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THE MICRO-MESOPOROUS SYSTEM OF ZRO_2-SIO_2-TIO_2 OXIDES AS CATALYST SUPPORT FOR DEHYDROGENATION PROCESSES

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INTRODUCTION

Recently, dehydrogenation of light alkanes to the corresponding olefins is one of the most studied catalytic processe[1,2]. Due to their high reactivity, light olefins are widely used as chemical building blocks for the production of polymers and many products and chemicals for everyday use. Herewith, propylene and ethylene are most important for the chemical industry. Until recently, they were obtained mainly as by-products of the processes of steam thermal and liquid phase catalytic cracking of the products of distillation of crude oil and associated petroleum gases. But the demand for pure propylene is far ahead of its production by these traditional methods. Therefore, an alternative, "non-oil" technology for the targeted production of propylene by direct catalytic dehydrogenation of propane (DHP) is developing at a faster pace[3]. This is also facilitated by the downward trend in world oil reserves, a decrease in the propylene content in its reprocessed products and a significant increase in the production of cheap natural shale gas; in which ethane and propane are also contained.

The main commercial technologies of DHP are based on two Cr_2O_3/Al_2O_3 and Pt-Sn/Al_2O_3 catalytic systems, but their periodic oxidative regeneration leads to a decrease in activity and structural stability due to particle agglomeration (sintering) and they must be replaced after 1–3 years of operation[4]. In addition, it is noted that the high cost of Pt as well as serious pollution issues caused by Cr restrict the further development of the

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[1] Sattler J.H.B., Ruiz-Martinez J., Santillan-Jimenez E., Weckhuysen B.M. Catalytic Dehydrogenation of Light Alkanes on Metals and Metal Oxides. Chem. Rev. 2014. V. 114. №. 20. P. 10613–10653. URL: https://doi.org/10.1021/cr5002436.

[2] Nawaz Z. Light alkane dehydrogenation to light olefin technologies: A comprehensive review.*Rev. Chem. Eng.* 2015. V. 31. № 5. P. 413–436. URL: https://doi.org/10.1515/revce-2015-0012**.**

[3] Макарян И.А., Рудакова М.И., Савченко В.И. Промышленные процессы целевого каталитического дегидрирования пропана в пропилен. *Междунар. научн. журнал «Альтернативная энергетика и экология»*. 2010. Т. 86. № 6. С. 67–81.

[4] Pham H.N., Sattler J.H.B., Weckhuysen B.M., Datye A.K. Role of Sn in the Regeneration of Pt/γ-Al_2O_3 Light Alkane Dehydrogenation Catalysts. *ACS Catal. 2016.* V. 6. № 4. P. 2257–2264. URL: https://doi.org/10.1021/acscatal.5b02917**.**

DHP industry, and to overcome these shortcomings, many scientific and industrial studies are aimed at the development of new catalysts for PDH[5,6].

Thus, authors of the paper[7] compared catalyst containing VOx groups supported on a mesoporous silicate with hexagonal ordered packing of cylindrical unified pores of the MCM-41 type, with CrO_x/MCM-41 and the industrial Pt–Sn/Al_2O_3 catalyst in the process DHP under the same conditions of operation and regeneration. They found that VO_x/MCM-41, both in oxidized and reduced form, works in a stream for a longer time and is stable in all DHP cycles, its activity can be completely restored by oxidative regeneration, that exceeds significantly industrial samples in terms of these indicators.

It was additionally established that the introduction of tetrahedrally coordinated Ti ions into the MCM-41 structure leads to an increase in the mesopore wall thickness and surface acidity and contributes to a more isolated position of VO_x groups supported on it from a solution of vanalyl acetylacetonate. This led to an increase in the conversion of propane in the process of dehydrogenation and to obtain a higher yield of propylene, compared with VO_x/MCM-41[8]. It was also determined that, in terms of productivity and selectivity for propylene, achieved at 550 °C, the VO_x/Ti-MCM-41 is close to the Pt-Sn/Al_2O_3, but it works more stably and is easily regenerated by short-term air purge.

As a support, alternative to alumina, for the catalysts for the dehydrogenation of light alkanes, the effect of ZrO_2 has been studied in sufficient detail[9]. Zirconium dioxide is considered as an ideal carrier for transition metals[10]. It is chemically stable, inactive in oxidative reactions, contains weakly amphoteric active centers, and interacts well with supported transition metal oxides, contributing to their highly dispersed arrangement and inhibiting sintering. But the use of ZrO_2 limits the fact that the surface of

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[5] Liu G., Zhao Z.-J., Wu T., Zeng L., Gong J. Nature of the Active Sites of VO_x/Al_2O_3 Catalysts for Propane Dehydrogenation. ACS Catal. 2016. V. 6. № 8. P. 5207–5214. URL: http:// DOI: 10.1021/acscatal.6b00893.

[6] Rodemerck U., Stoyanova M., Kondratenko E.V., Linke D. Influence of the kind of VO_x structures in VO_x/MCM-41 on activity, selectivity and stability in dehydrogenation of propane and isobutane. *J. Catal.* 2017. V. 352. P. 256–263. URL: https://doi.org/10.1016/j.jcat.2017.05.022 https://doi.org/10.1016/j.jcat.2017.05.022.

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[8] Зажигалов В.А., Коновалова Н.Д., Редькина А.В., Хоменко К.Н. Сравнительное исследование дегидрирования пропана на VO_x/MCM-41 и VO_x/Ti-MCM-41 с получением пропилена и водовода. *Укр. хім. журн.* 2013. V. 79. № 11. С. 63–72.

[9] Sattler J.H.B., Ruiz-Martinez J., Santillan-Jimenez E., Weckhuysen B.M. Catalytic Dehydrogenation of Light Alkanes on Metals and Metal Oxides. Chem. Rev. 2014. V. 114. №. 20. P. 10613–10653. URL: https://doi.org/10.1021/cr5002436.

