K.A. Shorayeva[1], B.K. Massalimova[1], Bespalko Yu.N.[2], V. A. Sadykov[2],

[1]M.Kh. Dulati Taraz State University, 080000 Taraz, Kazakhstan;
[2]Boreskov Institute of Catalysis, 630090 Novosibirsk, Russia.
E-mail: k.a.shorayeva@mail.ru, e-mail: massalimova15@mail.ru, dulia@yandex.ru, vasadykov@mail.ru

TESTING OF MO-CONTAINING CATALYSTS APPLIED TO AL-, AL/ZR-PILLARED CLAYS DURING THE OXIDATIVE DEHYDROGENATION OF ETHANE TO ETHYLENE

Abstract. The development of an alternative method for the oxidative dehydrogenation of ethane to ethylene is an important task in the presence of a suitable catalyst. Mo-containing catalyst systems applied to Al-, Al/Zr-columnar clays were prepared. The textural characteristics of the synthesized Al-, Al/Zr-columnar clays differ from the textural properties of natural clay with an increase in their specific surface from ~54 m^2/g to ~215 m^2/g. The LaNbMo and VMoTeNb catalyst systems applied to l-, Al/Zr-columnar clays showed higher activity and selectivity for oxidative dehydrogenation of ethane (ODH). A detailed characterization was achieved using XRD, adsorption of N_2, SEM, BET to study the texture properties of the synthesized catalysts. The highest activity and ethylene selectivity were shown by 10% VMoTeNb/PILCs and 20% VMoTeNb/PILCs catalysts. The lowest ethylene selectivity was exhibited by 10% LaNbMo/PILCs and 20% LaNbMo/PILCs catalysts. The results obtained indicate that the application of LaNbMo and VMoTeNb polyoxide active phases to Al-, Zr-columnar clays can improve the physical and mechanical properties of these types of catalysts due to changes in both the nature of the crystalline phase and the catalytic properties in oxidation reactions.
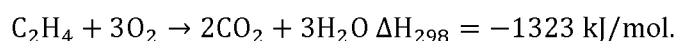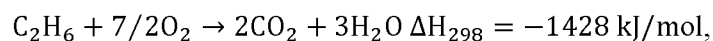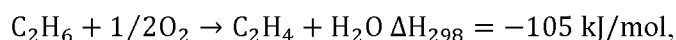**Keywords:** oxidative dehydrogenation; ethane ethylene; mechanism ethylene production.

1. Introduction

In recent years natural gas reserves and their rational use have been of great interest. Partly, natural gas can be attributed to renewable natural resources, since methane emission begins immediately with rotting biomass of animal and vegetable origin, and they renew faster than oil.

Currently, natural gas is widely used in the power industry and much less in the chemical industry due to some inertness of the gas. That is, many chemical reactions that have an industrial sense require too high costs to be economically viable [1, 2]. For example, the process of dehydration of light alkanes also presents a significant problem associated with their low reactivity, high energy consumption, and low selectivity [3-5].

One of the ways to intensify the dehydrogenation of alkanes is their oxidative dehydrogenation (ODE). In the case of oxidative dehydrogenation of ethane (ODE), these reactions are as follows:

$$C_2H_6 + 1/2O_2 \rightarrow C_2H_4 + H_2O \; \Delta H_{298} = -105 \text{ kJ/mol,}$$

$$C_2H_6 + 7/2O_2 \rightarrow 2CO_2 + 3H_2O \; \Delta H_{298} = -1428 \text{ kJ/mol,}$$

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 3H_2O \; \Delta H_{298} = -1323 \text{ kJ/mol.}$$

Despite the widespread use of steam cracking, fluid catalytic cracking, and catalytic dehydrogenation in the synthesis of olefins, intensive research is underway to develop oxidative dehydrogenation (ODH) catalysts for alkanes. This approach can significantly reduce the temperature of this process, which leads to higher selectivity and less coking of the catalysts [1, 3]. A number of catalysts have been proposed to improve ethane conversion and ethylene selectivity [6-10].

