

INFLUENCE of SHS-CATALYSTS PHASE STRUCTURE on FORMING PRODUCTS of PARTIAL METHANE OXIDATION

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Abstract

The activity of catalysts obtained by self-propagating high temperature synthesis in reaction of partial methane oxidation at atmospheric pressure was investigated. Basing on the compared results of X-ray analysis and gas chromatography analysis of reaction products, the dependence of compounds formation on the phase concentrations in the studied catalyst samples was found

Introduction

In connection with forecasts of oil reserves depletion every-growing attention is paid to searching alternative compounds that will serve in the nearest future as a source of obtaining products and semi-products of basic organic synthesis. Among such compounds the natural gas should be specified. Now the natural gas is used practically as a power generating source materials or present harmful emissions and petroleum gas flares resulting in environmental pollution [1]. Thus, the works aimed at synthesis of efficient catalysts and improvement of technology of partial methane oxidation are quite actual ones [2, 3].

This work presents the activity investigation results of the catalysts obtained by self-propagating high temperature synthesis in reaction of partial methane oxidation and the attempt was undertaken to find correlation between some reaction product yields and phase compositions of studied samples.

Experiment

The synthesis of SHS catalysts was carried out by methods elaborated in the Combustion Problems Institute [2]. The compounds containing lead, zinc and manganese were used as source charge components. The use of these components is explained by the fact that they proved to be catalysts making possible the efficient methane dehydromerization with formation of ethylene or methanol [4,5].

The components containing lead and zinc were supplied into the charge in amounts from 0 to 28% while the component containing manganese was fed from 0 to 16%. Besides these components there were fed into the charge the aluminum powder in amount up to 10%, magnesium sulfate (10%) and aluminum oxide in amounts from 23% to 65% as a ballast. The sample preparation consisted in weighting of source components, their further thorough grinding and steering in a porcelain mortar. The homogenization of obtained mixture was effected in the rotary mixer during 30 min. So prepared components were pressed to the 20 mm tablets under 25MPa pressure. Then the samples were weighted in the analytical balance

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and their height was measured. The SHS process was performed in a muffle furnace in air atmosphere. The samples were exposed for 3 minutes at 800 °C and then they were fired by flame of propane -oxygen burner at their upper end. The time of combustion wave propagating was measured and basing on its values the process rates were estimated. When the process accomplished, the SHS sample was immediately removed from the furnace and cooled in ambient air. Then it was weighted once more and its height was re-measured.

The investigation of catalytic activity of the SHS oxide catalysts in processes of interactions of natural gas in mixtures with oxygen of ambient air was carried out in the catalytic plant of flow running type in the X18H10T stainless steel micro-reactor of 5.5 mm inner diameter and 250 mm length. This micro-reactor was mounted vertically and heated with tubular electric furnace up to given temperature controlled by thermo-regulator. The amount of catalyst was constantly equal to 1.2cm³ in all experiments. The analysis of catalytic reaction products was carried out by chromatography methods based on the use of thermal conductivity detector.

Table 1. Initial composition of SHS catalysts, specific surface areas, methane oxidation product yield and phase composition

