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CONVERSION OF METHANOL INTO FORMALDEHYDE AND DIMETHOXYMETHANE ON BIFUNCTIONAL CATALYSTS

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***Abstract**: The oxidative conversion of methanol into formaldehyde and dimethoxymethane was studied in the presence of catalysts based on Zr alloys with V, Mo, Fe. The influence of the reaction temperature, contact time, alcohol, air ratio and pressure on the output of formaldehyde and dimethoxymethane was evaluated. The XRD and XPS analyses were performed to determine surface activity of the catalysts which showed a good efficiency. The dependence of final product yields on the reaction conditions and the state of the surface layer of catalyst were established.*

***Keywords**: methanol, catalysts, bimetallic alloys, oxidation, formaldehyde, dimethoxymethane.*

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Introduction

The selective oxidation of methanol to formaldehyde (FA) and dimethoxymethane (DMM) has drawn attention of researchers due to economic and environmental benefits arising from affordable and cheap raw materials. Formaldehyde is widely used in the polymer and resin industry, in the production of dimethoxymethane which is important chemical intermediate used as synthetic reagent and diesel fuel additive. DMM improves the lubricity of diesel fuel, has a high cetane number (> 80). Its use reduces smoke generation during fuel combustion. It is also an excellent solvent in the pharmaceutical and perfume industry due to its low toxicity. Recently, numerous efforts have been made to obtain catalysts for selective oxidation of methanol to DMM. Studies have shown that catalysts such as rhenium oxides [1], heteropoly acids [2], Cu-ZSM-5 [3], V_2O_5 / TiO_2 [4] and V-complex oxide catalysts [5, 6] are active in selective oxidation of methanol to DMM [5,6].

Experimental part

We conducted studies on the oxidation of CH_3OH on bifunctional catalysts — alloys of Zr with V, Mo, Fe, the preparation of which was reported in the previous study [7]. Initial alloys Zr-V; Zr-Mo; V-Fe were obtained through alloying pre-pressed metal samples in an arc furnace under high-purity helium atmosphere conditions following which an X-ray phase analysis was performed. Then, the obtained catalyst samples were preliminarily oxidized in an air stream at 873K for 2–3 hours, followed by treating with hydrogen at 873 K for one hour in a quartz reactor [8]. The oxidation of methanol was carried out at reaction temperature of 403–523 K in pulsed and flow modes (carrier gas - helium) by the ratio $O_2 : He = 1:3 \div 1:10$. A sample of catalyst was loaded into the reactor (an amount of 0.2-0.3 g), mixed with crushed glass of a particle size of 0.06–0.10 mesh. The reaction products were analysed by Gas Liquid Chromatography on Paropak-Q. In addition to formaldehyde (FA) and dimethoxymethane (DMM), a small amount of dimethyl ether (DME), as well as methylformate (MF) were found in the reaction products. The effect of the process temperature, contact time, and the ratio of $CH_3OH: O_2$ on the methanol conversion was studied. The activity of various catalyst samples was compared and their relationship with the content of the active component of the catalyst in the surface layer was investigated. X-ray diffraction (XRD) analyses of catalyst samples were performed ($ZrV_{0.3}$; Zr-V_2, Zr-Mo_2; Zr-$Fe_{0.5}$; $VFe_{0.2}$) before and after the redox treatment. The surface composition and valence state of catalyst components were defined by X-ray Photoelectron Spectroscopy (XPS) using an AE / ES 200B spectrometer [9].

Results and discussion

Initial samples of Zr-$V_{0,3}$; Zr-V_2; Zr-Mo_2; Zr-$Fe_{0.5}$, $VFe_{0.2}$ alloys did not show catalytic activity in the reaction of methanol oxidation at the temperature up to 672-773K, however, after O_2 + H_2-treatment, the activity of the catalysts increased drastically [10]. The activity of obtained Zr alloys with V, Mo, Fe samples in the reaction of the conversion of CH_3OH to DMM was evaluated and presented as a diagram in Fig.1. As shown, the highest activity among evaluated V-catalysts was apparent in $ZrV_{0.3}$ and $VFe_{0,2}$ samples where conversion of methanol at T423K was 76.6 - 80.0% respectively.

