are 23.5% and 23% at methane conversion of 99.4% and 99.8%, respectively. The resulting catalysts can be widely used in gas processing and petrochemicals.

Key words: self-propagating high-temperature synthesis, methane, synthesis gas, catalyst, partial oxidation.

Introduction

At present, the production of hydrocarbons and synthesis gas (selective catalytic oxidation of methane into synthesis gas), which produced by autothermal reforming is considered as a promising alternative process for conversion of hydrocarbons. For the production of synthesis gas, selective catalytic conversion of methane has been developed since 1990; it has a number of advantages over the process of water steam reforming [1-3]. Compared with the process of steam conversion, this process has such advantages as mild exothermicity, significant high efficiency, and a small reactor size. In synthesis gas, obtained by selective oxidation of methane, the ratio of H₂/CO is 2, according to the Fischer-Tropsch process. This ratio completely corresponds with the process of methanol and hydrocarbons synthesis. This process of selective catalytic oxidation of methane in a natural gas composition has become especially attractive for the production of liquid fuels in individual industries with the use of small installations. The exothermic nature of the process of selective catalytic oxidation, in terms of energy saving and capital inflows is cheaper than the traditional endothermic process [4-7]. In the case of a small reactor size, this makes it possible to ensure the efficiency of the process, significantly reduce the size and cost of equipment, and reduce the relative rates of consumption of raw materials and energy. The oxidation processes play a key role in modern chemical technology, because with their help more than 50% of the produced world chemical products have been obtained. In the last decade, new methods obtaining of synthesis gas by partial catalytic oxidation of methane in a mixture with insufficient content of oxygen at a short contact time are dynamically developed, and new ways of activating of methane and its reaction mixtures are being discovered [8-11]. Partial oxidation of alkanes to synthesis gas in comparison with the traditional method of steam conversion is just as simple, but it is carried out at a very low contact time. It is a promising approach for a new direction capable of producing products of different weight without forming carbon through small reactor as possible in size. At present, selective catalytic oxidation of carbons to synthesis gases and autothermal reforming is considered as a promising alternative process for

steam conversion. Since the nearest time, researcher of methane reformers are began to show interest in catalysts based on noble metals, because of their low sensitivity to coke formation and high activity and stability. Series of metal catalysts on the basis mg-stabilized, Al-coated noble metals of Ru, Rh, Ir, Pt and Pd were investigated by CH₄ and CO₂ mixed reforming in synthesis gases industry [12-14].

Experimental part

For the study, less important catalysts embedded in the carrier with a total mass of 5g were made by the SHS method (self-propagating high-temperature synthesis). Catalysts were prepared by measuring a certain amount of elements, mixing with a carrier, after that totally dissolving in water at 80°C, drying each catalyst at the temperatures (T) 300-500°C, making the form of ash. Catalysts were prepared from dry salts of systematic metal (crystals). The content of gas composition before reaction and after reaction was analyzed by chromatographic method through "CHROMOS-1000" chromatogram. The chromatographic peaks were determined using calibration curves. These calibrating curves were carried out using pure substances by programmed chromatogram "CHROMOS-1000". The short descriptions of universal device that investigates the catalyst, which used for production hydrogen-containing substances from methane in a composition of natural gas by method of selective catalytic oxidation.

The reaction gases: CH₄ + Ar, O₂ + Ar are supplied to the mixer balloon. The gas speed is regulated by means of a crane and a soft regulator, is taken by a rheometer and placed in a carrier. Mixing gases is supplied into the reactor with a catalyst. The reactor is heated with the help of two: the first microwave oven gas is preliminarily heated to 573K, while the second is heated up to the temperature of the reaction, regulated by Lattre. The oven, those preliminary heats gases is connected to millivoltmeter through thermocouple and the temperature of reaction oven is regulated by two thermocouples connected to millivoltmeter and which located on the catalyst layer [15-21].