[10] Yamaguchi T. Application of ZrO_2 as a catalyst and a catalyst support. *Catal. Today*. 1994. V. 20. P. 199–217. URL: https://doi.org/10.1016/0920-5861(94)80003-0.

this oxide during heat treatment is significantly reduced due to the growth of crystallites by the surface diffusion mechanism that accompanies the transformation of the t-ZrO_2 phase modification into m-ZrO_2[11]. A support obtained by hydrolysis of $ZrOCl_2$ can change its surface from 360 m^2/g to 20 m^2/g and texture from microporous to mesoporous and macroporous, depending on the processing temperature, from 110 to 650°C[12]. It was shown that the dispersion of the active component layer on it, which separates the support particles from each other, suppresses their surface diffusion and increases the thermal stability of the texture of the support, can contribute to maintaining the ZrO_2 surface[13]. In the dehydrogenation of light alkanes, the activity of the Cr_2O_3/ZrO_2 catalyst was significantly higher than that of the samples of Cr_2O_3 supported on Al_2O_3 or SiO_2. This was explained by the more isolated arrangement of active centers on the surface of zirconium dioxide and the presence of oxygen anionic vacancies involved in the dissociative adsorption of alkane[14]. Zirconia can also be stabilized by synthesizing its mixed system with silicon dioxide[15]. This makes it possible to create materials with a developed surface, a porous defective structure, and with significantly greater strength of acid sites that are active in the process of hydrocarbon dehydrogenation[16].

In work[17], for example, chromium-containing zirconium-silicate xerogels Cr/Si/Zr/O were tested as catalysts for DHP and it was shown that they are much more active at lower temperatures, in comparison with Cr/Si/Al/O, and exhibit 100% propylene selectivity on propylene. Vanadium-containing zirconium silicate xerogels in DHP have not been studied.

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[11] Mercera P.D.L., van Ommen J.G., Doesburg E.B.M., Burggraaf A.J., Ross J.R.H. Zirconia as a Support for Catalysts Evolution of the Texture and Structure on Calcination in Air. *Appl. Catal.* 1990. V. 57. P. 127–148. URL: https://doi.org/10.1016/S0166-9834(00)80728-9.

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It should be noted that recently, zirconia promoted by metal oxides, increasing the number of active structural anionic vacancies, is considered as an alternative type of unconventional catalysts with a defective structure, capable of replacing spent catalysts for non-oxidative dehydrogenation of light alkanes containing Cr or Pt[18,19].

Based on this and the positive results obtained in the process of DHP on vanadium oxide deposited on Ti-MCM-41 and Cr-containing zirconium silicate xerogel, the task was posed in this work:

– synthesize xerogels of mixed ZrO_2-SiO_2 oxide, modify them with TiO_2 additives, test the obtained systems as supports of various amounts of vanadium oxide for catalysts of the propane dehydrogenation to propylene process and compare them with the properties of the previously studied V_2O_5/Ti-MCM-41[20].

1. Experimental part

Zirconium silicates are widely used in various industries from ceramic materials and coatings, optical sensors, materials for electronics to ion exchangers, sorbents and heterogeneous catalysts. Their thermal and mechanical resistance and unique physicochemical properties depend on the method of their synthesis and the Zr/Si ratio. To obtain highly dispersed porous ZrO_2–SiO_2 mixed oxides with a developed surface, the most commonly used sol–gel method is hydrolysis of the corresponding organo-organic compounds (alkoxides) followed by conversion of hydrolysis products into sols, gels, and xerogels as the final materials[21]. However, the relatively high cost of alkoxides, their sensitivity to atmospheric moisture and fire hazard do not allow their use on a large scale, in large-tonnage production of sorbents and catalysts. ISPE NAS of Ukraine proposed a patent for a sol gel method for producing spherically granulated zirconium silicate using only available salts of elements and aqueous solutions of ordinary bases (hydroxides) and mineral acids as precursors[22].

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[18] Otroshchenko T., Bulavchenko O., Thanh H. V., Rabeah J., Bentrup U., Matvienko A., Rodemerck U., Paul B., Kraehnert R., Linke D., Kondratenko E.V. Controlling activity and selectivity of bare ZrO2 in non-oxidative propane dehydrogenation. *Appl.Catal. A: Gen*. 2019. V. 585. P. 117189–117199. URL: https://doi.org/10.1016/j.apcata.2019.117189.

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The mixed oxide ZrO_2-SiO_2 was synthesized according to the patent by carrying out the following reactions: $2\ K_2CO_3 + ZrOCl_2 \rightarrow K_2[ZrO(CO_3)_2]$,

$$K_2[ZrO(CO_3)_2] + Na_2SiO_3 \rightarrow ZrO_2 \,.\, SiO_2 \,.\, n\ H_2O$$

Solutions of the carbonate complex of zirconium and sodium metasilicate were fed into a flow reactor, where a mixed sol of zirconium oxyhydrate and silicic acid was formed, which droplet entered the column, passed through a layer of water-immiscible liquid (undecane) and turned into strong Zr-Si hydrogel spheres. They were washed with distilled water and transferred to the active H-form by treatment with a HCl solution. After drying at 130°C and calcination at 450°C, hard spherical granules of the Zr-Si xerogel with a diameter of 200–700 μm were obtained.

The modification of Zr-Si oxide with titanium dioxide was carried out by adding a $TiCl_4$ solution to the synthesis gel so that the amount of added TiO_2 was 3 wt. % from mass SiO_2. This value was chosen for comparison, as the maximum amount of titania that can be introduced into the MCM-41 system without destroying its structure[23]. The molar ratio of ZrO_2 / SiO_2 / TiO_2 oxides in the gel was 0.6 / 1 / 0.02. The granules of the dried and calcined sample were designated Zr-Si(Ti).