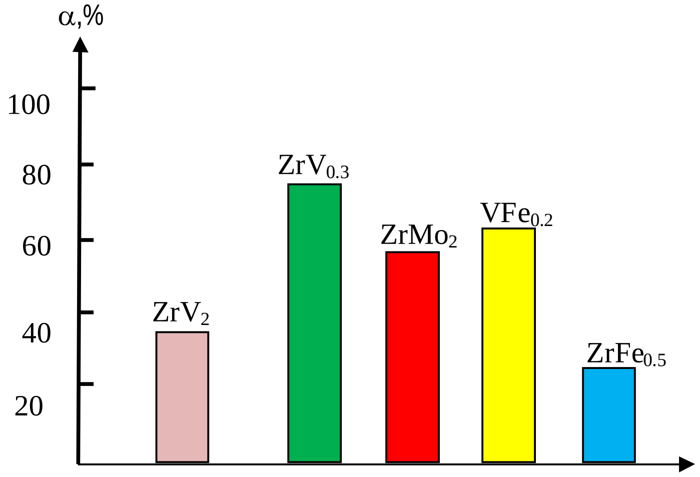

Fig. 1. Catalytic activity of catalyst samples in the oxidation reaction of CH_3OH T- 423K; P - 0.15 MPa, ratio of alcohol : air = 1 : 4

Bimetallic catalysts Zr-$V_{0.3}$ and V-$Fe_{0.2}$ showed oxidizing and reducing properties, which are necessary for the oxidation of methanol in formaldehyde followed by condensation of CH_2O and methanol with formation of DMM :

$$2\ CH_3OH + CH_2O \rightarrow CH_3–O–CH_2–O–CH_3 + H_2O$$

The influence of reaction conditions such as temperature, pressure, ratio of alcohol/air on the yields of final products was studied for the catalyst Zr-$V_{0.3.}$ As can be seen from the Fig.2, the peak of DMM is at temperatures below 473K (about 403-423K). In this temperature range, the effect of the alcohol/air ratio was studied and shown in Fig.3. With the increasing alcohol/air ratio, the selectivity of DMM decreases, while the selectivity of DME and MF increases. The pressure in the system has a great influence on the methanol oxidation process and DMM yield, as can be seen from Fig.4. With the increasing pressure in the system to 0.15 MPa, the selectivity of DMM increases, and then decreases.

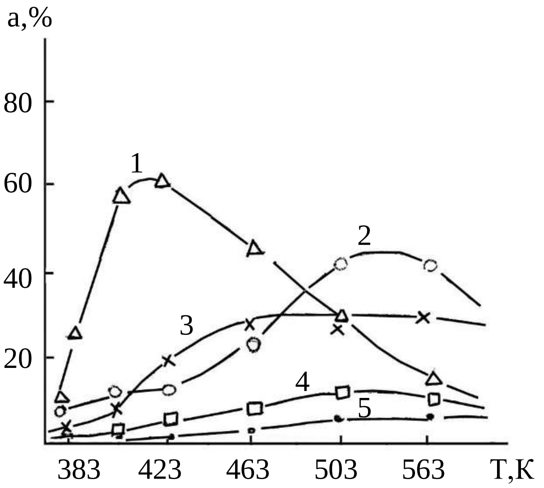

Fig. 2. Dependence of the yield of products of oxidation CH_3OH on temperature: temperature: catalyst $ZrV_{0.3.}$
1 - DMM, 2 - DME, 3 - FA, 4 - MF, 5 - CO_2.

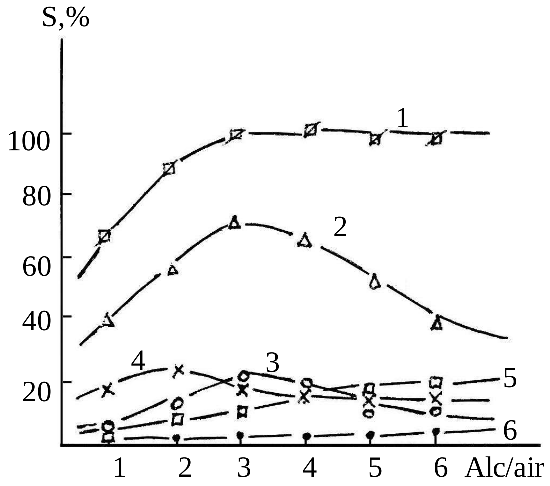

Fig. 3. Dependence of selectivity of products oxidation CH_3OH on the ratio of alcohol: air:catalyst $ZrV_{0.3}$, T=423K.
1 - conversion of CH_3OH
2 - DMM, 3-DME, 4-FA, 5 - MF, 6-CO_2