No	PbO %	ZnO %	K ₂ O %	Al ₂ O ₃ %	S _{sp} m ² /g	H ₂ vol%	O ₂ vol%	CH ₄ vol%	CO vol%	CO ₂ vol%	CH ₃ vol%	C ₂ H ₆ vol%	H ₂ O vol%	CH ₃ OH vol%	CH ₄ OH vol%
1	0	0	0	0	0.19	-	1.86	0.75	0.05	2.20	0.42	1.89	2.06	-	0.71
2	14	14	8	44	0.21	-	6.76	2.72	-	1.82	-	3.97	2.72	-	2.82
3	7	7	4	52	0.74	-	3.76	0.60	-	1.20	-	3.28	1.81	-	1.78
4	28	28	16	8	0.22	-	9.08	4.28	0.16	2.45	0.12	1.19	2.23	-	1.18
5	21	21	12	26	0.08	-	6.04	5.20	-	3.81	0.54	2.81	0.23	-	1.05
6	0	14	4	62	1.94	-	7.35	4.14	-	0.23	2.23	3.04	2.33	1.25	2.23
7	14	7	16	43	0.15	0.28	0.48	0.24	0.42	1.16	4.57	2.68	1.88	2.91	-
8	7	28	12	31	0.22	-	3.10	4.39	-	3.55	0.78	3.44	5.20	2.82	3.51
9	28	21	0	31	0.48	0.17	1.31	5.43	-	3.89	1.67	3.16	3.07	2.45	2.89
10	21	0	8	51	0.69	0.47	6.59	4.94	0.31	4.01	1.21	2.43	4.15	1.11	1.83
11	0	7	12	61	2.48	-	8.17	3.22	-	2.88	0.61	2.89	3.38	-	2.38
12	14	28	0	38	0.33	-	7.00	4.77	-	3.38	0.36	2.82	3.69	-	2.41
13	7	21	8	44	0.73	0.11	1.45	7.07	-	3.35	0.67	4.26	2.59	-	3.32
14	28	0	4	28	0.29	0.23	5.90	5.98	0.08	2.71	0.75	3.81	3.04	0.63	2.38
15	0	14	16	29	0.18	-	0.82	5.54	0.02	3.82	1.21	3.36	4.36	2.81	2.11
16	0	28	8	44	0.25	0.60	3.16	5.42	1.18	3.57	1.70	3.78	3.73	3.28	1.81
17	14	21	4	41	1.17	0.43	0.72	2.75	0.69	7.02	2.07	3.33	8.36	1.81	1.24
18	7	0	16	57	1.12	0.62	1.84	2.93	2.43	4.02	1.71	2.28	3.48	2.57	1.62
19	28	14	12	26	0.12	0.40	0.48	5.16	5.31	5.11	4.89	5.97	2.16	3.13	2.42
20	21	7	0	52	0.72	0.76	0.35	41.48	1.40	5.54	1.80	3.92	5.01	4.57	2.76
21	0	21	16	43	0.52	0.37	1.77	46.21	1.03	6.28	1.28	1.70	5.96	0.84	2.04
22	14	0	12	54	0.62	0.60	2.28	52.24	1.91	3.24	2.84	3.02	3.16	4.53	4.16
23	7	14	0	59	0.72	0.28	4.18	43.42	1.23	4.76	1.38	4.51	3.38	2.74	2.28
24	28	7	8	37	0.55	-	4.21	36.57	0.27	4.82	1.41	1.22	4.97	0.25	1.12
25	21	28	4	27	1.14	0.71	1.59	33.40	1.43	3.99	2.57	1.80	3.64	1.55	2.88

Continued of the Table 1

No	Fe-Al ₂ O ₃ %	PbO %	Al ₂ O ₃ %	Pb/(Sb+O) m	PbO/Sb ₂ O ₃ m	ZnAl ₂ O ₄ %	0.62ZnAl ₂ O ₄ · 0.28FeAl ₂ O ₃ %	0.62ZnAl ₂ O ₄ · 0.58FeAl ₂ O ₃ %	K ₂ Al ₂ O ₇ %	K ₂ FeAl ₂ O ₇ %	0.7Al ₂ O ₃ · 0.3MgAl ₂ O ₄ %
1	30	0	0	0	0	0	0	0	0	0	0
2	44	0	0.5	22	0	15	5	5	58	24	6
3	62	0	1.8	10	0	10	0	0	35	0	15
4	8	4	0	0	0	0	72	0	25	0	0
5	28	2	0	0	0	10	0	0	60	105	0
6	62	0	2.5	0	0	30	0	10	53	0	0
7	43	0	0	17	0	10	0	0	75	0	6
8	30	0	1	0	0	27	10	5	133	115	0
9	31	0	2.5	30	35	56	0	2	0	0	7
10	51	10.5	0.5	0	0	0	0	0	33	0	7
11	61	5	4	0	0	33	10	0	120	70	0
12	38	2	2.5	36	17	75	0	10	0	0	0
13	44	0	2.0	0	0	33	5	6	120	61	0
14	48	9	0	0	0	0	0	0	15	0	7
15	20	0	0	0	0	0	7	0	68	57	0
16	44	0	3.0	0	0	60	0	0	120	57	0
17	41	2	3.0	30	14	50	0	10	64	12	0
18	37	3	0	10	0	0	0	0	81	81	0
19	28	0.6	0	0	0	8	6	4	25	71	0
20	52	0	2.0	52	60	38	0	11	0	0	0
21	43	0	1.0	0	0	15	10	5	120	78	0
22	54	3	0	8	0	0	0	0	30	18	4
23	39	0	2.0	0	0	30	0	2	0	0	5
24	37	7	0.5	17	37	11	0	3	49	59	0
25	27	0	2.0	21	31	69	6	4	67	51	0