Vanadium oxide on the xerogels of the samples, as before, on the Ti-MCM-41 structure, was applied based on their moisture capacity by the traditional method of impregnating their surface with an aqueous solution of ammonium metavanadate in oxalic acid, in which it is formed a compound $(NH_4)_2[VO(C_2O_4)_2 \cdot H_2O] \cdot H_2O$ called the vanadium oxalant complex. Since its sorption is carried out from acidic solutions with a $pH < 2$, the surface hydroxyl groups of the support attach a proton and its surface is charges positively, according to the following reaction: Support-OH + $H^+ \rightarrow$ $(\text{Support-}OH_2)^+$. In this case, even at room temperature, a ligand exchange reaction occurs, in which part of the ligand of the metal complex is exchanged with the functional groups of the oxide support with the formation of covalently bound vanadium[24]:

$$x\ (\text{Support-}OH_2)^+ + [VO(C_2O_4)_2 \cdot H_2O]^{2-} \rightarrow$$

$(\text{Suppoer-}O)_x[VO(C_2O_4)_{2-x}] + x\ H_2C_2O_4 + H_2O$, where $x = 1$ or 2

The decomposition reaction of the vanadium oxalant complex during calcination in an oxygen atmosphere can be written as:

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[23] Koyano K.A., Tatsumi T. Synthesis of titanium-containing MCM-41. *Microporous Material*. 1997. V. 10. P. 259–271. URL: https://doi.org/10.1016/S0927-6513(97)00016-3

[24] Karakoulia S.A., Triantafyllidis K.S., Lemonidou A.A. Preparation and characterization of vanadia catalysts supported on non-porous, microporous and mesoporous silicates for oxidative dehydrogenation of propane (ODP). *Microp. Mesop. Mater*. 2008. V. 110. P. 157–166. URL: https://doi.org/10.1016/j.micromeso.2007.10.027

$$2(NH_4)_2[VO(C_2O_4)_2] + 2{,}5O_2 \rightarrow 4NH_3{\uparrow} + 8CO_2{\uparrow} + 2H_2O + V_2O_5$$

The catalysts were prepared by the applying of 5, 10, 15 and 20 wt. % V_2O_5, they were dried at 130°C and calcined in air at 450°C. They were designated as x% V_2O_5 /Zr Si or x % V_2O_5 /Zr-Si(Ti), which indicated on the % of the active phase per unit mass of the support.

Nitrogen adsorption isotherms for the traditional analysis of the texture of the samples were obtained according to the standard procedure after vacuum treatment at 423 K on an ASAP 2405N Micromeritics instrument. The pore size distribution was calculated by the theory of the nonlocal density functional NLDFT[25].

An analysis of the microstructure and elemental composition of the support was determined by scanning electron microscopy (SEM) using a JEOL JSM 7001F scanning electron microscope with an Oxford Instruments microanalyzer system.

X-ray diffraction patterns of the studied samples were recorded on a DRON-4-07 diffractometer in the Cu Kα radiation of the anode line with a Ni filter in the reflected beam with Bragg – Brentano geometry.

The propane dehydrogenation reaction was carried out in a 30 cm long quartz flow reactor using samples of – 0.85 g of – 1 cm^3 volume placed in the middle of the reactor. The working mixture contained 7 vol. % propane in argon. Its flow rate was varied from 9 to 18 ml/min, setting the contact time with the catalyst (τ) ~ 7 or 3.5 s. Before measurements, the catalyst was kept for at least an hour in the stream of the reaction mixture at 250–300°C. Then the temperature of the reactor was increased by 25°C ~ every 30 minutes to 675°C after achieving constant analysis results. Propane and the products of its dehydrogenation reaction – propylene (C_3H_6), methane, ethane and ethylene (C_xH_y) in ml, were analyzed on a silica gel column using a flame-sedation detector. The data were processed as the degree of conversion of propane – X (C_3H_8), product formation selectivity – S (C_3H_6), S (C_xH_y) and propylene yield – Y (C_3H_6).

2. Results and discussion

Tables 1 and 2 show microphotographs and elemental analysis of the surface layer of Zr-Si and Zr-Si(Ti) samples supports obtained by SEM. As can be seen, in the samples of xerogels dried and calcined at 450°C, the atomic ratio Zr / Si = 0.37–0.44, it turned out to be less than their initial content in sols – 0.6. For the obtained atomic ratios Si / Zr: 2,27–2,71, which are close to 2,

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[25] Ustinov E.A., Do D.D., Jaroniec M. Adsorption of argon and nitrogen in cylindrical pores of MCM-41 materials: application of density functional theory. *Appl. Surf. Sci.* 2005. V. 252. P. 1013–1028. doi:10.1016/j.apsusc.2005.01.122.

and which, according to the Tanabe rule[26] and the Thomson model[27], approximately corresponds to the maximum Brönsted acidity of mixed ZrO_2-SiO_2 oxides, the Hammet acidity function may be $H_0 \geq -8.2$[28]. However, as shown by measurements by the indicator method, at synthesized zirconium silicates $H_0 \geq -3$. This can be explained by the influence of the residual potassium content in the samples, which has a basic character, as can be seen from the data of elemental analysis in tabl. 1 and 2. But since the strength of the H-Ti-MCM-41 acid sites[29] corresponds to the range of $-3.0 \geq H_0 \geq +3.3$, the close value of the Gamet function $H_0 \geq -3$ in the obtained zirconium silicates is interesting for comparisons with samples Ti-MCM-41.

Table 1

Surface topography and distribution of elements of a sample of Zr-Si

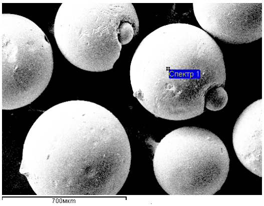
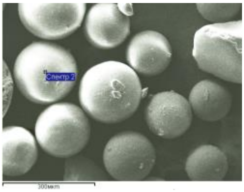
	Element	Weighting %	Atomic %	Compounds, %	Formula	Ratio of elements
	Si K	23.43	22.25	50.13	SiO_2	Zr/Si = 0,44 Si/Zr = 2,27 K/Si = 0,099
	Cl K	0.81	0.61	0.00		
	K K	3.22	2.20	3.88	K_2O	
	Zr L	33.45	9.78	45.18	ZrO_2	
	O	39.09	65.16			
	Total	100	100	100		

Table 2

Surface topography and distribution of elements of a sample of Zr-Si(Ti)

	Element	Weighting %	Atomic %	Compounds, %	Formula	Ratio of elements
	Si K	25.91	23.78	55.43	SiO_2	Zr/Si = 0,37 Si/Zr = 2,71 Ti/Si = 0,017 K/Si = 0,034
	K K	1.22	0.80	1.47	K_2O	
	Ti K	0.73	0.40	1.23	TiO_2	
	Zr L	31.00	8.76	41.88	ZrO_2	
	O	41.13	66.27			
	Total	100	100	100		

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[26] Танабе К. Катализаторы и каталитические процессы. Москва : Мир, 1993. 176 с.