Results and discussion

If catalyst composition included several types of metal it can be changed, by can change the catalytic properties. At the same time, if the catalyst composition includes more active components, this increases the stability of the components, provides strength to coking and etching [5]. Thus, we determine the effect of the catalyst on the production of the targeted methane 12.5%Mg-12.5%Mn-12.5%Co-12.5%Al/ 50% CO(NH₂)₂ (T = 900°C, space velocity (W) = 2500 h⁻¹). When studying a mixture of hydrocarbons close to real, following experiments such as the effect of temperature on the catalyst at temperatures of 300 and 600°C, as well as the conversion of methane to the desired product were carried out (Table 1). Consider the effect of the catalyst to reaction at a temperature of 300°C. And so in this situation methane conversion is 99.4%, H₂ yield is 65% and CO yield is 23.5%, respectively, selectivity is H₂ 99.1%, at CO is 71.6%. When obtaining catalyst at 400°C, methane conversion decreases to 98.2%, respectively the yield of H₂ would be 64% and CO would be 20%, accordingly selectivity of H₂ decreases to 98.7%, CO can observe a decline to 61.7%. Conversation of methane at a temperature of 500°C and 600°C is 98.5%, H₂ yield degreases to 63.1%, 17.1% and 60.5 CO yield and 18, respectively decreasing noticed at selectivity and H₂ is 95.6% and 90.3% , Co is decreased to 51,8 % and to 53.7% (Table1). Thus, during the selective production of desired product, the process parameters of the process of oxidizing a mixture of hydrocarbon products close to reality can be optimized by changing the temperature.

Table 1 - Influence of preparation temperature on the CH₄ conversion and yield and selectivity of H₂ and CO for the oxidation of methane into synthesis gas on the 12.5% Mg - 12.5% Mn - 12.5% Co - 12.5% Al / 50% CO(NH₂)₂ catalyst at W = 2500 h⁻¹

Catalysts which prepared at T, °C	Conversion CH ₄ , %	Yield, %		Selective, %	
		H ₂	CO	H ₂	CO
300	99.4	65.0	23.5	99.1	71.6
400	98.2	64.0	20.0	98.7	61.7
500	98.5	63.1	17.1	95.6	51.8
600	98.5	60.5	18.0	90.3	53.7

As shown in following (Table.2) 41% Mg-3%Mn-3%Co-3%Al / 50% CO(NH₂)₂ (T = 900°C, W = 2500 h⁻¹), conversion of methane obtained at 300°C temperature of up to 600°C will increase to 37.1% from 19.8% at 300-600°C and changing of selectivity in H₂ and CO yield is noticed.

Yield of formed H₂ increases from 15.4% at 300°C and increases to 19.4% CO at 400°C, and then can be decreased to 7.6% at 500°C, can be increases back to 22% at below 600°C and the amount of CO decreases to 6.3% at 300°C, to 5.2% at 400°C and to 2.1 at 500°C, will be able to see grow up to 6.8 at 600°C back. As well as, the selectivity temperature of H₂ decreases from 114.9% to 83.3 and Co decreases from 68.3% to 94%. At present, the selective oxidation of hydrocarbons and autothermal reforming is alternative to the traditional processes [6].

Table 2 - Influence of preparation temperature on the CH₄ conversion and yield and selectivity of H₂ and CO for the oxidation of methane into synthesis gas on the 41% Mg - 3% Mn - 3% Co - 3% Al / 50% CO(NH₂)₂ catalyst at W = 2500 h⁻¹

Catalysts which prepared at T, °C	Conversion CH ₄ , %	Yield, %		Selective, %	
		H ₂	CO	H ₂	CO
300	19.8	15.4	6.3	114.9	94.0
400	20.5	19.4	5.2	134.7	72.2
500	21.1	7.6	2.1	95.0	52.5
600	37.1	22.0	6.8	83.3	68.3