The helium was used as a gas carrier at feed rate up to 60 cm³/min. The Porapak Q and molecular sieves CaX were used as sorbents. The chromatogram data proceeding was performed by methods of interior normalization and absolute calibration [6].

The investigations were carried out varying volume rates of reaction component feed (1500–5500 h⁻¹, reactor temperature (650–850°C), methane-air ratios (1:1-5:1) and SHS catalyst compositions. The experiments were carried out basing on the multi-factor planning [7]. The matrix of experiment planning and reaction product yields in function of varied factors is given in the Table 1.

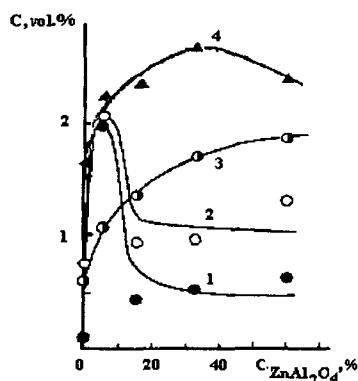
Results and discussion

The investigation of catalytic activity enabled to find the following available principal reaction products: CO, CO₂, H₂O, C₂H₄, C₂H₆, CH₂O, CH₃OH, N₂ traces as well as non-reacted initial components: CH₄, O₂ and N₂.

As regards catalysis the formation of certain compounds or their fragments during reaction running process is occurred at separate active centers located, as a rule, on the catalyst surfaces. These centers may represent both individual atom groups and complex atomic or molecular formations.

They may have divers nature, pH, charges etc. [8-11]. As is generally known from the literature [8, 9] the catalyst components perform certain functions. So, the hydrogenating properties of catalysts are due to such available metals as Ni, Co, Fe as well as their polymerizing effects are caused by hardly reduced oxides, of which are: ThO₂, MnO, MgO, TiO₂, Cr₂O₃, Al₂O₃, ZnO, SiO₂ etc., moreover, some ones, i.e. Al₂O₃, ZnO, having dehydrating functions. In process of catalysts synthesis there are formed new phases those effects on the yield of either compounds may be very substantial.

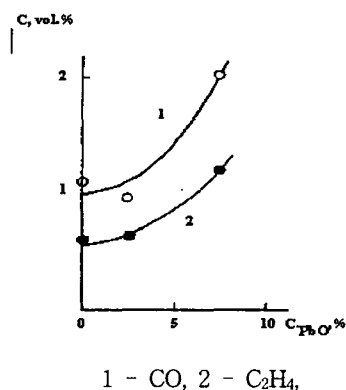
This paper presents results of catalytic activity investigation of 25 catalyst samples obtained by SH-synthesis method. Moreover the results of the X-ray phase analysis of these ceramic contacts were obtained. In the end, there was elaborated a database where the data of chromatography analysis are referred to the compound yields resulted of methane catalytic oxidation. To reveal effects of available phases on the variations of either substance concentrations the data statistic processing was carried out by method of passive experiment [8]. The results of data proceedings are presented in diagram form.



1 - CO, 2 - C₂H₄, 3 - CH₂O, 4 - CH₃OH.
Fig.1. Dependence of reaction product yield on ZnAl₂O₄ phase.

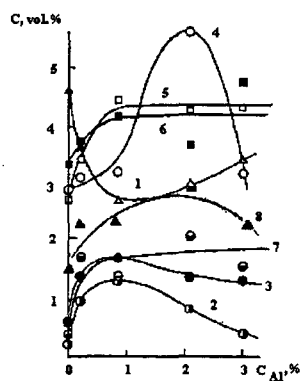
The Fig. 1 shows dependence of formation of some compounds in the catalyst volume on the ZnAl₂O₄ phase concentration. It is evident that the

availability of this phase effects on the methanol yield, its maximum concentration being observed at 30-45% concentrations of this phase. The increase in concentrations of this phase in the catalyst results in a progressive increase of formaldehyde yields. The small ZnAl₂O₄ (4-6 %) concentrations cause the catalytic process to run toward to formation of ethylene and carbon oxide.