[27] Thomas C.L. Chemistry of cracking catalysts. *Ind. Eng. Chem.* 1949. V. 41. P. 2564–2573.

[28] Bosman H.J.M., Kruissink E.C., van der Spoel J., van den Brink F. Characterization of the acid strength of ZrO_2-SiO_2 mixed oxides. *J. Catal.* 1994. V. 148. P. 660–672. URL: https://doi.org/10.1006/jcat.1994.1253.

[29] Зажигалов В.А., Коновалова Н.Д., Редькина А.В., Хоменко К.Н. Сравнительное исследование дегидрирования пропана на VO_x/MCM-41 и VO_x/Ti-MCM-41 с получением пропилена и водовода. *Укр. хім. журн.* 2013. V. 79. № 11. С. 63–72.

Isotherms of Nitrogen adsorption-desorption for the synthesized zirconium silicates (Fig. 1a) belong to type IV isotherms characteristic of porous bodies with the shape of an H2 type hysteresis loop in which the desorption branch has a rather large horizontal part. Loops of type H2 are observed for some silica gels and the so-called corpuscular systems, the pores of which are of an indefinite nature with narrow “throats” and various wider cavities. This is also confirmed by the picture of the distribution of pores by the size of the radii characteristic of micro-mesoporous systems (Fig. 1, b).

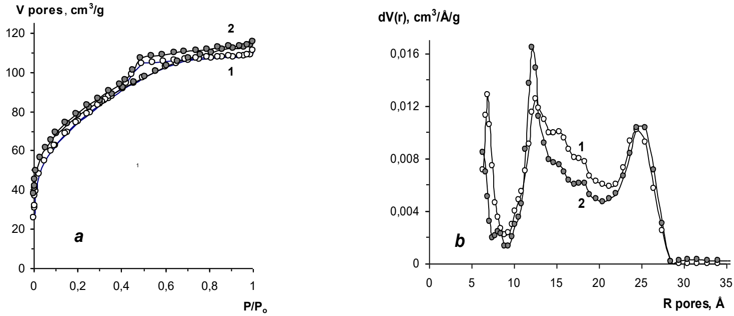

Fig. 1. Nitrogen adsorption-desorption isotherms (*a*) and calculation of pore size distribution at radius size by DFT method (*b*) for samples: *1* – Zr-Si; *2* – Zr-Si(Ti)

The main texture parameters of supports and catalysts containing 5 to 20 wt. % vanadium oxide are given in the table 3. It is seen that, as an increasing amount of V_2O_5 is deposited, the specific surface and pore volume of V_2O_5/Zr-Si gradually decreases, as that was observed[30] for ZrO_2 with a developed surface (> 300 m^2/g) and for micro- and mesoporous silicate carriers[31]. On the contrary, the texture parameters of V_2O_5/Zr-Si(Ti) samples remain approximately constant, as in work[32] when V_2O_5 was deposited on ZrO_2 calcined at 450–500°C with a relatively low surface (~ 160 m^2/g).

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[30] Khodakov A., Yang J., Su S. Iglesia E., Bell A.T. Structure and Properties of Vanadium Oxide–Zirconia Catalysts for Propane Oxidative Dehydrogenation. *J. Catal*. 1998. V. 177. P. 343–351. URL: https://doi.org/10.1006/jcat.1998.2143.

[31] Karakoulia S.A., Triantafyllidis K.S., Lemonidou A.A. Preparation and characterization of vanadia catalysts supported on non-porous, microporous and mesoporous silicates for oxidative dehydrogenation of propane (ODP). *Microp. Mesop. Mater*. 2008. V. 110. P. 157–166. URL: https://doi.org/10.1016/j.micromeso.2007.10.027.

[32] Khodakov A., Olthof B., Bell A.T., Iglesia E. Structure and Catalytic Properties of Supported Vanadium Oxides: Support Effects on Oxidative Dehydrogenation Reactions. *J. Catal.* 1999. V. 181. P. 205–216. URL: https://doi.org/10.1006/jcat.1998.2295.

The test data on the activity of the obtained catalysts with increasing temperature of the propane dehydrogenation reaction are shown in Fig. 2 and 3.

Table 3

Textural parameters of zirconium silicates and supported vanadium oxide catalysts

Sample	Specific surface area, S_{BET}, m^2/g	Total pore volume V_{Σ}, cm^3/g	Average pore diameter D, A^o
Zr-Si	264.3	0.178	26.9
5% V_2O_5 / Zr-Si	202	0.130	25.78
10% V_2O_5 / Zr-Si	152.6	0.094	24.69
15% V_2O_5/ Zr-Si	136.6	0.109	31.96
20% V_2O_5 / Zr-Si	127.7	0.101	31.6
Zr-Si(Ti)	275.8	0.187	27.18
5% V_2O_5 / Zr-Si(Ti)	255	0.168	26.35
10% V_2O_5 / Zr-Si(Ti)	278.3	0.202	29.1
15% V_2O_5 / Zr-Si(Ti)	250.8	0.156	24.93
20% V_2O_5 / Zr-Si(Ti)	280	0.184	26.36