Ethane ODE is performed on a solid catalyst in which ethane reacts with an oxidizing agent, usually oxygen. When comparing the ODH of ethane with existing commercial processes, a number of advantages are noted: there is no thermodynamic limitation (ΔGR, 298K$°$=-128 kJ/mol); the reaction is exothermic (ΔHR, 298K$°$=-106 kJ/mol), which eliminates the need for energy; a limited number of reaction products (COx and ethylene) is observed; catalyst deactivation with coke does not occur due to the presence of oxygen in the reaction medium [8]. Therefore, the development of an alternative method for the oxidative dehydrogenation of ethane to ethylene in the presence of a suitable catalyst has become an urgent task.

Based on this, the goal of this study is to develop new catalytic systems applied to columnar clays in order to obtain an environmentally friendly and economically viable catalyst, designed to increase ethane conversion and ethylene selectivity.

2. Experimental part
2.1 Catalytic synthesis
Research objects are polyoxide catalyst systems deposited on columnar clays capable of catalyzing the process of oxidative dehydrogenation of ethane to ethylene.

2.1.1 Mechanical activation of natural clays

To activate natural kaolinite clays, the AGO-2 high-voltage planetary mill was used. The grinding was carried out with steel balls with a diameter of 8 mm and a total weight of 200 g in 150 ml water-cooled steel drums. The ratio of balls' mass to the mass of mixture (M) was 20:30. The rotational speed of the drums was 1200 rpm (40g). To ensure a low level of powder contamination in the steel grinding medium, the natural lining of the working surface of drums and balls, obtained by preliminary activation of a similar mixture, leading to the coating of the surface of the balls and the inner surface of the drums with the processed composition, was used [11].

2.1.2 Synthesis of columnar clays

Pre-cleaned and ground natural clays with particle diameters up to 0.25 mm were incubated for 24 hours at room temperature for complete hydration., Aluminum and zirconium hydroxocomplexes were used as intercalating solutions (hydrolysis of aqueous solutions of aluminum chloride (0.2 M) and zirconium chloride (0.2 M) in aqueous NaOH solution (0.5 M)). Pillarization was carried out by slowly adding intercalating agent to clay samples, followed by washing of chlorine ions. The obtained Al-, Zr-columnar clays were dried for one day at room temperature, then they were calcined at 500 $°$C for 5 hours.

2.1.3 Preparation of catalysts

Mixed oxides LaNbMo and MoVTeNb with nominal atomic ratios La:Nb:Mo=1:0.8:0.2 and V:Mo:Te:Nb=0.3:1:0.23:0.12 were prepared. The synthesis of the catalysts included the following stages: 1) an aqueous solution containing ammonium paramolybdate (Merck, 99%), telluric acid (Sigma-Aldrich, 98%) and ammonium metavanadate (Sigma-Aldrich, 99.5%), was prepared with constant stirring at 80 °C FROM; separately 2) an aqueous solution of niobium oxalate (ABCR Laboratories, 99%) was also prepared at 80 °C. 3) then, a solution of niobium oxalate was added to a mixture containing ammonium paramolybdate, telluric acid and ammonium metavanadate with vigorous continuous stirring. The resulting mixture turned into a suspension, which was cooled to room temperature. Using the impregnation method, the prepared polyoxide system was applied onto the surface of Al-, Al/Zr-columnar clays by the volume of moisture capacity. Then, the catalyst samples were dried at 50 °C for gradual evaporation of water. The catalysts were first thermally treated at 310 °C for 1 h, then they were calcined at 700 °C for 3 h in a stream of nitrogen.

2.2 Characterization of catalysts
2.2.1 Study of physico-chemical properties of the catalysts

The texture characteristics of columnar clays were studied using nitrogen adsorption and desorption isotherms using the BET method (Brauner-Emmett-Teller) on a SORBTOMETR-M device (Russia). The

change in the phase composition of the catalysts was monitored using x-ray phase analysis on a general-purpose diffractometer DRON-4-0.7 with CuKα radiation (Russia).

