

Catalytic Oxycondensation of Methane

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Abstract

*The catalyst with composition of $(\text{Mn}_2\text{O}_3)_x * (\text{Na}_2\text{MoO}_4)_y * (\text{ZrO}_2)_z$, fabricated on the basis of “sol-gel” technology for the reaction of oxycondensating methane has been chosen and an influence of different factors to the catalyst activity, as well as to the reaction efficiency studied. Kinetic objective laws of the process of oxycondensating methane in the presence of the optimal catalyst with composition of $(\text{Mn}_2\text{O}_3)_x * (\text{Na}_2\text{MoO}_4)_y * (\text{ZrO}_2)_z$ were studied in different values of initial substances partial pressures and temperature in differential reactor condition, as well as a kinetic model of the process was developed. A kinetic equation, which satisfy the reaction of oxycondensating methane in differential reactor condition was chosen and evaluated its adequateness. Proceeding mechanism of the process based on studying kinetic objective laws of fabrication reaction of ethylene from methane, as well as technological scheme of the catalytic oxycondensation reaction of methane have been offered.*

Key words: methane, ethylene, oxycondensation, nanocatalyst, kinetics, mechanism, technological scheme.

Introduction

Sensible use of oil and gas allows chemical industry to develop still in high level. In order to economically use oil and natural gas an employment of high effective, less waste, economical, ecological safe technologies, as well as environment protection problem is of particular attention [1].

At present one of the methods with the brilliant future to process natural gas is an oxycondensation reaction of it [2]. It passed more than 30 years since oxycondensation reaction of methane investigated, but the reaction has not been inculcated in industry yet, because of not creating a stable catalyst, which possess high activity and efficiency.

There are a number of works on preparation of C_2 – hydrocarbons from methane in one stage they stand out for their high economical effectiveness

[3,4]. At the same time the problems on choosing more effective catalysts, studying the objective laws of the reaction proceeding, modeling and optimizing the process for the process are still being left actual.

A method with the brilliant future to prepare catalyst for oxycondensation reaction of methane is a “sol-gel” technology. Use of nanocatalysts leads to the improvement of ecological characteristics of the processes and technologies in industry, to the decrease of harmful wastes thrown away into atmosphere, to the development of ecological pure types of alternative energy resources, to the production of new products and materials. Following abovementioned creation of new methods of the production of synthetic substances based on local raw materials and industrial wastes, which are important for national economy, as well as

creation of wasteless, ecological pure, high quality and competitive technologies is actual.

Experimental

Oxycondensation reaction of methane has been studied in flowing differential reactor in laboratory condition. The reactor was a quartz tube and its length 650 mm, inner diameter 8 mm. The catalyst size was 0,25-0,5 mm. Methane : oxygen was sent to the reactor in 2 : 7-1 volume ratio with 1:15 l/hour rate. The temperature has been changed in interval of from 700 to 850°C. Oxycondensation reaction of methane was carried out in flowing reactor in usual atmosphere pressure. Gas products of the reaction were analyzed by chromatographic method.

The catalyst with composition of $(Mn_2O_3)_x * (Na_2MoO_4)_y * (ZrO_2)_z$ was prepared for oxycondensation reaction of methane on “sol-gel” method. Phase composition analysis was conducted in DRON-4,0 (CuK $_{\alpha}$ – radiation) diffractometer, particles size in Scanning Electron Microscopy (JSM – 6380 LV) and emission Electron microscopy (EMV – 100 BR).

Results and discussion

To study kinetic objective laws of oxycondensation reaction of methane the influence of partial pressures of methane and oxygen to the formation rate of ethylene was examined in 700 – 800° C temperature and in 600 – 1200 hour⁻¹ values of volumetric rate.

When study the influence of reagents partial pressures to the objective laws of the process proceedings the partial pressure of the second gas kept unchanged, while changing that of the first one. Pure argon gas in a required amount has been injected to the reaction zone to keep linear rate unchanged. In order to keep the specific rate constant the catalyst volume was adjusted to the investigation condition.