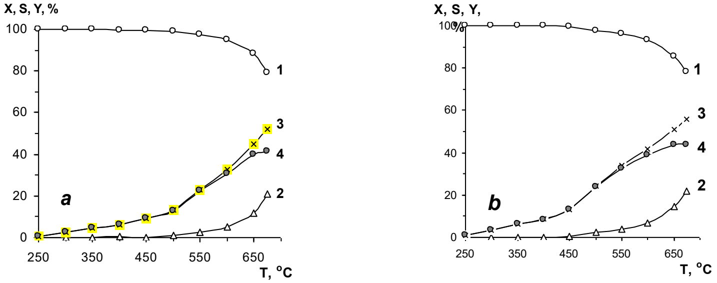

Fig. 2. The change in catalytic parameters with increasing temperature of the propane dehydrogenation reaction on 10 %V_2O_5/ Zr-Si (*a*) and 10 %V_2O_5/ Zr-Si(Ti) (*b*). *1* – S (C_3H_6), *2* – S (C_xH_y), *3* – X (C_3H_8), *4* – Y (C_3H_6). Contact time – 3,5 s

In a mixture, containing 7 vol. % propane in argon, at a contact time of 3.5 s, greater propylene yield ~ 40–45 mol. % was obtained at 650°C on samples containing 10 wt. % vanadium oxide. At low temperatures – up to 550°C, the catalysts show an almost 100% selectivity for propylene, which decreases to 90 – 80 mol. % with increasing temperature to 650–675°C (Fig. 2). In this case, the catalyst, modified by the introduction into the support of titanium oxide – 10 % V_2O_5 / Zr-Si(Ti), in the entire range of temperature increase shows the yield of propylene by 5–10% more than 10% V_2O_5 / Zr-Si.

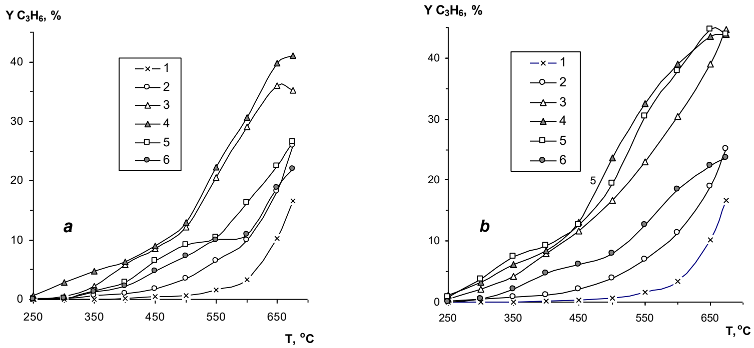

Fig. 3. Dependence of the yield of propylene from the reaction temperature of the propane dehydrogenation on catalysts: V_2O_5/ Zr-Si (*a*) и V_2O_5/ Zr-Si (Ti) (*b*). *1* – reaction without catalyst. *2* – on supports. When applying on its: *3* – 5% V_2O_5, *4* – 10% V_2O_5, *5* – 15% V_2O_5, *6* – 20% V_2O_5. Contact time – 3,5 s

At high temperatures, the endothermic reaction of propane dehydrogenation can proceed without a catalyst by a radical chain mechanism, forming predominantly propane degradation products, since much less energy is needed to break the C–C bond than to break the C–H bond[33]. To overcome the high binding energy C–H, it is necessary to use special catalysts that significantly accelerate the DH process. At the same time, the amount of undesirable by-products becomes insignificant, since undesirable reactions proceed more slowly. Various heterogeneous mechanisms of propane dehydrogenation with the participation of acidic centers of the catalyst in the activation of propane with the formation of propyl-carbenium ions[34], a stepwise oxidation-reduction mechanism with the participation of oxygen atoms of the active sites of the catalyst have been proposed[35]. A heterogeneous-homogeneous mechanism is also proposed, according to which the active centers of the catalyst surface contribute to the

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additional activation of propane with the formation of propyl radicals that continue the chain reaction in the reactor volume[36].

As can be seen in fig. 3, in an empty reactor, after 500°C, a propane dehydrogenation reaction proceeds with the formation of propylene and the zirconium silicate supports themselves catalyze this process noticeably. The supporting of 5 and 10 wt. % V_2O_5 on Zr-Si at 650°C leads to an increase in the yield of propylene from 17 to 35 and 40 mol. %, respectively, but it decreases sharply at 15 and 20 wt.% V_2O_5. The introduction of TiO_2 into the structure of ZrO_2-SiO_2 contributes to an increase in the yield of propylene by ~ 10 mol. % and leads to its lower decrease and only when applying 20 wt % V_2O_5.

The specific surface area of the catalysts decreases significantly after increasing the temperature during the reaction to 675°C (Fig. 4). But if for V_2O_5 /Zr-Si after 10% deposition of vanadium oxide it decreases to ~ 70 m^2/g, then S_{BET} for V_2O_5 / Zr-Si (Ti) is set at the level of 150 m^2 /g.

This changes the surface density of vanadium atoms before and after the propane dehydrogenation reaction, whose calculation is shown in Fig. 5, where the layer levels of mono and polyvanadates are noted. The surface density of vanadium atoms in the monolayer of monovanadates corresponds to 2.3 VO_x /nm^2, and in the monolayer of polyvanadates to 7.5 VO_x /nm^2, that was theoretically calculated[37].

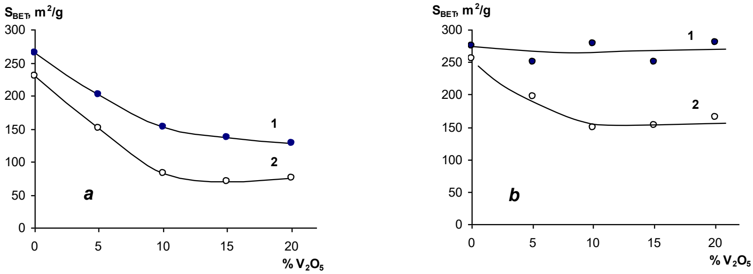

Fig. 4. The dependence of the specific surface area of the catalysts from the amount of V_2O_5 supported (wt. %) on Zr-Si (*a*) and Zr-Si (Ti) (*b*). *1* – initial catalysts, *2* – after the propane dehydrogenation reaction