2.2.2 Statistical processing of data

Statistical analysis was performed with a help of SPSS Statistical Program (version 16, Chicago, Illinois, USA) using semi-logarithmic regression analysis Graphpad PRISM Software (San Diego, California, USA).

2.3 Catalytic test

2.3.1 Reactor plant with on-line chromatographic analysis

Catalytic experiments were carried out in an automated laboratory flow reactor with on-line chromatographic analysis of the components of the reaction mixture. A quartz tube reactor with an internal diameter of 10 mm and 200 mm in length was equipped with two thermocouples, one of which showed the temperature of the wall of the reactor, and the other measured the temperature of the catalyst layer. All runs were performed by feeding a mixture, consisting of ethane (C_2), oxygen (O_2) and nitrogen (N_2) as a diluent in the ratio $C_2H_6:O_2:N_2 = 10:10:80$, into the reactor. The purity of ethane, oxygen, and nitrogen used in this work was 99.7 vol. %, 99.996 vol. %, and 99.999 vol. %, respectively. The gas flow rate was quantified using independent mass flow temperature controllers.

2.3.2 Reaction conditions

For a typical experiment, 0.60 g of a heat-treated catalyst with an average particle size of 150 μm was charged to the reactor. Before carrying out the reaction, the composition of the gas mixture was checked using GC, and was preheated to 140 °C. A blank experiment, conducted at 480 °C, confirmed the absence of transformations of both ethane and oxygen in the absence of a catalyst.

The reaction was carried out for 6 hours. In all experiments, the carbon balance was in the range of 100% ± 2.0%. For systematical study of the effect of temperature and contact time on the catalytic behavior of LaNbMo and VMoTeNb catalysts, the first series of experiments were carried out in accordance with the factorial design of the experiment. The partial pressures of ethane, oxygen, and nitrogen at the inlet were fixed at 7.0, 5.5, and 65.5 kPa, respectively.

3. Results and discussion

3.1 Texture characteristics of columnar clays

The specific surface of Al-, Al/Zr-columnar clays was determined using indicators of nitrogen adsorption and desorption isotherms by the BET method on a SORBTOMETR-M device (Russia) (table 1).

Table 1 - Textural characteristics of Al-, Al/Zr-columnar clays

№	Compound	S_{BET}, m^2/g	$V_{pore\ ads}$, cm^3/g	$V_{pore\ des}$, cm^3/g	$V_{micropore,C}$ m^3/g	Average pore diameter, A	$D_{pore\ ads}$, A	$D_{pore\ des}$, A
1	glina MM	53.7097	0.115297	0.119158	0.002722	95.0805	139.1295	117.4108
2	Al-PILCs	173.1012	0.048405	0.061924	0.049691	26.6481	111.0876	51.2044
3	Al/Zr-PILCs	216.3813	0.046253	0.061939	0.063175	24.3099	105.5924	48.1946

Note: V pore ads/des – by method BJH;
Average pore diameter: 4V/A BY BET;
BJH adsorption/desorption average pore diameter: 4V/A.

The textural properties of the synthesized Al-, Al/Zr-columnar clays are shown in table 1. The specific surface of natural clay treated with intercalating agents increased from ~54 m^2/g to ~215 m^2/g.

