

**INFLUENCE OF THE POROUS STRUCTURE OF V<sub>2</sub>O<sub>5</sub>-ZrO<sub>2</sub>-SiO<sub>2</sub> CATALYST ON REACTION OF PROPANE DEHYDROGENATION**

*Antonina Redkina*<sup>1, \*</sup>, *Nadezhda Konovalova*<sup>1</sup>, *Nikolay Kravchenko*<sup>1</sup>,  
*Volodymyr Strelko*<sup>1</sup>

<https://doi.org/10.23939/chcht16.02.259>

**Abstract.** A spherically granular, amorphous, mesoporous catalyst was obtained by supporting V<sub>2</sub>O<sub>5</sub> on synthesized by direct sol-gel method of ZrO<sub>2</sub>-SiO<sub>2</sub> hydrogel and was identified by SEM, XRD and N<sub>2</sub> adsorption / desorption. It is shown that its hydrothermal and alcohol treatment increases the specific surface, volume and width of pores and leads to an increase in the yield of propylene in the reaction of propane dehydrogenation and decreases the temperature of reaching its high values.

**Keywords:** propane dehydrogenation, propylene, vanadium oxide, zirconium silicates.

## 1. Introduction

At present, the supported vanadium oxides are ones of the most promising alternative catalysts for dehydrogenation of propane (DHP) to propylene, which is a large-tonnage semi-product of the chemical industry and serves as the main raw material for producing polypropylene, propylene oxide, acrylonitrile, polyurethane foam and many other products.<sup>1-3</sup> The need for pure propylene significantly exceeds its production volumes by traditional methods of thermal and catalytic cracking of petroleum distillation products; therefore, the target DHP is developing at a faster pace, which is also facilitated by the production of cheap shale gas containing significant amounts of propane.<sup>4,5</sup> The main commercial technologies of DHP are based on two catalytic systems: Cr<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> and Pt-Sn/Al<sub>2</sub>O<sub>3</sub>, 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.<sup>5,6</sup> In addition, it is noted that the high cost of Pt, as well as serious pollution issues caused by Cr, restrict further development of the DHP industry, and to overcome these shortcomings, many scientific and industrial studies are aimed at the development of new catalysts for DHP.<sup>1-3</sup>

It was shown<sup>7</sup> that a catalyst with VO<sub>x</sub> groups supported on a mesoporous ordered silicate system of the MCM-41 type, in comparison with industrial catalysts, works for a longer time in the stream in all DHP cycles and can be completely reduced by oxidative regeneration. An increase in the acidity of MCM-41 by introducing Ti ions into its structure led to an increase in the selectivity of the formation and yield of propylene and to achieve a performance close to Pt-Sn/Al<sub>2</sub>O<sub>3</sub>.<sup>8</sup> Herewith, it was noted that the maximum catalytic characteristic achieved on VO<sub>x</sub>/Ti-MCM-41 depends on both the acidity of the sample surface and its pore volume.<sup>9</sup>

The supported vanadium oxide was widely studied and showed the greatest efficiency in the exothermic process of oxidative dehydrogenation of propane ODHP,<sup>10</sup> but herewith, the lower selectivity and yield of propylene due to its further oxidation were obtained. Cavani *et al.*<sup>10</sup> noted that both with ODHP and with DHP, an increase in the yield of propylene can be achieved by increasing the surface area of the catalysts and changing their porous structure and chemical nature, which can initiate the additional passing of high-temperature radical homogeneous reactions. The formation of free radicals in such reactions can occur on the active sites of the surface of the catalysts (heterogeneous onset of homogeneous reactions) and they can be more selective than a completely heterogeneous process. For example, Liu *et al.*<sup>1</sup> explain the beginning of the DHP reaction on VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> by the formation of propyl radicals associated with vanadium.