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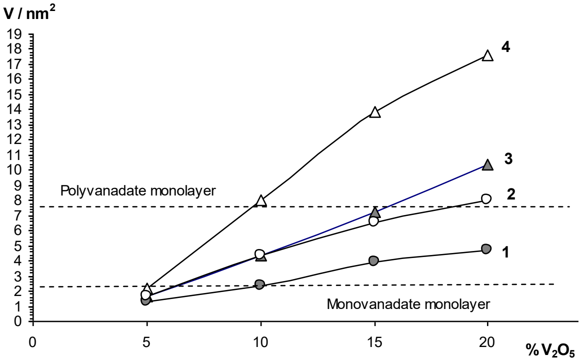

Fig. 5. The surface density of the VO_x groups, in depending from the amount of vanadium oxide supported on Zr-Si(Ti), before – *1* and after the reaction – *2* and on Zr-Si, before –*3* and after the propane dehydrogenation reaction – *4*

As can be seen (fig. 5), the V /nm^2 value of V_2O_5 / Zr-Si (Ti) before and after the reaction is lower or between the levels of the mono and polyvanadate layers and on 1/3 exceeds the latter after of work under supporting 20 % V_2O_5, which leads to a decrease in the yield of propylene. In the case of low active catalysts 15–20 % V_2O_5 / Zr-Si, on the contrary, the V /nm^2 value after the reaction is 2 and 2.5 times higher than the level of the polyvanadate layer. Based on the results obtained, in accordance with[38], it can be concluded that both isolated monovanadates and polyvanadate groups of vanadium oxide are active in the selective dehydrogenation of propane, the amount of which does not exceed their monolayer coating of the carrier surface. It is also seen that the composition of the carrier affects the state and distribution of active sites. Similar to the conclusions made in[39], one can notice that the presence of TiO_2 in the composition of the carrier leads to a greater isolation of the supported V_2O_5 groups and that the ability of vanadium to activate C–H bonds weakens with an increase in VO_x density, as a result of which the number of bonds V-O-M (M – atom metal of support) decreases due to the inclusion of vanadium in the formation of V-O-V bridge bonds and the observed decrease in activity indicates the effect bonds of V-O-support on the kinetically significant stages of the DHP reaction.

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The data of x-ray phase analysis of the catalysts before and after the propane dehydrogenation reaction are shown in Fig. 6 and 7. It is seen that the initial samples with vanadium oxide, as well as the supports calcined at 450°C, are in the amorphous state before the reaction (Fig. 6, a). After increasing the temperature during the reaction to 675°C, the diffraction patterns of the catalysts show reflections of the tetragonal phase (t-ZrO_2) with maxima at (2θ) 30.2; 34.8; 35.3; 50.3; 50; 59.6 and 60° (JCPDS map number 79-1976). These peaks (Fig. 7) are much sharper and larger for V_2O_5 /Zr-Si (Ti) than for V_2O_5 / Zr-Si (Fig. 6, b).

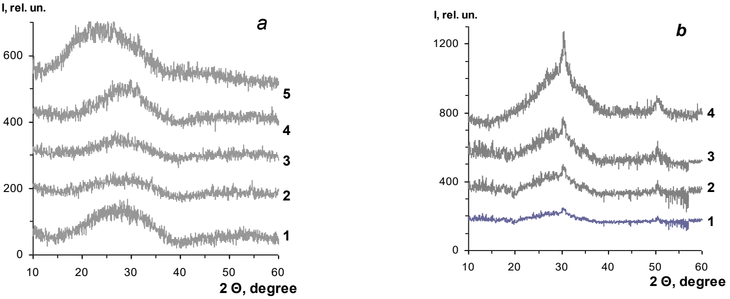

Fig. 6. Diffraction patterns of samples calcined at 450°C before the DHP reaction (a): *1* – Zr-Si and Zr-Si (Ti); *2* – 5% V_2O_5 /Zr-Si; *3* – 5% V_2O_5 / Zr-Si(Ti); *4* – 20% V_2O_5 /Zr-Si; *5* – 20% V_2O_5 /Zr-Si (Ti). And after the reaction at 250-675°C on Zr-Si (b), when supporting V_2O_5: *1* – 5%, *2* – 10%, *3* – 15%, *4* – 20 wt. %

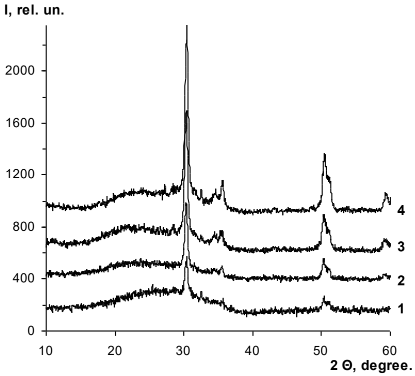

Fig. 7. Diffraction patterns of the V_2O_5/Zr-Si(Ti) samples after the reaction of DHP at 250-675°C, on which at V_2O_5 supported in the wt %: *1* – 5%, *2* – 20%, 3 – 15%, *4* – 10%

With an increase in the amount of supported vanadium oxide in the composition of the catalysts, the intensity of t-ZrO_2 reflections on fig.6,b and 7 changes approximately to the same extent as during the 500° calcination of samples of 2–30 V_2O_5/ZrO_2 in work[40] and at heat treatment of 2–18% V_2O_5/ZrO_2 at 450°C in[41]. In work[42], this was observed with an increase in ZrO_2 to 60 wt. % in mixed ZrO_2-SiO_2 oxides obtained by the sol-gel method and calcined at 600°C.