It can be seen from Figure 1 that the specific surface (SBET, m^2/g) of natural clay grows when it is pillared with intercalating agents of aluminum and zirconium. The average pore diameter of Al-, Al/Zr-columnar clays gradually decreases compared to natural clay. In this case, the average micropore volume (Vmicropore, cm^3/g) in all the studied samples remains unchanged.
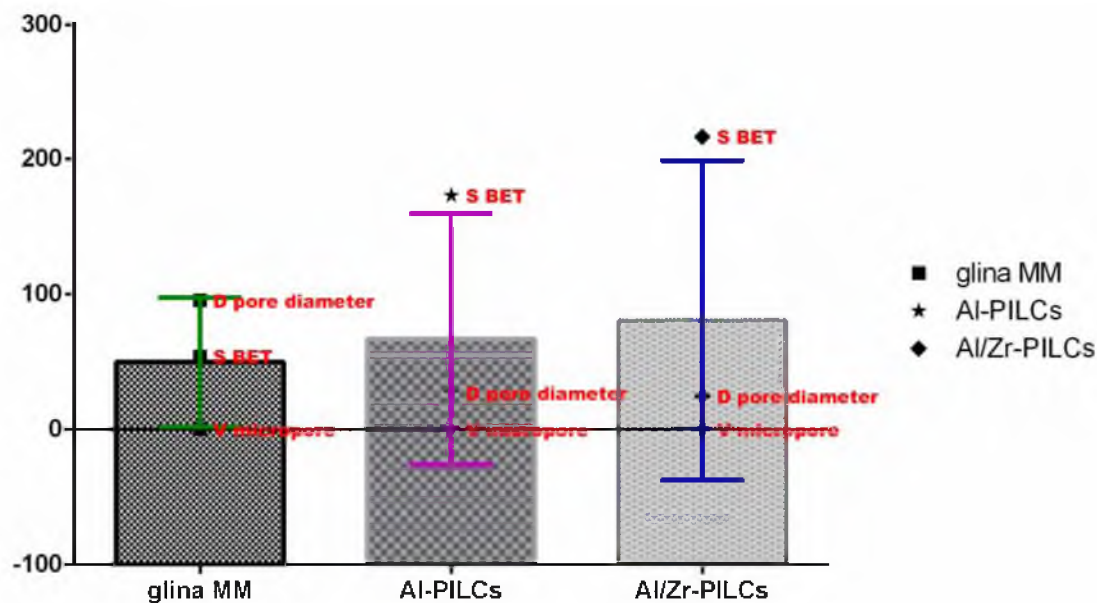
Figure 1 - Comparison of the texture properties of natural clay with Al-, Al / Zr-columnar clays

3.2. Catalytic testing

Catalytic properties of the polyoxide LaNbMo and VMoTeNb catalysts applied to Al-, Zr-columnar clays in the oxidative dehydrogenation reaction of ethane (ODE) were studied. The synthesized samples were tested in a flow reactor with on-line chromatographic analysis of the reaction mixture components. The test results are shown in table 2 and in figure 2.

Table 2 - Catalytic properties of polyoxide catalysts LaNbMo and VMoTeNb applied
to columnar clays in the oxidative dehydrogenation of ethane

| № | Sample | Tp., °C | t, c | X, % | Selectivity,% | |
					C_2H_4	CO_x
1	10% LaNbMo/PILCs	400	5,52	10,2	36,1	63,9
		430	5,52	14,6	35,3	64,7
		460	5,52	21,0	35,3	64,7
2	20% LaNbMo/PILCs	400	3,36	0,8	34,1	65,9
		430	3,36	1,5	38,0	62,0
		460	3,36	2,6	44,7	55,3
3	10% VMoTeNb/PILCs	420	5,52	49,3	91,9	8,1
		441	5,52	65,3	87,7	12,3
		461	5,52	79,6	81,3	18,7
4	20%VMoTeNb/PILCs	417	5,52	47,4	90,9	9,1
		440	5,52	62,9	87,6	12,4
		460	5,52	80,6	78,8	21,2