<sup>1</sup> Institute of Sorption and Problem Endoecology of NAS of Ukraine, 13, Gen. Naumov Str., Kyiv 03164, Ukraine

\* [antonina.redkina@ukr.net](mailto:antonina.redkina@ukr.net)

© Redkina, A.; Konovalova, N.; Kravchenko, N.; Strelko, V., 2022

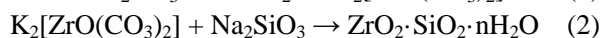
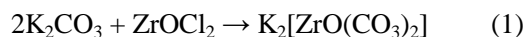
Recently, zirconia promoted by metal oxides is also considered as an alternative type of catalyst capable of replacing spent catalysts of non-oxidative DHP. It has been shown that the active sites in such systems are structural anionic oxygen vacancies near coordination-unsaturated Zr atoms, which cause propane activation.<sup>11-13</sup>

Previously,<sup>14</sup> we studied the properties of spherically granulated micro-mesoporous zirconium silicate (Zr-Si) xerogels as supports of vanadium oxide in the DHP reaction. It was shown that on V<sub>2</sub>O<sub>5</sub>/Zr-Si, at a shorter contact time of the reaction mixture, a higher propylene yield was obtained than on V<sub>2</sub>O<sub>5</sub>/Ti-MCM-41, which has a structure with regular hexagonal packing of cylindrical mesopores with the same diameters. But with a longer contact time, at the temperatures above 823 K, the propylene yield on V<sub>2</sub>O<sub>5</sub>/Zr-Si became lower. It was concluded that the system of tortuous micro-mesopores of the Zr-Si xerogel can impede the development of the DHP reaction by a heterogeneous-homogeneous mechanism.

In this work, the task was to increase the specific surface area of the vanadium-zirconium-silicate catalyst and to change its porous structure, as well as to determine the influence of these parameters on the proceeding of the propane dehydrogenation reaction to propylene.

## 2. Experimental

Spherically granular highly dispersed porous ZrO<sub>2</sub>-SiO<sub>2</sub> oxide was obtained by methods, described in detail previously<sup>14</sup>. We used the direct sol-gel synthesis and the droplet coagulation of the zirconium silicate hydrogel, using the aqueous solutions of the accessible salts, with concentrations necessary for the obtaining the Zr/Si = 0.6 in the synthesised sol, according to the following reactions:



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 403 K and calcination at 823 K, hard spherical granules of the Zr-Si xerogel with a diameter of 200–700 μm were obtained.

The preparation of Zr-Si catalysts with 10 wt% supported V<sub>2</sub>O<sub>5</sub> is described in detail by Redkina and co-workers.<sup>14,15</sup> The Zr-Si xerogel was impregnated with a solution of ammonium metavanadate salt (NH<sub>4</sub>VO<sub>3</sub>) in oxalic acid (H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>) with pH < 2, in which the resulting vanadium oxalate complex exchanges ligands with the functional groups of the support to form covalently bound vanadium oxide.<sup>16</sup> Since compounds containing tetravalent V show a high degree of vanadium incorporation into the porous silicate matrix,<sup>17</sup> vanadium oxide was supported on Zr-Si hydrogel by diffusion of a 10 % aqueous solution of VOSO<sub>4</sub> salt into the pores of the gel spheres, followed by precipitation of vanadium hydroxide with NH<sub>4</sub>OH and washing with water to pH = 7. A portion of the hydrogel was then subjected to hydrothermal treatment (HTT) in steel autoclaves at 523 K for 5 h. After HTT, a portion of the catalyst was further decanted with alcohol for 12 h. After application of vanadium oxide and various processing, all samples were dried at 403 K and calcined for 4 h in air at 823 K. The catalyst supported on xerogel was designated as V<sub>2</sub>O<sub>5</sub>/Zr-Si, and the samples on Zr-Si hydrogels were designated as V<sub>2</sub>O<sub>5</sub>-Zr-Si.

Isotherms of low temperature nitrogen adsorption were measured according to the standard procedure on an ASAP 2405 N Micromeritics instrument, after vacuum treatment at 473 K. The distribution pores from the radius sizes were calculated using the DFT density functional theory.