It is well known that pure zirconia, depending on the temperature range, can be in three characteristic crystalline modifications. At room temperature, the monoclinic form (m-ZrO_2) is stable, which transforms into a metastable tetragonal structure at temperatures around 1 170°C and then into a stable cubic crystalline form at even higher temperatures. However, upon heating mixed oxides, the tetragonal ZrO_2 phase is formed first at low temperatures and remains stable over a fairly wide temperature range. This is based on the Oswald step transition rule[43], according to which if a substance can be in more than one form, then a less stable state is formed at first. With decreasing temperature, the transition from t-ZrO_2 to m-ZrO_2 is accompanied by an increase in the lattice volume by 3–5%, which is enough to exceed the elastic limits and lead to the destruction of even small grains[44]. Materials based on zirconium dioxide are widely used in many fields, therefore, to increase their strength much attention is paid to the study of t-ZrO_2 stabilization in mixed oxides. That can occur by replacing zirconium cations with oxide cations, which lead to the formation of oxygen vacancies or by structural similarity between the tetragonal phase and the phase of the amorphous precursor[45].

The observed stabilization of t-ZrO_2 by silicon dioxide is explained by the fact that the amorphous silica matrix, with a large amount of it in ZrO_2-SiO_2 gels[46], or a thin film of amorphous SiO_2, with its content of 2–10%[47], do not allow ZrO_2 particles to grow to a critical size of 30 nm for the

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transition to the monoclinic phase. The size of ZrO_2 particles can be approximately estimated from the width of their reflections in the diffractogram of Fig. 7 using the Debye-Scherrer formula[48]:

$$d = k\lambda / \beta \cos \theta,$$

where d is the average crystallite size; k is a coefficient of 0.94 for x-ray analysis; λ is the wavelength of the radiation used ($CuK_\alpha = 1.54$ Å); β is the peak width at half height (in radians); θ is the diffraction angle.

Such an assessment shows that with an increase in the amount of the supported V_2O_5 from 5 to 20 wt. % crystallite size varies ~ from 16 to 19 nm. In this case, the diffraction patterns of the samples (Fig. 6, b and 7) did not reveal reflections of vanadium oxide, which indicates its finely dispersed state.

The authors explain the stabilization of t-ZrO_2 in a double – V_2O_5-ZrO_2[49] or triple – V_2O-ZrO_2-SiO_2[50] oxide system by dissolving vanadium ions in the tetragonal phase of zirconia (to a maximum of 5 mol %), with the formatiqon after annealing at 450^{o}C solid solution t-ZrO_2-V, in which V^{4+} replace Zr^{4+}. This leads to a slight distortion of the t-ZrO_2 lattice and its further conversion to m-ZrO_2 will depend on the vanadium content.

It was shown in[51] that titanium ions to 20 mol. % can be homogeneously dispersed into the structure of ordered porous zirconium dioxide, which is much larger than the number of tetrahedrally coordinated titanium ions, which can be isomorphically incorporated into micro- and mesoporous silicates without breaking their structure (~ 3 wt.%[52]). This is determined by the difference in the ionic radii of the elements: Zr^{4+} (0.82 Å) > Ti^{4+} (0.64 Å) > Si^{4+} (0.39 Å) [53]. Moreover, due to the strong interaction between Zr and Ti ions, the strength and heat resistance of optimally modified ZrO_2 significantly increase.

Figure 8 compares the yields of propylene obtained by increasing the temperature of the propane dehydrogenation reaction on synthesized micro-mesoporous zirconium silicate xerogels and on the ordered mesoporous titanosilicate with the MCM-41 structure, with the same amount of active phase of 5 wt. % V_2O_5 and at contact time of the reaction mixture with catalysts in 3.5 s.

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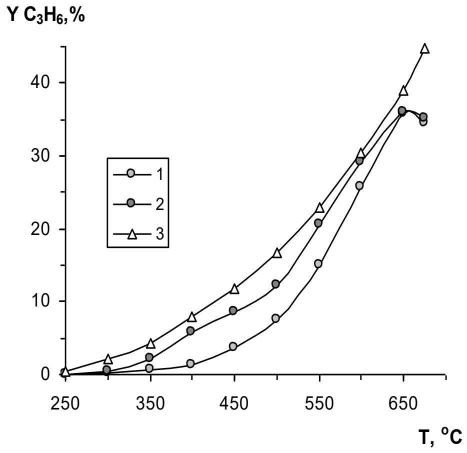

Fig. 8. Comparison of the yield of propylene from the temperature of the reaction of propane dehydrogenation on 5 wt. % of the V_2O_5 supported on: *1* – Ti-MCM-41, *2* – Zr-Si, *3* – Zr-Si(Ti). Contact time –3.5 s

Ti-MCM-41 was obtained by template hydrothermal synthesis from titanoaerosil[54], it contains 1,4 wt. % implanted Ti^{4+} ions or 0,02 mol TiO_2 with respect to SiO_2 and has uniform hexagonal packed cylindrical pores with a diameter of ~ 3.5 nm.

As can be seen, depending on the carriers of vanadium oxide, the propylene yield changes in the following order: Zr-Si(Ti) > 0.6Zr-Si > Ti-MCM-41 and it accordingly increases almost proportionally with increasing reaction temperature from 250 to 650°C. It is also seen that the introduction of zirconium and additionally titanium into the composition of the silicate support allows one to reduce the temperature of reaching the same values of Y (C_3H_6) by almost 50–100°C, in comparison with Ti-MCM-41.

However, increasing the contact time to 7 s (Fig. 9) practically does not affect the propylene yield on V_2O_5 /Zr-Si(Ti), but increases it by V_2O_5 /Ti-MCM-41, so that after 550°C the Y (C_3H_6)` on this sample becomes much larger than on vanadium-zirconium-titanium silicate.

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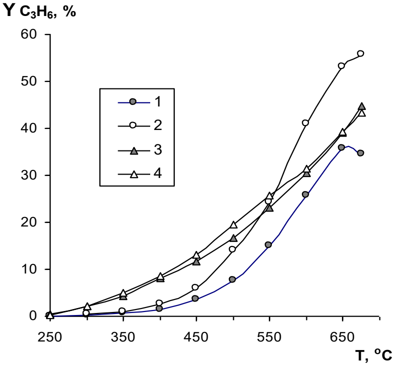

Fig. 9 The dependence of propylene yield from the temperature of the DHP reaction at different contact times of the reaction mixture with catalyses 5% V_2O_5 /Ti-MCM-41, *1* – τ = 3,5 s; *2* – τ = 7 s; and 5 % V_2O_5 /Zr-Si(Ti), *3* – τ = 3,5 s; *4* – τ = 7 s

This can be explained by the fact that the disordered structure of the ZrO_2-SiO_2 xerogel prevents the additional development of a homogeneous radical reaction in the volume of its tortuous micro- and mesopores, whereas the increase in the contact time of the reaction mixture with active vanadium and titanium-containing centers on the walls of cylindrical mesopores of the ordered MCM-41 structure helps to increase the degree of propane conversion and the development of the reaction according to a heterogeneous-homogeneous mechanism.