Note: PILCs – Al/Zr-pillared clays

For the initial reaction mixture (vol. %) the components (table 2, figure 2) were taken in the following ratios $C_2H_6:O_2:N_2 = 10:10:80$.
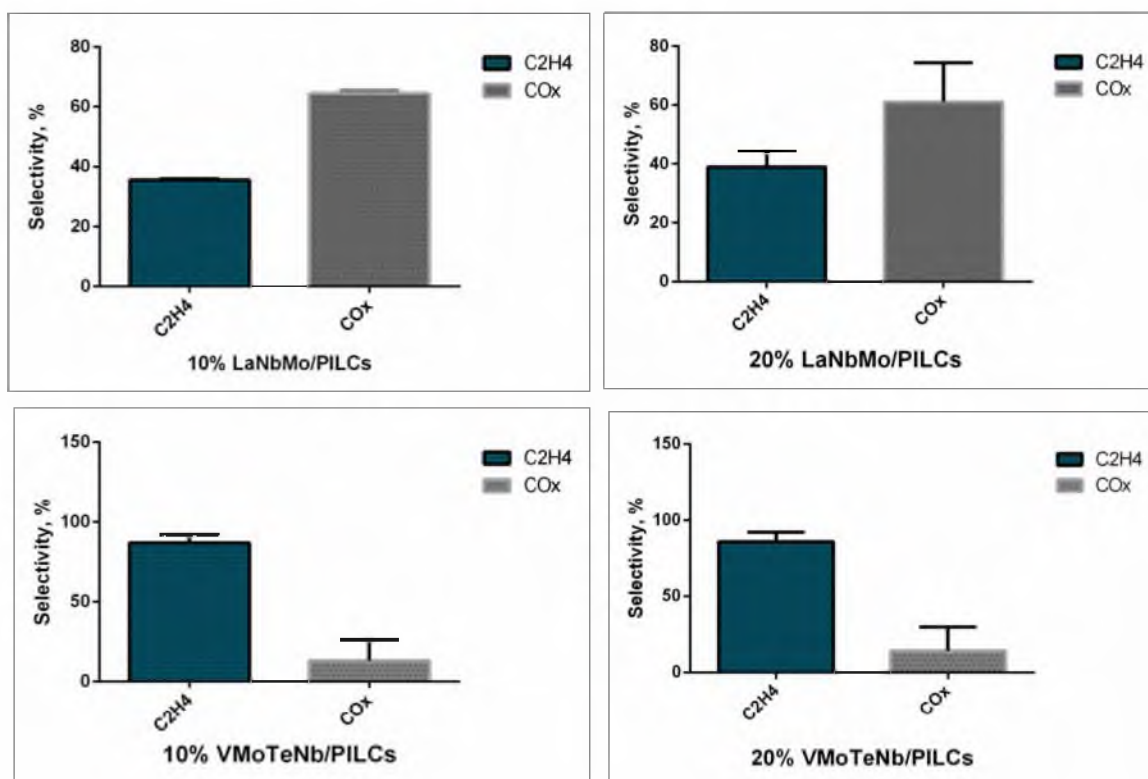
Figure 2 - Oxidative dehydrogenation of ethane to ethylene with LaNbMo and VMoTeNb polyoxide catalysts

The results of catalytic tests of the polyoxide LaNbMo and VMoTeNb catalysts (Figure 2) applied to Al-, Al/Zr-columnar clays showed that catalysts with the chemical composition of VMoTeNb have high selectivity during the oxidative dehydrogenation of ethane to ethylene, despite the active mass in them.

Mixed metal oxides MoVTeNbO have low surface area, which limits their potential industrial use. The inclusion of metal oxides on the substrate improves the mechanical properties of the catalysts and, as a rule, modifies their catalytic behavior, which can adversely affect the catalytic activity [10, 12].

It is known [10, 13] that Mo-containing catalysts applied to natural supports (alumina, modified clays, zeolites) have a higher reactivity than alumina.

Conclusions. The results obtained indicate that the deposition of LaNbMo and VMoTeNb polyoxide active phases on Al-, Zr-columnar clays can improve the physical and mechanical properties of these types of catalysts by changing the nature of the crystalline phase, as well as catalytic properties in oxidation reactions

К.А. Шораева[1], Б.К. Масалимова[1], Ю.Н. Беспалко[2], В.А. Садыков[2]

[1] М.Х. Дулати атындағы Тараз мемлекеттік университеті, Тараз, Қазақстан;
[2] Г.К. Боресков атындағы катализ институты, Новосібір, Ресей

Al-, Al/Zr-БАҒАНАЛЫҚ САЗБАЛШЫҒЫНА ОТЫРҒЫЗЫЛҒАН Mo-ҚҰРАМДЫ КАТАЛИЗАТОРЛАРДЫ ЭТАНДЫ ЭТИЛЕНГЕ ТОТЫҚТЫРА ДЕГИДЛЕУ ҮДЕРІСІНДЕ СЫНАУ