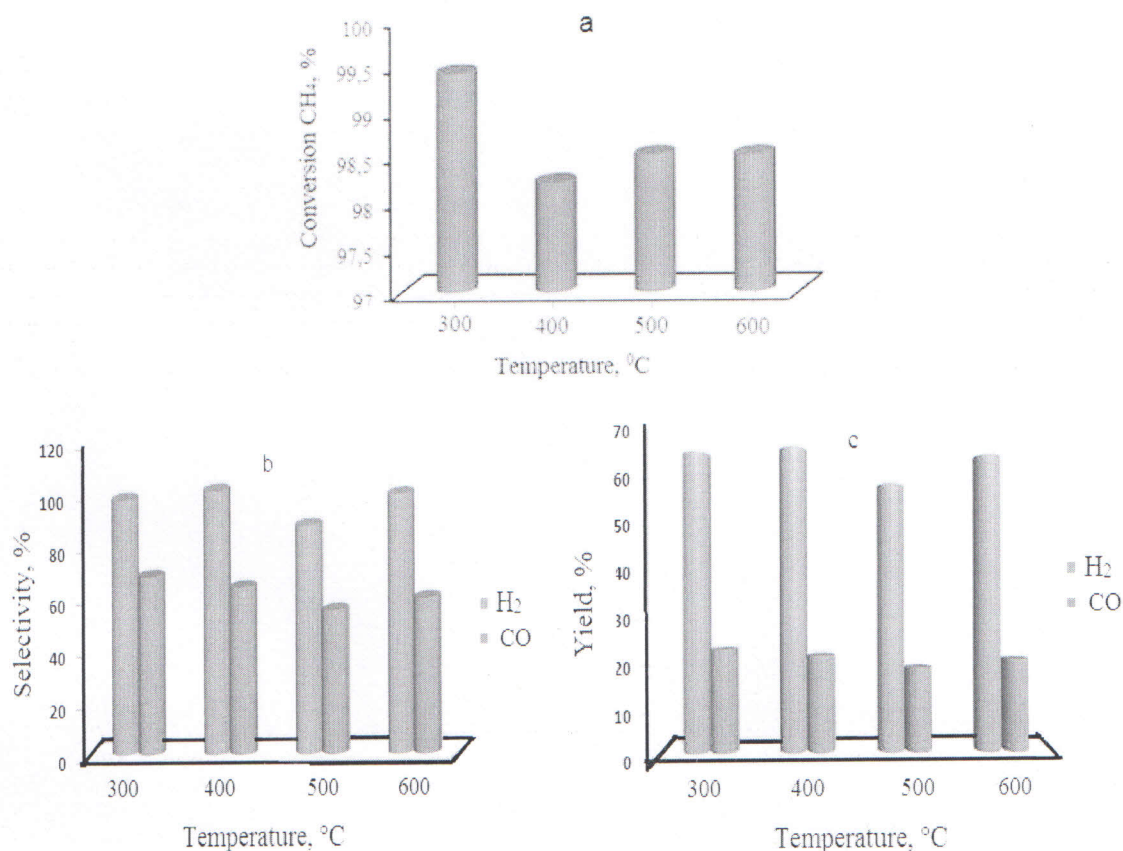


Figure 1 – Oxidative conversion of methane into synthesis gas (CH₄ conversion (a), H₂ and CO selectivity (b) and yield of H₂ and CO (c) on the 3% Mg - 41% Co - 3% Mn - 3% Al / 50% CO(NH₂)₂ catalyst prepared at different temperatures (from 300 to 600°C)

Known catalysts disadvantages are need to activate them in advance before carrying out the reaction, decreasing of catalyst activity at certain time, large amount of metals (10%), carbon formation and metal loss at high temperature. In this context, for direct process of selective catalytic oxidation of methane (SCO) from natural gas composition, currently, effective and stable, low interest rates catalysts have been investigated [7]. 3%Mg- 41%Co-3%Mn-3%Al / 50% CO(NH₂)₂ (T = 900°C, W = 2500 h⁻¹), the catalysts obtained at 300°C to 600°C temperature for the reaction of methane conversion at 300-600°C temperature during the reaction is equal to similar value, from 98.5% to 98.8% and selectivity and the yield of H₂, CO is changed. Yield of produced H₂ increases from 67% at 300°C to 68% at 400°C and H₂ yield decreases to 59.7% at 500°C, in contrast increases to 66% at 600°C, the amount of CO decreases from 23% at 300°C to 21.5% at 400°C and to 18.7% at 500°C again will be able to see grow up to 20.5% at 600°C. As well as, at these temperatures of selectivity of H₂ increases from 98.2% at 300°C to 101.5% at 400°C, decreases to 88% at 500°C and increases at 600°C to 100%. If CO selectivity at 300-500°C decreases to 55.1% from 68.4% it will be 59.7% at 600°C (Figure 1).

Table 3 - Influence of preparation temperature on the CH₄ conversion and yield and selectivity of H₂ and CO for the oxidation of methane into synthesis gas on the 3% Mg - 3% Co - 41% Mn - 3%Al / 50% CO(NH₂)₂ catalyst at W = 2500 h⁻¹

Catalysts which prepared at T, °C	Conversion CH ₄ , %	Yield, %		Selective, %	
		H ₂	CO	H ₂	CO
300	32.5	17.8	4.4	80.9	40.0
400	26.8	18.9	3.6	93.6	52.1
500	28.5	19.3	5.3	96.5	53.0
600	30.5	19.5	4.7	97.5	47.0