CONCLUSIONS

Thus, from the behavioral work on the study of the textural, physicochemical, and catalytic properties of the micro-mesoporous zerconium silicate xerogel as a support of vanadium oxide in the process of propane dehydrogenation to propylene, the following main conclusions can be drawn:

1. Sol-gel synthesis of double $0.6ZrO_2$-SiO_2 and triple $0.6ZrO_2$-SiO_2-$0.02TiO_2$ oxides from water solution of available element salts, supplemented by simple coagulation technology in a drop, made it possible to obtain their strong spherical granules having, after calcining at 450°C, the developed surface ~ 300 m^2 g and amorphous bimodal micro-mesoporous structure with pore diameters ~ 1,4; 2,7 and 5 nm.

2. Application by wet impregnation from a solution of ammonium metavanadate in oxalic acid 5 to 20 wt. % V2O5 on the obtained xerogels it showed that the specific surface area of Zr-Si based catalysts at that

gradually decreases by almost two, while its values for Zr-Si(Ti) based samples practically does not change.

3. In the process of propane dehydrogenation with a gradual increase in temperature to 675 °C, the surface of the catalysts decreases, but in V_2O_5 /Zr-S(Ti) remains twice as large as in V_2O_5 /Zr-Si.

4. As the X-ray phase analysis of the samples after the reaction shows, this can be explained by the fact that the addition of TiO_2 to zirconium silicate promotes greater crystallization of ZrO_2 in the metastable tetragonal phase, which, according to the literature, stabilizes the structure and surface size of the sample.

5. As a result of this, the positions of the active sites of vanadium oxide on Zr-Si(Ti) become more isolated than on Zr-Si. The surface density of vanadium atoms on Zr-Si(Ti) only at applying 20 wt. % V_2O_5 after reaction slightly exceeds the monolayer of polyvanadates, leading to a decrease in the yield of propylene. While at the supporting of 15–20 wt. % V_2O_5 on Zr-Si, this overshoot takes place in 2 and 2,5 times.

6. Comparative testing of the activity of catalysts with increasing reaction temperature from 250 to 650°C in a reaction mixture containing 7 vol. % propane in an inert gas and at its contact time of 3,5 s shows that the propylene yield depends on the composition of vanadium oxide supports and decreases on them in this order: Zr-Si(Ti) > Zr-Si > Ti-MCM-41.

7. In this case, the introduction of zirconium and additionally titanium into the structure of the porous silicate support can significantly reduce the reaction temperature at which the same yields of propylene are obtained on V_2O_5 /Ti-MCM-41. Its maximum yield under these reaction conditions is ~ 45 mol. % is achieved on a sample of 10% V_2O_5 /Zr-Si(Ti) at 650°C.

8. Increasing the contact time to 7 s practically does not affect the propylene yield on V_2O_5 /Zr-Si(Ti) and significantly increases it on V_2O_5 /Ti-MCM-41 at temperatures above 550°C. It is possible that, in contrast to the ordered structure of homogeneous, cylindrical mesopores – Ti-MCM-41, the system of tortuous micro-mesopores of zirconium-silicate xerogel prevents the development of the reaction by a heterogeneous-homogeneous mechanism and contributes to a decrease in the yield of propylene at high reaction temperatures.

SUMMARY

In order to achieve the possibility of replacing expensive Pt-Sn / Al_2O_3 or toxic Cr_2O_3 / Al_2O_3 catalysts for the dehydrogenation of light alkanes, in the dehydrogenation reaction of propane to propylene it were studied the properties of vanadium oxide supported on xerogels of the Zr and Zr, Ti-containing oxide micro-mesoporous silicates. The obtained data were compared with the activity of V_2O_5 supported on mesoporous titanosilicate with an ordered hexagonal packing of uniform cylindrical pores of the Ti-MCM-41 type, studied earlier and showing promising results.

The supports were synthesized by the sol-gel method from aqueous solutions of the available salts of $ZrOCl_2$, K_2CO_3, Na_2SiO_3 and $TiCl_4$, maintaining the following molar ratio of oxides in the $0.6ZrO_2$-SiO_2 and $0.6ZrO_2$-SiO_2-$0.02TiO_2$ sols. The use of simple technology coagulation in a drop with subsequent calcination of the resulting hydrogels made it possible to obtain strong spherical granules of xerogels having a develope0 \d surface of ~ 300 m^2/g with an amorphous structure and pore diameters of ~ 1.4; 2.7 and 5 nm. The supporting 5 to 20 wt. % V_2O_5 `on the surface of the samples was carried out by their impregnation with a solution of ammonium metavanadate. For the study it were used methods of scanning electron microscopy, low-temperature nitrogen adsorption, X-ray phase analysis, and gas chromatography. The reaction was carried out in a flowing quartz reactor, without filling its the empty volume with an inert filler. It is shown that the obtained V_2O_5/ZrO_2-SiO_2 catalyst makes it possible to lower the temperature of achieving high yields of propylene and further increase its yield by modifying the support with titanium dioxide, which strengthens the catalyst structure, stabilizes the surface area and promotes more isolated position of the active sites. However, the disordered structure of Zr-Si xerogels with sinuous micro- and mesopores, in comparison with Ti-MCM-41, probably prevents the development of the reaction by a heterogeneous-homogeneous mechanism and reduces yield of propylene at high temperatures and the times of reaction mixture contact with catalysts.

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