Аннотация. Олефиндер синтезінде бу, сұйық каталитикалық крекингтің және каталитикалық дегидрогенизацияның кеңінен қолданылуына қарамастан, алкандарды тотықтыра дегидлеу (ODH) катализаторларын құру бойынша қарқынды зерттеулер жүргізілуде. Этанды тотықтыра дегидлеу (ЭТД)

қатты катализаторда орындалады, онда этан тотықтырғышпен, ягни оттегімен әрекеттеседі. Этанды этиленге дейін тотығу арқылы дегидрлендіруді жүзеге асыру үшін жоғары селективті катализатор дайындау басты міндет болып саналады.

Осылайша қоспалар құрамы: La:Nb:Mo = 1:0.8:0.2 және V: Mo:Te:Nb = 0.3:1: 0.23:0,12 болатын Al-, Al/Zr-бағаналы сазбалшықтарга отырғызылған LaNbMo және MoVTeNb катализаторы дайындалды. Бағаналы саздың құрылымдық сипаттамасы ВЕТ әдісін қолдана отырып, азот адсорбциясы және десорбция изотермаларының көрсеткіші негізінде зерттелді. Синтезделін алынган Al-, Al/Zr-бағаналық сазбалшықтың құрылымдық сипаттамасы табиги сазбалшық құрылымынан үстіңгі қабытының ~54 м²/г-ден 15215 м²/г дейін өсуі арқылы ерекшеленеді.

Автоматтандырылған online хроматографиялық анализ орнатылган зертханалық ағынды реакторда каталитикалық тәжірибе жүргізу барысында Al-, Al/Zr-бағаналық сазбалшық бетіне отырғызылган LaNbMo және VMoTeNb каталитикалық жүйелері этанның тотықтыра дегидрленуіне (ЭТД) қатысты өте жоғары белсенділік пен селективтілік танытты.

Синтезделген катализаторлардың құрылымдық қасиеттері XRD, N₂, SEM, ВЕТ адсорбция әдістері негізінде сипатталды. Ең жоғары белсенділік пен этилен селективтілігін 10% VMoTeNb/PILCs және 20% VMoTeNb/PILCs катализаторлары көрсетті. Этиленнің ең төмен селективтілігін LaNbMo/PILC 10% және LaNbMo/PILCs 20% катализаторлары көрсетті.

Al-, Al/Zr-бағаналы сазбалшықтарга отырғызылган LaNbMo және VMoTeNb катализаторларының каталитикалық сынақ нәтижесін сараптауда химиялық құрамы VMoTeNb катализаторының этиленге тотығу арқылы дегидрлену үдерісінде құрамындагы белсенді массалардың мөлшеріне қарамастан жоғары селективті екендігін көрсетті.

Аралас металл оксидтері MoVTeNb аз көлемді үстіңгі бетке ие, бұл олардың өнеркәсіптік қолданылуын шектейді. Металл оксидтерін субстратқа қосу катализатордың механикалық қасиетін жақсартады және, әдетте, каталитикалық белсенділікке теріс әсер етуі мүмкін каталитикалық әрекетті өзгертеді.

Алынган нәтижелер Al-, Zr-бағаналы сазбалшықтарга отырғызылған полиоксидтік белсенді фазалы LaNbMo және VMoTeNb катализаторларының тотығу реакциясындагы кристалл фаза мен каталитикалық қасиеттерінің жақсаратындыгын көрсетті.

Түйін сөздер: тотықтыра дегидрлеу, этан, этилен, механизм, этилен өндірісі.