1 - CO, 2 - C₂H₄,
Fig.2. Dependence of reaction product yield on the PbO phase.

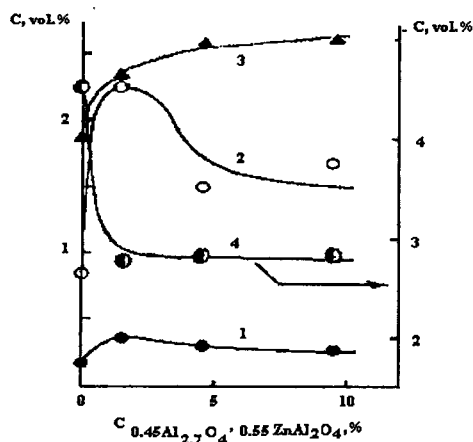
The available lead oxide phase in the catalyst (fig.2) contributes to the increase in carbon oxide and ethylene concentrations in the reaction products.



1 - O₂, 2 - CO, 3 - C₂H₄, 4 - C₂H₆,
5 - CO₂, 6 - H₂O, 7 - CH₂O, 8 - CH₃OH.
Fig.3. Dependence of reaction product yield on the Al phase.

As is obvious from the fig. 3, the catalytic properties are showed too by small concentrations of phase of aluminum metal remained in the samples after SH synthesis completed. Thus, its effects on the yields of methanol, formaldehyde, ethane, ethylene, oxygen and carbon oxide was found.

For methanol and ethane concentration curves the maximum is observed located in the zone of approximate 2% Al concentration. The changes in concentrations of water vapor, carbon dioxide and formaldehyde are observed at concentrations of aluminum metal phase up to 1% with further going up to plateau. The decrease of oxygen concentrations in the reaction products is occurred in the 0 to 1% Al concentration range. Apparently, all these processes may be attributed to the chemical sorption of the compounds on the metal surface.



1 - H₂, 2 - CH₂O, 3 - CH₃OH, 4 - O₂

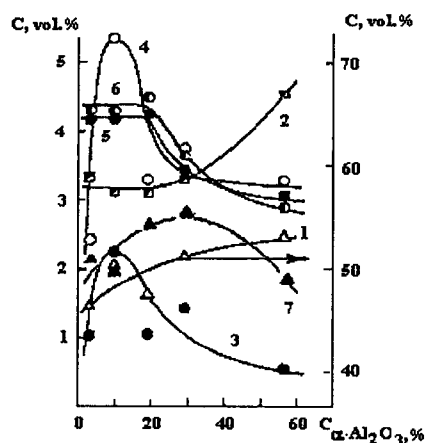
Fig.4. Dependence of reaction product yields on the phase $0.45\text{Al}_{2.7}\text{O}_4 \cdot 0.55\text{ZnAl}_2\text{O}_4$

The fig. 4 represents the dependence of the yields of methane oxidation reaction products on the $0.45\text{Al}_{2.7}\text{O}_4 \cdot 0.55\text{ZnAl}_2\text{O}_4$ phase concentrations in catalyst sample. It is evident that the increase in this phase concentration results in increase of formaldehyde concentrations and in decrease of methane and oxygen concentrations in the reaction products. The methanol concentrations passe through

the maximum at 2% concentration of this phase available in catalyst composition.