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

X-ray diffraction patterns were recorded on a DRON-4-07 diffractometer using Cu K $\alpha$  radiation from the anode line with a Ni filter in the reflected beam with Bragg–Brentano geometry.

The DHP reaction was carried out in a flow quartz reactor of 30 cm long and 0.7 cm in diameter; 0.85 g of the catalyst (volume 1 cm<sup>3</sup>) was placed in the middle of the reactor. The flow rate of the mixture containing 7 vol % of propane in argon, was maintained as 18 mL/min and its contact time with the catalyst was 3.5 s. After holding the samples in the reaction mixture for at least a one hour at 523–573 K, the temperature of the reactor was increased by 25 K every 30 minutes to 923–948 K. Propane and the products of its dehydrogenation reaction – propylene (C<sub>3</sub>H<sub>6</sub>), methane, ethane, and ethylene (C<sub>x</sub>H<sub>y</sub>)

were analyzed on a chromatographic column filled with silica gel using a flame ionization detector. The catalytic parameters were determined as the degree of propane conversion  $X(C_3H_8)$ , product selectivity  $S(C_3H_6)$ ,  $S(C_2H_4)$  and propylene yield  $Y(C_3H_6)$ .

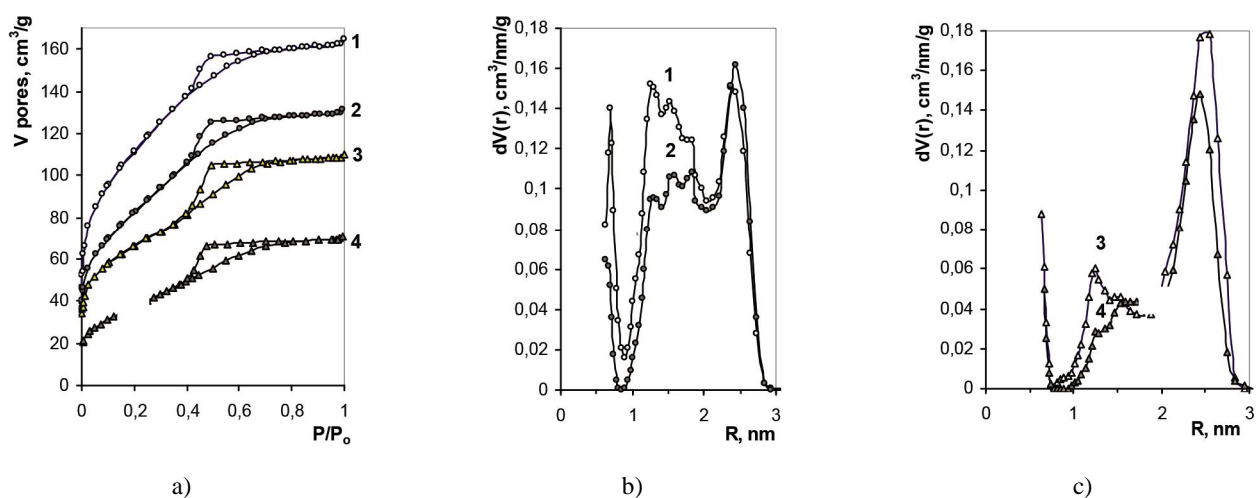
### 3. Results and Discussion

It is known that zirconium dioxide is one of the best supports for catalytically active metal oxides,<sup>18</sup> since it is chemically stable, inactive in oxidative reactions, has weak amphoteric properties and interacts well with transition metals, contributing to their highly dispersed surface location and inhibiting them sintering. However, the possible relatively large  $ZrO_2$  surface ( $\sim 300 \text{ m}^2/\text{g}$ ), obtained by drying amorphous  $Zr(OH)_4$ ,<sup>19</sup> significantly decreases during its further calcination in air at high temperatures. This is due to the growth and agglomeration of crystallites by the mechanism of surface diffusion and leads to a change in the modifications of the formed crystalline  $ZrO_2$  phase. It was shown<sup>20</sup> that the thermostability of  $ZrO_2$  can be improved by preliminary dispersing a monolayer of the active component on its surface, which, separating the crystallites of the support from each other, prevents their growth to critical sizes. In this case, a much larger surface area of the catalyst is obtained after the impregnation of zirconia hydrogel with solutions of salts of active elements than when its xerogel is impregnated.<sup>20</sup> It stabilizes the state of  $ZrO_2$  and the synthesis of its mixed oxide with  $SiO_2$ . This allows not only to create a support with a developed