К.А. Шораева[1], Б.К. Масалимова[1], Ю.Н. Беспалко[2], В.А. Садыков[2]

[1] Таразский государственный книверситет имени М.Х. Дулати, Тараз, Казахстан;
[2] Институт катализа имени Г.К. Бореского, 630090 Новосибирск, Россия

ИСПЫТАНИЕ МО-СОДЕРЖАЩИХ КАТАЛИЗАТОРОВ, НАНЕСЕННЫХ НА Al-, Al/Zr-СТОЛБЧАТЫЕ ГЛИНЫ, В ПРОЦЕССЕ ОКИСЛИТЕЛЬНОГО ДЕГИДРИРОВАНИЯ ЭТАНА В ЭТИЛЕН

Аннотация. Несмотря на широкое использование парового крекинга, флюид-каталитического крекинга и каталитического дегидрирование при синтезе олефинов, ведутся интенсивные поиски по разработке катализаторов окислительного дегидрирования (ODH) алканов. ОДЭ этана выполняется на твердом катализаторе, в котором этан реагирует с окислителем, обычно кислородом. Разработка альтернативного способа окислительного дегидрирования этана в этилен является актуальной задачей в присутствии подходящего катализатора.

Таким образом, были приготовлены катализаторы – смешанные оксиды LaNbMo и MoVTeNb с номинальными атомными отношениями La:Nb:Mo=1:0,8:0,2 и V:Mo:Te:Nb=0,3:1:0,23:0,12, нанесенные на Al-, Al/Zr-столбчатые глины. Были изучены текстурные характеристики столбчатых глин по показателям изотерм адсорбции и десорбции азота по методу БЭТ. Результаты данного исследования показали, что текстурные свойства синтезированных Al-, Al/Zr-столбчатых глин отличаются от текстурных свойств природной глины с увеличением их удельной поверхности от ~54 м²/г до ~215 м²/г.

При проведении каталитических эксперименов на автоматизированном лабораторном проточном реакторе с on-lineхроматографическим анализом каталитические системы LaNbMo и VMoTeNb, нанесенные на Al-, Al/Zr-столбчатые глины проявляли более высокую активность и селективность в отношении окислительного дегидрирования этана (ODH).

Детальная характеристика была достигнута с использованием XRD, адсорбции N₂, SEM, БЭТ для изучения текстурных свойств синтезированных катализаторов. Наибольшую активность и селективность по этилену показали 10% VMoTeNb /PILCs и 20% VMoTeNb /PILCs катализаторы. Наименьшей селективностью по этилену обладали 10% LaNbMo/PILCs и 20% LaNbMo/PILCs катализаторы.

Результаты каталитических испытаний полиоксидныхLaNbMo и VMoTeNb катализаторов, нанесенных на Al-, Al/Zr-столбчатые глины, показали, что при окислительном дегидрировании этана в этилен высокую селективность имеют катализаторы с химическим составом VMoTeNb, несмотря на содержание в них активной массы.

Смешанные оксиды металлов MoVTeNb имеют низкую площадь поверхности, что ограничивает их потенциальное промышленное применение. Включение оксидов металлов на подложку улучшает механические свойства катализаторов и, как правило, модифицирует их каталитическое поведение, что может оказывать неблагоприятное влияние на каталитическую активность.

Полученные результаты исследования свидетельствуют о том, что нанесение на Al-, Zr-столбчатые глины полиоксидных активных фаз LaNbMo и VMoTeNb может улучшить физические и механические свойства катализаторов этих типов за счет изменения как природы кристаллического фазы и каталитические свойства в реакциях окисления.

Ключевые слова: окислительное дегидрирование; этан; этилен; механизм; производства этилена.

Information about authors

K.A. Shorayeva– 3-year PhD student of specialty chemistry, M.Kh. Dulati Taraz State University, Tole bi str. 60, Taraz, Kazakhstan. E-mail: k.a.shorayeva@mail.ru.

B.K. Massalimova– candidate of chemical sciences, associated professor, manager of the department of "Chemistry and chemical technology", M.Kh. Dulati Taraz State University, Tole bi str. 60, Taraz, Kazakhstan. E-mail: massalimova15@mail.ru.

Yu.N. Bespalko – candidate of chemical sciences, Boreskov Institute of Catalysis, Novosibirsk, Russia. E-mail: dulia@yandex.ru

V.A. Sadykov– doctor of chemical sciences, professor, Boreskov Institute of Catalysis, Novosibirsk, Russia. E-mail: vasadykov@mail.ru.

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