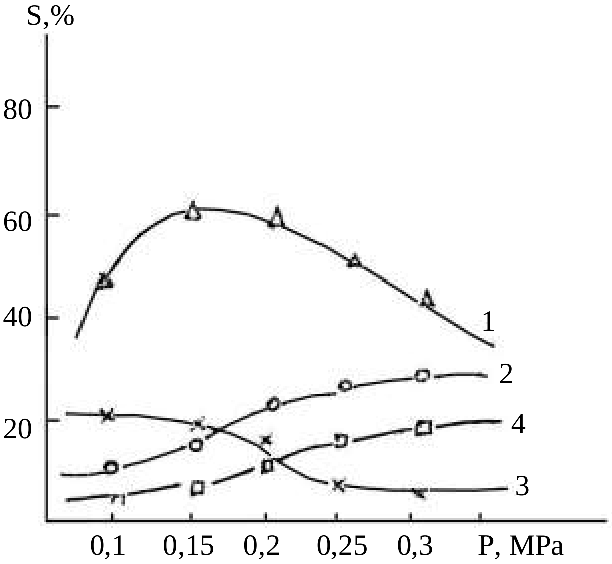

Fig. 4. Dependence of selectivity of reaction products on air pressure: $ZrV_{0.3}$; T-423K.
1- DMM, 2- DME, 3 - FA, 4- MF

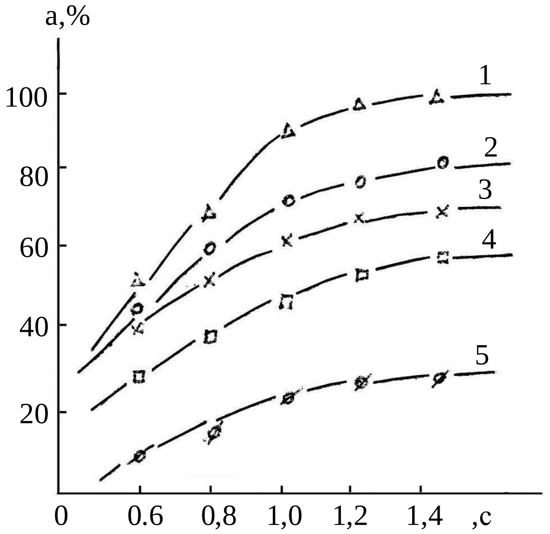

Fig. 5. Effect of contact time on the reaction oxidation CH_3OH over catalytic systems: T - 423K. 1- $ZrV_{0,3}$ 2-$VFe_{0,2}$
3-$ZrMo_2$ 4-ZrV_2 5-$ZrFe_{0,5.}$

The influence of the contact time on conversion of CH_3OH at T 423K; pressure - 0.15 MPa on the samples of catalysts is shown in Fig.5 from which it can be seen that the optimal contact time is $\tau = 1.2$ sec. for $ZrV_{0,3}$.

The maximum yield of formaldehyde and the formation of DMM occured at temperatures below 423 K indicating that a lower reaction temperature contributes to a higher conversion of methanol into DMM. However, the formation of dimethyl ether and methyl formate began to increase at a high reaction temperature. In the presence of O_2, the hydrogenated vanadium oxide (sample $ZrV_{0.3}$ after

O_2+H_2- treatment O_2+H_2-) showed a good activity with DMM selectivity of 67.0% wt. After two hours, the reaction reached a steady state and remained stable for more than 20 hours.

The XRD analyzes of catalyst samples after oxidative treatment in an air stream at a temperature of 873 K for 2–3 hours indicated deep phase changes in the surface layer and the formation of V, Mo, Zr oxides and other non-stoichiometric compositions [8]. Vanadium and molybdenum oxides as more active metals, segregated on the surface of the catalysts, and oxides of Zr and zirconium remained as a catalyst support. Schematically, the structure of such catalyst can be represented in Fig.6. The diffusion of oxygen in such crystalline structures was facilitated which led to an increase in the activity of the catalyst.