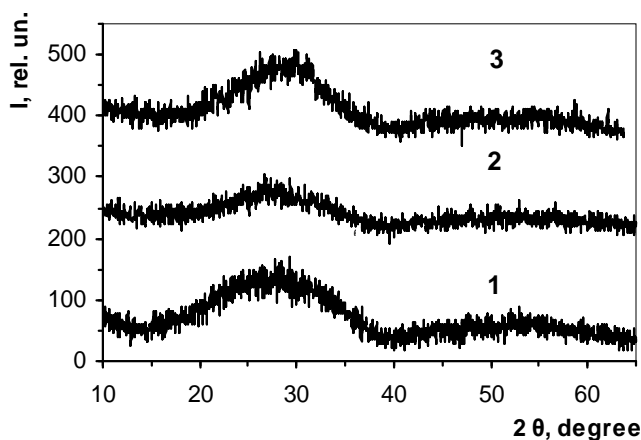
surface and porous structure, but also with a greater strength of acid sites active in the dehydrogenation of hydrocarbons.<sup>21</sup>

An additional way for regulation of the porous structure of zirconium silicates is to conduct HTT of their hydrogels, which helps to strengthen the bonding of elements in their polymer skeleton and to obtain xerogels with a larger specific surface and pores volume after calcination.<sup>22</sup> And also, replacing intermicellar water in hydrogels with alcohol or another organic liquid with a low surface tension, which reduces the capillary compressive strength of the gel skeleton during drying, leads to an increase in the volume and pore diameter of the obtained samples.<sup>23</sup>

From the results shown in Fig. 1a, it can be seen that the type of nitrogen adsorption/desorption isotherms in the obtained hydrogel and xerogel of zirconium silicate and catalysts with supported vanadium oxide does not change and refers to type IV isotherms with  $H_2$  hysteresis loops.<sup>24</sup> The desorption branch in isotherms has a rather large horizontal part, characteristic of corpuscular systems, the pores of which are of an indefinite nature with narrow "throats" and various wider cavities. This is also confirmed by the distribution of pores by radius sizes, characteristic for micro-mesoporous systems (Fig. 1b). The pore volume of the samples decreases both upon calcination and upon deposition of vanadium oxide, especially when applied to Zr-Si xerogel (Fig. 1a). The change in pore size distribution (Fig. 1b) in every case occurs in the direction of increasing pores with a large radius.



**Fig. 1.** Isotherms of low-temperature nitrogen adsorption (a) and the nature of the pore size distribution of radiuses (b, c) for the  $0.6Zr$ -Si hydrogel, dried at 403 K (1); xerogel obtained by further calcination at 823 K (2); samples of catalysts with V introduced in structure of the hydrogel –  $V_2O_5$ -Zr-Si (3), and with V supported on the surface of xerogel –  $V_2O_5$ /Zr-Si (4)



**Fig. 2.** X-ray diffraction patterns of Zr-Si support (1);  $V_2O_5$ /Zr-Si catalyst (2) and  $V_2O_5$ -Zr-Si catalyst (3)