Findings on studies of the influence of methane partial pressure to oxycondensation process by having linear rate of gas flow constant in different values of the temperature and volumetric rate were presented in table 1.

Table 1 Examination results of the influence of methane partial pressure in different specific volumetric rate and temperatures ($P_{total} = 0,1$ MPa; $P_{O_2} = 0,014$ MPa)

Specific volumetric rate of methane, ml/ml.cat.hour	Partial pressure of methane, MPa	Conversion level of methane to ethylene, %			Formation rate of ethylene, S%		
		T=700°C	T=750°C	T=800°C	T=700°C	T=750°C	T=800°C
600	0,017	8,8	14,3	20,6	6,7	8,4	10,6
800	0,017	7,6	11,5	17,4	5,6	7,2	8,8
1000	0,017	6,7	9,1	13,5	5,2	6,4	7,6
1200	0,017	5,8	8,5	9,7	4,8	5,8	6,5
600	0,025	18,4	20,8	24,5	7,2	9,5	12,8
800	0,025	15,2	17,6	21,0	6,4	8,2	11,3
1000	0,025	13,0	15,2	18,6	5,6	6,4	10,0
1200	0,025	10,6	12,8	14,4	4,8	5,0	8,1
600	0,033	25,8	27,4	28,6	23,2	34,6	41,8
800	0,033	24,6	30,2	35,8	41,9	54,5	57,8
1000	0,033	23,4	33,2	42,8	64,3	72,8	81,4
1200	0,033	20,8	28,5	39,2	48,8	62,5	75,9

As it is shown from the table in the same values of specific volumetric rate and temperature the total conversion of methane decreases, while its partial pressure increases. The influence of oxygen partial pressure to the kinetic objective laws of methane oxycondensation reaction has been

studied in the values of 700 – 800°C and in specific volumetric rate of 600 – 1200 hour⁻¹. The partial pressure of oxygen was changed from 0,014 MPa to 0,01 MPa. In that time the partial pressure of methane was kept constant (0,033 MPa). Findings are presented in table 2.

Table 2 Examination results of the influence of oxygen partial pressure in different specific volumetric rate and temperatures ($P_{total} = 0,1 \text{ MPa}$; $P_{CH_4} = 0,033 \text{ MPa}$)

Specific volumetric rate of methane, ml/ml.cat.hour	Partial pressure of oxygen, MPa	Conversion level of methane to ethylene, %			Selectivity compared with ethylene, S%		
		T=700°C	T=750°C	T=800°C	T=700°C	T=750°C	T=800°C
600	0,010	17,2	20,8	24,6	9,8	12,3	14,5
800	0,010	14,8	18,4	21,2	8,2	10,0	11,3
1000	0,010	10,4	14,0	17,8	6,4	8,5	9,8
1200	0,010	7,7	11,2	15,5	4,9	6,0	7,5
600	0,012	20,5	23,8	27,2	15,0	20,4	24,8
800	0,012	18,2	20,0	24,5	13,2	17,5	19,9
1000	0,012	15,8	17,4	21,1	10,7	14,8	16,2
1200	0,012	13,9	16,2	18,7	8,5	11,2	13,8
600	0,014	25,8	27,4	28,6	23,2	34,6	41,8
800	0,014	24,6	30,2	35,8	41,9	54,5	57,8
1000	0,014	23,4	33,2	42,8	64,3	72,8	81,4
1200	0,014	20,8	28,5	39,2	48,8	62,5	75,9

As it is shown from the table total conversion of methane, as well as formation efficiency and selectivity of ethylene decreases with the decrease of oxygen partial pressure. As a result of kinetic investigations an improvement of the process indices has been observed with the increases of contact time and temperature.