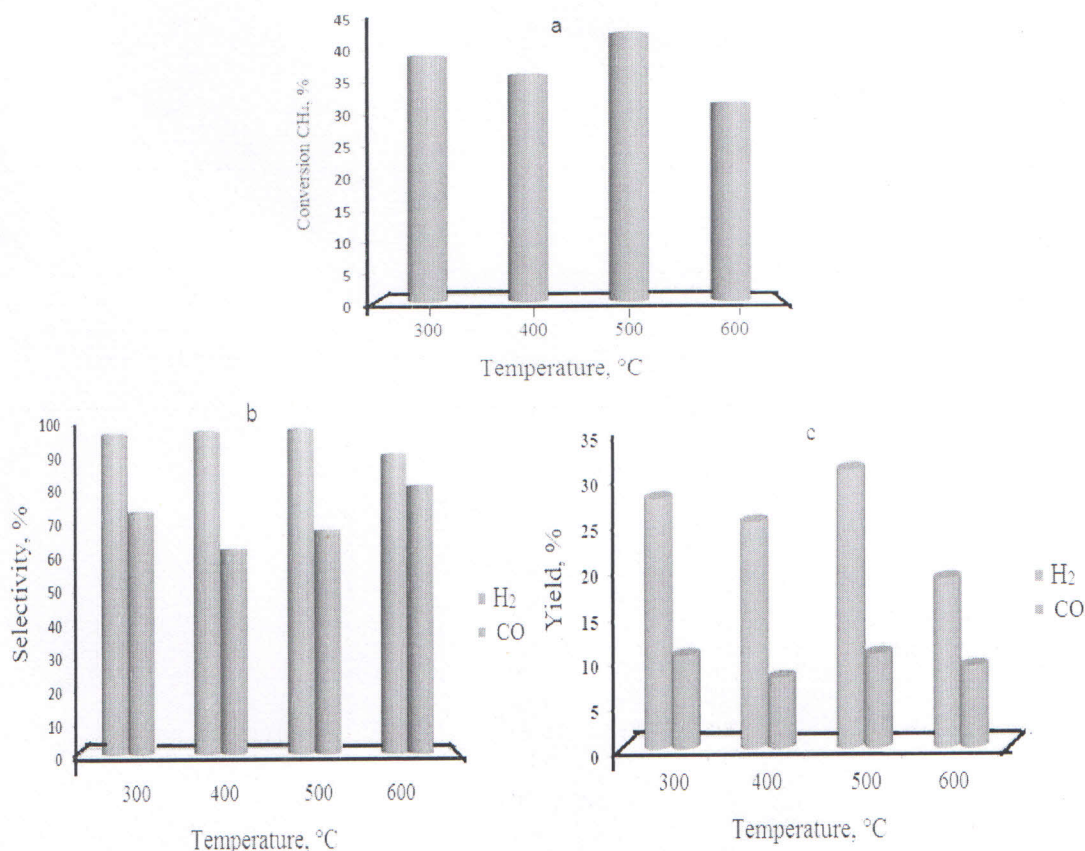


Figure 2 - Oxidative conversion of methane into synthesis gas (CH₄ conversion (a), H₂ and CO selectivity (b) and yield of H₂ and CO (c)) on the 3% Mg - 3% Co - 3% Mn - 41% Al / 50% CO(NH₂)₂ catalyst prepared at different temperatures (from 300 to 600°C)

It was shown that methane processing using a combination of different catalysts in appropriate situation in relation to high temperatures and O₂, H₂O and CO₂ is used as an oxidation. If the catalyst includes several metals in the composition, the catalytic properties can be changed by changing the proportion of catalysts [8]. As well as 3%Mg-3%Co-3%Mn-41% Al / 50% CO(NH₂)₂ (T=900°C, W = 2500 h⁻¹), supposes that you begin from 300°C to 600°C temperature of the catalysts for the reaction of methane conversion at 300-600°C increases to 32.3% from 40% and there are selective changes on yield of H₂, CO. Yield of generated H₂ decreases from 27,6% at 300°C to 25% at 400°C, the yield of H₂ decreases to 30.8% at 500 ° C, till 18.7% at 600°C.

The amount of CO decreases from 10.4% at 300°C to 7.9% at 400°C and at 500°C started from 10.5% at 600°C, and again, we can see a decrease of up to 9.1. As well as, if the selectivity of H₂ in the temperature range 300-500°C increases up from 98.5% to 100, at 600°C the yield decreases to 92. CO selectivity at 300-500°C decreases to 68.6% from 74.3% and at 600°C, we can see the increase of 82.3% (Figure 2).