X-ray phase analysis carried out in the range of reflection angles  $2\theta = 10\text{--}70^\circ$  for the synthesized supports and catalysts, which are calcined in air at 823 K (Fig. 2), showed the presence of only an amorphous halo on the

diffraction patterns of all samples. The absence of phase reflections of vanadium oxides may indicate their highly dispersed state on the surface of supports. The phase reflections of metastable tetragonal zirconium dioxide  $t\text{-ZrO}_2$  usually appear already at 673 K upon calcination of the dried hydrogel  $ZrO_2$ <sup>25</sup> and at 773 K in the diffraction pattern of a 10 %  $VO_x/ZrO_2$  sample.<sup>26</sup> The absence of  $t\text{-ZrO}_2$  reflections in our case is consistent with the data presented by del Monte,<sup>27</sup> who showed that the amorphous matrix, with  $SiO_2$  content of  $\geq 50\%$  in the binary  $ZrO_2\text{-}SiO_2$  oxide, contributes to the preservation of the amorphous state of  $ZrO_2$  to a calcination temperature 1073 K of the mixed oxide.

Table 1 shows examples of SEM micrographs and elemental analysis of the surface layer of vanadium oxide catalysts obtained by diffusion of an aqueous solution of the  $VOSO_4$  salt into a matrix of spheres Zr-Si hydrogel –  $V_2O_5$ -Zr-Si and by applying of vanadium oxide by impregnation of the  $NH_4VO_3$  salt oxalate solution of the calcined Zr-Si xerogel –  $V_2O_5$ /Zr-Si.

**Table 1.** Topography of surface and distribution of elements in the granules surface layer of  $V_2O_5$ -Zr-Si and  $V_2O_5$ /Zr-Si catalysts

		Element	% by weight	Atomic %	Compounds, %	Formula	Ratio of elements
$V_2O_5$ -Zr-Si		Si K	21.58	20.45	46.16	$SiO_2$	Zr/Si = 0.47 Si/Zr = 2.16 V/Si = 0.14
		V K	5.57	2.91	9.95	$V_2O_5$	
		Zr L	32.49	9.48	43.89	$ZrO_2$	
		O	40.36	67.15			
		Total	100	100	100		
$V_2O_5$ /Zr-Si		Si K	22.26	20.88	47.62	$SiO_2$	Zr/Si = 0.43 Si/Zr = 2.31 V/Si = 0.14
		V K	5.63	2.91	10.06	$V_2O_5$	
		Zr L	31.33	9.05	42.32	$ZrO_2$	
		O	40.78	67.16			
		Total	100	100	100		

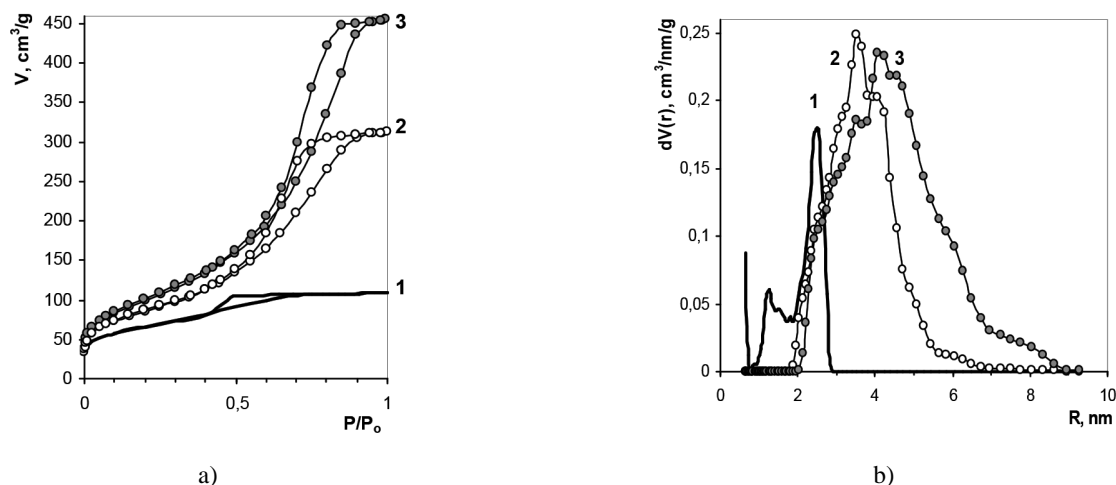
It is seen that the amount of  $ZrO_2$  in the prepared, samples is less than that in the synthesis sol; therefore, the real Zr/Si ratio in them is  $\sim 0.43\text{--}0.47$  and the  $SiO_2$  content in the mixed oxide is higher than  $ZrO_2$ . The average amount of supported vanadium oxide in both catalysts is approximately 10 wt %  $V_2O_5$ . Moreover, analyses at many points on the surface of  $V_2O_5$ -Zr-Si granules show a  $V_2O_5$  content varying in the range of 9.5–11 wt %. Similar analyses of this sample  $V_2O_5$ /Zr-Si show a wider distribution of  $V_2O_5$  – from 7 to 12 wt %. This is consistent with the data obtained by Zhao and co-workers<sup>20</sup>, who showed that the deposition of the active phase on the support hydrogel contributes to a more isolated and uniform arrangement of the active sites of