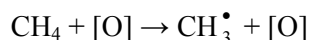
The increase of methane : oxygen ratio leads to the drop of methane and oxygen conversion. Falling formation of the products down was proved with the injection of ethane, ethylene, carbon monoxide and carbon dioxide to the reactor. And increase in contact time leads to rising of methane and oxygen conversion, as well as to the drop of selectivity with respect to ethylene. As the temperature rises, conversion of

methane increases and the selectivity with respect to ethane, as well as to ethylene decreases. With the increase of methane : oxygen ratio the selectivity with respect to ethane rises, the selectivity with respect to ethylene remains unchanged.

Oxygen conversion increases with the temperature rise. If an oxygen conversion reaches 95 % at 0,9 sec., the contact time makes 0,009 sec in 1000° C.

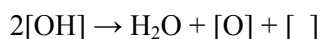
The process selectivity decreases with the increase of oxygen conversion. But the dependence with the temperature has a complex character. With the temperature increase up to 700-800°C the process selectivity decreases, then it increases in 850-950 °C.

The oxycondensation reaction of methane goes on homogen - heterogen mechanism. Activation of methane occurs in solid, oxide catalyst surface. In an active center of the catalyst one hydrogen atom is separated from methane molecule and methyl radical forms. Ethane molecule is formed by recombination of methyl radicals in gas phase:

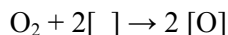


Here [O] – an active center with oxygen in the catalyst surface; [OH] – an adsorbed hydroxygroup in the catalyst surface.

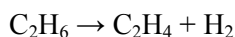
Further the process occurs on the following scheme: from two adsorbed hydroxygroups water molecule and oxygen space in the catalyst surface form:



Then regeneration of oxygen center happens:



Dehydrogenation of ethane by forming ethylene occurs at the temperature of higher than 700°C in gas phase or in the active center of the catalyst surface:



Kinetic objective laws of the oxycondensation process of methane in the

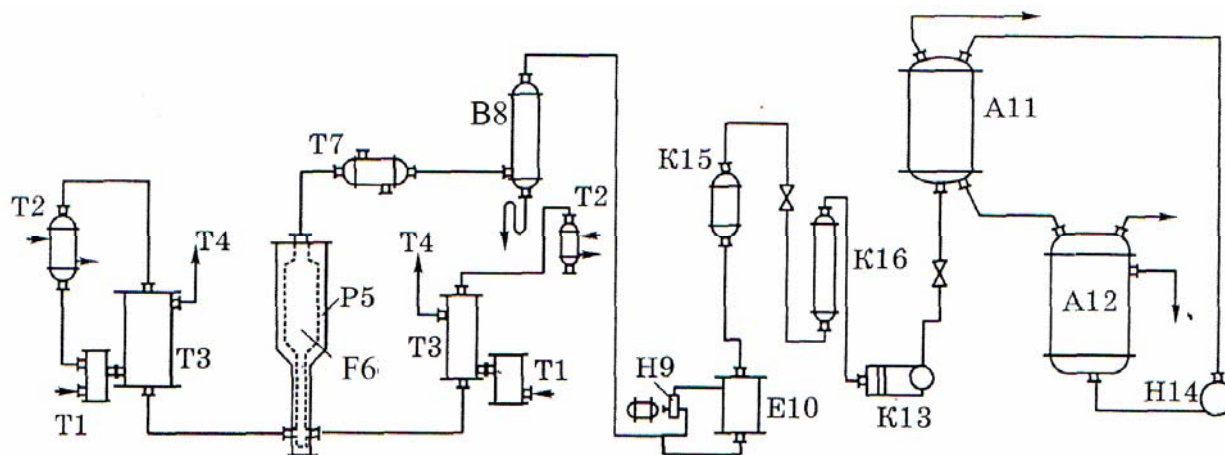
presence of an optimal catalyst with composition of $(\text{Mn}_2\text{O}_3)_x \cdot (\text{Na}_2\text{MoO}_4)_y \cdot (\text{ZrO}_2)_z$ has been studied in different values of the partial pressure and the temperature in differential reactor condition and a kinetic model of the process developed.