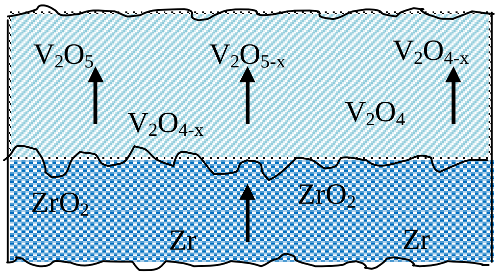

Fig. 6. Schematic structure of Zr- $V_{0..3}$ catalyst after O_2 - treatment.

Further, the obtained samples were hydrogenated in a stream of hydrogen at 873K for 1 hour. As shown by the results of XPS analyses, the conditions of O_2 + H_2 processing led to changes not only in the surface layer of the catalyst but in the valence state of active components of the alloys as well [9]. The redox treatment affects only the surface layer of the alloy, however, the bulk structure of the catalyst remained unchanged, as shown by physicochemical studies. The increased activity of the catalyst was associated with the appearance of vanadium, molybdenum in the intermediate oxidation state in the samples of the most active catalysts - $ZrV_{0.3}$; VFe $_{0,2}$; Zr-Mo_2:

$$V^{5+} \leftrightarrow V^{4+} \leftrightarrow V^{3+};$$

$$Mo^{4+} \leftrightarrow Mo^{5+} \leftrightarrow Mo^{6+}.$$

The observed increased activity of such a catalytic system is apparently a result of a combination of qualitative changes in the surface composition of the catalyst due to the segregation of the corresponding metal of variable valency (vanadium or molybdenum) on the surface of the alloy and further realization of its optimal oxidation level under the influence of the reaction condition.

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METANOLUN FORMALDEHİDƏ VƏ DİMETOKSİMETANA BİFUNKSİONAL KATALİZATOR ÜZƏRİNDƏ CEVRİLMƏSİ

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Metanolun formaldehidə və dimetoksimetana çevrilməsi Zr-n V, Mo, Fe ilə ərintiləri əsasında katalizatorların iştiraki ilə öyrənilmişdir. Metanolun müxtəlif maddələrə selektiv oksidləşməsi oksigenin iştirakı ilə yüksək aktivlik qöstərmiş və bimetalik Zr–V, Zr–Mo, V–Fe katalizatorların səthində aparılmışdır. Oksidləşmə reaksiyanın gedişinə, reaksiya məhsullarının çıxımına, reaksiyanın temperaturuna, kontakt müddətinin, təzyigin və ilkin maddələrin spirt : O_2 mol nisbətinin təsiri öyrənilmişdir. Katallizatorların səthi aktivliklərini müəyyən etmək məgsədi ilə RFA və RFES analizləri aparılmışdır. Reaksiya məhsulların çıxımlarının reaksiyanın aparılma şəraitindən və katalizatorun səthinin vəziyyətindən asıllığı müəyyən edilmişdir. Katalizatorun aktiv mərkəzlərində metanoldan DMM alınmasının mexanizmı haqda ilkin fərziyyə irəli sürülmüşdür.

Açar sözlər: *metanol, katalizatorlar, bimetallik ərintilər, oksidləşmə, formaldehid, dimetoksimetan.*

ПРЕВРАЩЕНИЯ МЕТАНОЛА В ФОРМАЛЬДЕГИД И ДИМЕТОКСИМЕТАН НА БИФУНКЦИОНАЛЬНЫХ КАТАЛИЗАТОРАХ

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Окислительное превращение метанола в формальдегид и диметоксиметан изучали в присутствии катализаторов на основе сплавов Zr с V, Mo, Fe. Изучено влияние температуры реакции, времени контакта, соотношения спирт/воздух, давления на выход формальдегида и диметоксиметана. Проведены РФА и РФЭС анализы для исследования поверхностной активности катализаторов, проявивших хорошую эффективность. Установлена зависимость выходов конечных продуктов от условий проведения реакции и состояния поверхностного слоя катализатора.

Ключевые слова: *метанол, катализаторы, биметаллические сплавы, окисление, формальдегид, диметоксиметан.*