the catalysts. The average Si/Zr ratio in both samples is 2.16–2.31, close to 2, which, according to the Tanabe rule, approximately corresponds to the maximum Brønsted acidity of mixed  $ZrO_2\text{-}SiO_2$  oxides and so the Hammett acidity function can be  $H_0 \geq -8.2$ .<sup>28</sup>

The HTT of the 10 %  $V_2O_5$ -Zr-Si sample before calcining (Fig. 3) changes the shape of the hysteresis loop on the isotherm – the horizontal part on the desorption branch becomes shorter, indicating that the difference between the diameters of the “throats” and “cavities” in the porous structure of the catalyst decreases and the type of the hysteresis loop H2 transforms into H1, which is typical for systems with a developed mesoporous structure.<sup>24</sup> Micropores disappear, the radius

of the mesopores increases and their size distribution becomes close to uniform. Decantation of the sample with ethanol after HTT leads to a narrowing of the

shape of the hysteresis loop on the isotherm, indicating an additional equalization in size of increasing pore radius.



**Fig. 3.** Isotherms of low-temperature nitrogen adsorption/ desorption (a) and the nature of the pore size distribution of radiuses (b) for 10 %  $V_2O_5$ -Zr-Si catalysts obtained by depositing vanadium oxide on Zr-Si hydrogel (1), subjected to preliminary hydrothermal treatment before calcination (2) and further decantation with alcohol (3)

**Table 2.** Textural parameters of zirconium silicates and vanadium oxides catalysts

Sample	Sequential processing	Specific surface area $S_{BET}$ , $\text{m}^2/\text{g}$	Total pore volume $V_a$ , $\text{cm}^3/\text{g}$	Diameter mesopore $D_{DFT}$ , nm	Average pore diameter, nm
Zr-Si	D	389.3	0.255	2.50	2.62
Zr-Si	D, C	292.2	0.203	4.89	2.79
10 % $V_2O_5$ / Zr-Si	D, C	152.6	0.109	4.89	2.87
10 % $V_2O_5$ -Zr-Si	D, C	234.0	0.170	5.09	2.90
10 % $V_2O_5$ -Zr-Si	HTT, D, C	303.7	0.483	7.03	6.37
10 % $V_2O_5$ -Zr-Si	HTT, DE, D, C	358.1	0.706	8.14	7.88

Notes: D is drying, C is calcination, HTT is hydrothermal treatment, DE is decantation with ethanol.

Table 2 shows the results of the calculation of the texture parameters from the desorption branches of the isotherms of nitrogen adsorption/desorption for the synthesized zirconium silicates and vanadium oxide catalysts after their various sequential processing, indicated in the footnotes of the table. It can be seen that the catalyst obtained by impregnating the Zr-Si hydrogel with a solution of vanadyl sulfate salt has a larger pore volume and its specific surface area on  $80 \text{ m}^2/\text{g}$  higher than that the sample formed by the interaction of the oxalate complex of ammonium metavanadate with OH groups of the Zr-Si xerogel. After HTT, the specific surface area of the catalyst increases by another  $70 \text{ m}^2/\text{g}$ , the pore volume grows by almost 3 times, the diameter of mesopores raises to 7 nm. When decanting with