A kinetic equation, which satisfy the oxycondensation reaction of methane in differential reactor condition was offered and its adequateness evaluated:

$$W = \frac{k \cdot K_{\text{CH}_4} \cdot P_{\text{CH}_4} \cdot K_{\text{O}_2} \cdot P_{\text{O}_2}}{(1 + K_{\text{CH}_4} \cdot P_{\text{CH}_4} + K_{\text{O}_2} \cdot P_{\text{O}_2})^2}$$

The following optimal conditions have been chosen for carrying out the oxycondensation reaction of methane on the basis of adequate kinetic equation: $T = 800^\circ\text{C}$; $P_{\text{CH}_4} = 0,033$ MPa; $P_{\text{O}_2} = 0,014$ MPa; volumetric rate – 1000 hour^{-1} ; linear rate - $\omega = 2,2$ cm/sec; the catalyst size – 2-4 mm. In given condition the yield of the reaction on ethylene made 42,8 %.

Based on findings a technological scheme of the catalytic oxycondensation reaction of methane has been offered. A technological scheme of ethylene preparation by oxycondensating natural gas is presented in the following figure. It consists of two stages.



Technological scheme of ethylene preparation from natural gas and air.

T1 - furnaces; T2 - tubular preheaters; T3 - coil preheaters; T4 – outlet pipes for heating gases; P5-reactor; F6-ceramic balls; T7-tubular condenser; B8-barometric scrubber; H9-vacuum pump; E10-water collector; A11-absorber; A12-desorber; K13-compressor; H14-pump; K15-column for acetylene absorption; K16-column for CO₂ absorption.

A. Main stages

1. Oxycondensation of natural gas
2. Absorption of ethylene
3. Desorption of ethylene

B. Subsidiary stages

1. Adsorbent regeneration.

Oxycondensation of natural gas, absorption and desorption of ethylene

First natural gas is heated with water steam up to 110-120°C in tubular preheater (2), then it is heated with heating gases up to 500 °C in coil preheater (3). At the same time air is also heated up to 350-400 °C by this method. Heated gases are injected into the reactor, where they get mixed and passing through nozzle (6) (ceramic balls with the diameter 40 mm) interact with each other. The heat required for endothermic reaction is obtained by burning a part of methane given to the process.

The reaction is carried out in the temperature of 750-800 °C (in atmosphere pressure). Duration of gases stay in the zone of high temperature makes less than one second. 750 m³ methane and 1500 m³ air are put hourly through the furnace with the diameter of 1.3 m and height of 2.0 m. Gaseous products of the reaction, getting out of the reactor (5) are cooled in condenser (7), then are cooled in barometric scrubber (8) and washed off soluble admixtures.

Further the reaction products are directed to separation and to isolation of ethylene. No reacted methane is returned to the production cycle.

Oxicondensation gases are sent with the help of compressor K13 to the absorber A11, where ethylene is absorbed by ethyl alcohol. After saturation absorbent is sent to the desorpter A12, from there ethylene is isolated by heating. The solvent is cooled up to -20°C in order to increase solubility of ethylene in ethyl alcohol.

Oxicondensation gases are preliminary purified from C₂H₂ in column K15 with N-methylpyrrolidine and from CO₂ in column K16 with monoethanolamine.

Conclusions

- i) Catalyst with composition of (Mn₂O₃)_x * (Na₂MoO₄)_y * (ZrO₂)_z based on “sol-gel” technology has been chosen for oxicondensation reaction of methane.
- ii) With the presence of chosen optimal catalyst with composition of (Mn₂O₃)_x * (Na₂MoO₄)_y * (ZrO₂)_z kinetic objective laws of the process of oxicondensating methane were studied in different values of initial substances partial pressures and temperature in differential reactor condition, as well as a kinetic model of the process was developed.
- iii) A kinetic equation satisfying oxicondensation reaction of methane in differential reactor condition has been chosen and estimated its adequateness.
- iv) Flowing mechanism of the process based on studying kinetic objective laws of preparation reaction of ethylene from methane and technological scheme of catalytic oxicondensation reaction of methane have been offered.

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