Conclusion

The influence of catalyst composition and ratio of element on selective oxidation of the methane of natural gas into synthesis gas have been investigated. The 12.5% Mg - 12.5% Co - 12.5% Mn - 12.5% Al / 50% CO(NH₂)₂ and 3% Mg - 41% Co - 3% Mn - 3% Al / 50% CO(NH₂)₂ catalysts, which prepared at 300°C are most active among them the series of 12.5% Mg - 12.5% Mn - 12.5% Co - 12.5% Al / 50% CO(NH₂)₂, 41% Mg - 3% Mn - 3% Co - 3% Al / 50% CO(NH₂)₂, 3% Mg - 41% Co - 3% Mn - 3% Al / 50% CO(NH₂)₂, 3% Mg - 3% Co - 41% Mn - 3%Al / 50% CO(NH₂)₂, 3% Mg - 3% Co - 3% Mn - 41% Al / 50% CO(NH₂)₂ catalysts, which prepared from 300 to 600°C at W = 2500 h⁻¹, τ = 1.44 s, process temperature - 900°C. It was determined that the yields of H₂ are 65% and 67%, CO yields are 23.5% and 23% at methane conversions 99.4% and 99.8%, accordingly.

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ПАРЦИАЛЬНОЕ ОКИСЛЕНИЕ МЕТАНА В СИНТЕЗ-ГАЗ В ПРИСУТСТВИИ Mg-Mn-Co-Al КАТАЛИЗАТОРОВ

Аннотация. В настоящей статье представлены результаты исследования процесса парциального окисления метана в синтез-газ на Mg-Mn-Co-Al катализаторах, приготовленных методом самораспространяющегося высокотемпературного синтеза в растворе. Испытания проводились в интервале температур 300–600 °С при различном соотношении компонентов катализатора при варьировании условий реакции. В настоящее время парциальное окисление метана в синтез-газ является альтернативным процессом среди традиционных методов. Было установлено, что 12.5% Mg - 12.5% Co - 12.5% Mn - 12.5% Al / 50% CO (NH₂)₂ и 41% Mg - 3% Co - 3% Mn - 3% Al / 50% CO (NH₂)₂ катализаторы, приготовленные при 300 °С, являются наиболее оптимальными для селективного получения синтез-газа из метана при 900 °С и W = 2500 ч⁻¹. Показано, что выходы водорода составляют 65% и 67%, а выходы CO – 23.5% и 23% при конверсии метана 99.4% и 99.8%, соответственно. Полученные катализаторы могут широко использоваться в газопереработке и нефтехимии.

Ключевые слова: самораспространяющийся высокотемпературный синтез, метан, синтез-газ, катализатор, парциальное окисление.

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МЕТАНДЫ Mg-Mn-Co-Al КАТАЛИЗАТОРЛАРЫ ҚАТЫСЫНДА СИНТЕЗ ГАЗҒА ДЕЙІН ПАРЦИАЛДЫ ТОТЫҚТЫРУ

Аннотация. Мақалада метанды ерітіндіде өздігінен таралатын жоғары температуралық әдіспен дайындалған Mg-Mn-Co-Al катализаторлары қатысында синтез-газға дейін тотықтыру үрдісінің зерттеу жұмыстары ұсынылған. Реакцияның жүру шарттарын өзгерте отырып, 300-600 °С температура аралығында катализаторлардың құрамындағы заттардың әр түрлі қатынасында зерттеу жүргізілді. Қазіргі уақытта метанды синтез газға парциалды тотықтыру дәстүрлі әдістердің ішінде баламалы үдеріс болып табылады. Метаннан синтез газды талғамды тотықтыру үшін 300 °С температурада дайындалған екі 12.5% Mg - 12.5% Co - 12.5% Mn - 12.5% Al / 50% CO(NH₂)₂ және 41% Mg - 3% Co - 3% Mn - 3% Al / 50% CO (NH₂)₂ катализаторларының оңтайлы екені анықталды. Зерттеу жұмыстарының нәтижесі бойынша сутектің шығымы 65% және 67%, ал СО шығымы 23,5% және 23%, метанның конверсиясы сәйкесінше 99.4% және 99.8% екені анықталды. Алынған катализаторларды газ өндеуде және мұнай химиясы өндірісінде кеңінен қолдануға болады

Тірек сөздер: өздігінен таралатын жоғары температуралық синтез, метан, синтез газ, катализатор, парциалды тотықтыру.