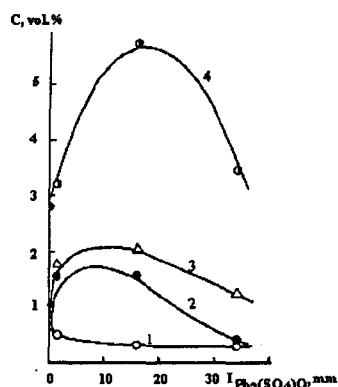
The available aluminum oxide phase substantially effects on the methane catalytic oxidation process running out. As is evident from the Fig.5 the maximum methanol yield is observed at $\alpha\text{-Al}_2\text{O}_3$ concentrations up to 25-40%. With increase of this phase concentrations in the catalyst from 0 to 10% there is observed increasing of ethane and ethylene concentrations in the methane oxidation reaction products while the further increase of the former results in decrease of above mentioned compound yield. In concentration range of $\alpha\text{-Al}_2\text{O}_3$ phase there is observed insignificant but marked decrease in formation of water and carbon dioxide in reaction of partial methane oxidation and depression of oxygen and methane consumption.

Among the phases revealed by X-ray analysis there are some ones for which the concentrations are expressed rather in per-units than in percents that because of primary standard lack. Therefore the dependencies obtained referring on such data are mostly of quality nature. These phases are: $\text{K}_2\text{Al}_{22}\text{O}_{34}$, $\text{Pb}_2(\text{SO}_4)\text{O}$, $\text{KMg}_2\text{Al}_{15}\text{O}_{25}$.



1 - CH₄, 2 - O₂, 3 - C₂H₄, 4 - C₂H₆, 5 - CO₂,
6 - H₂O, 7 - CH₃OH

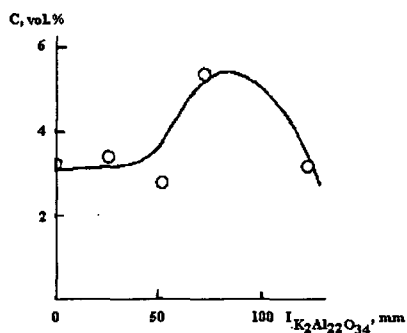
Fig. 5. Dependence of reaction product yields on the phase $\alpha\text{-Al}_2\text{O}_3$



1 - H₂, 2 - CO, 3 - C₂H₄, 4 - C₂H₆
 Fig. 6. Dependence of reaction product yields on the phase Pb₂(SO₄)O

As shown in the fig.6. the available Pb₂(SO₄)O phase in zone of its 5-15 mm reflex line intensity results in increase of ethylene and carbon oxide concentrations and at 2-3 mm - in increase of hydrogen concentrations. In the range of reflex line intensity from 15 to 20 mm the phase Pb₂(SO₄)O passes through the maximum of ethane yield.

For K₂Al₂₂O₃₄ and KMg₂Al₁₅O₂₅ phases the mostly marked effects are found as regards to increase of ethane yield with passage of its concentration curve through the maximum values corresponding to the reflex line intensity of these phases in 90 mm range for K₂Al₂₂O₃₄ and 20 mm range for KMg₂Al₁₅O₂₅ (fig.7 a,b).



1 - H₂, 2 - CO, 3 - C₂H₄, 4 - C₂H₆
 Fig. 7(a). Dependence of ethane yield on the phase K₂Al₂₂O₃₄

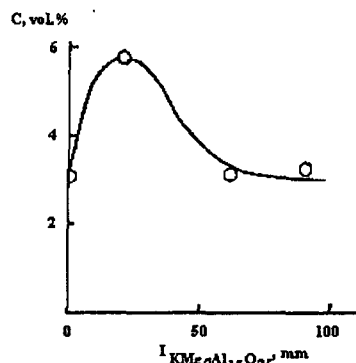


Fig. 7(b). Dependence of ethane yield on the phase KMg₂Al₁₅O₂₅

Conclusions

Thus, the obtained plots are evidences that the phases of catalyst compositions are involved in formation of reaction products of partial methane oxidation by quite direct way. The concentrations of certain catalyst phases are of very considerable importance for catalytic process running. Moreover, it is evident that on the phase surface there are occurred conversion processes involving rather few compounds than the sole one. There is found that the mostly marked effects on the methanol and formaldehyde yields in the reaction products of partial methane oxidation are exerted by availability of such phases as ZnAl₂O₄, α-Al₂O₃, Al, 0.45Al_{2.7}O₄ · 0.55ZnAl₂O₄ and KMg₂Al₁₅O₂₅.

There is shown that the application of multi-factors experiment planning makes easy to follow correlation between the catalyst composition and obtained products of catalytic reaction basing on a limited series of experiments.

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