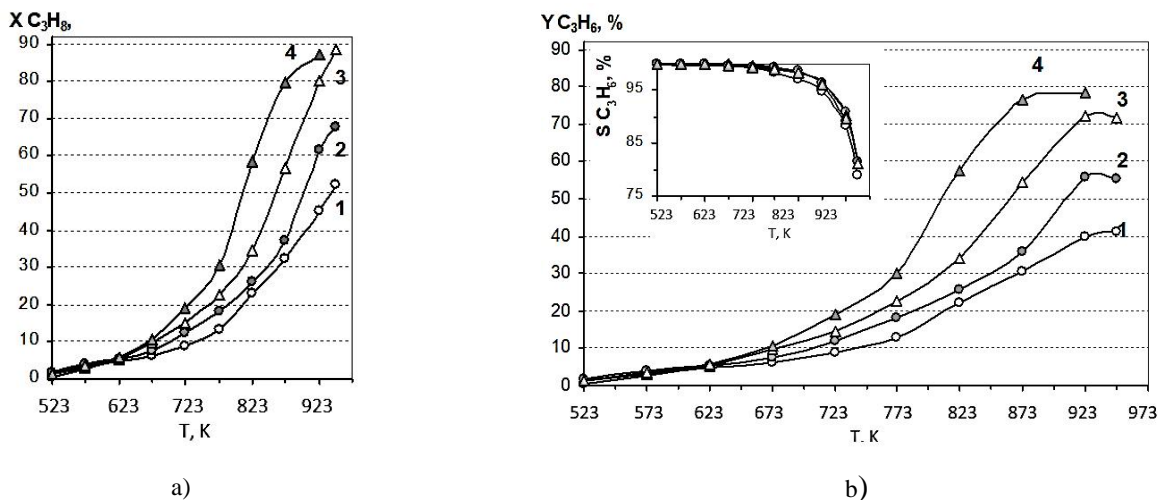
ethanol, the volume increases by 1.5 times, additionally by  $50 \text{ m}^2/\text{g}$ , the specific surface grows and the diameter of the mesopores becomes more than 8 nm.

The change in the porous structure of oxide vanadium-zirconium silicates carried out during synthesis and subsequent treatments has a significant effect on their catalytic characteristics in DHP, shown in Fig. 4, depending on the temperature of the reaction.

The transition from a catalyst with  $V_2O_5$  supported on a Zr-Si xerogel to that applied on a Zr-Si hydrogel and subjected to further hydrothermal and alcohol processing is accompanied by an increase in their specific surface area, pore volume and diameter, and an increase in their spatial order when the micro-mesoporous structure is converted to uniformly mesoporous. As can be seen

(Fig. 4 a), such changes in the structure of the samples lead to an increase in the degree of propane conversion during DHP, especially at reaction temperatures above 773 K, when conditions are created for initiating homogeneous or heterogeneous/homogeneous radical

reactions, the importance of their contribution to the general process of DHP, pointed out by Cavani *et al.*<sup>10</sup> Wherein, the highest values of  $X(C_3H_8)$  are achieved on the catalyst with the highest specific surface area and pore volume (Fig. 4a, Table 2).



**Fig. 4.** Change in the degree of conversion of propane (a), the selectivity of propylene formation and propylene yield (b), with an increase in the temperature of the propane dehydrogenation reaction on the catalysts containing 10%  $V_2O_5$  on Zr-Si oxides, obtained by applying vanadium oxide on Zr-Si xerogel (1), on a hydrogel (2), subjected to preliminary hydrothermal treatment (3) and further decantation with alcohol (4). The reaction mixture is 7%  $C_3H_8$  in argon. Contact time is 3.5 s

The selectivity of propylene formation in all samples (Fig. 4b) is almost the same and close to 100 % up to a reaction temperature of 773 K. Then it decreases to levels of ~90 % and 80 % with increasing temperature to 923 K and 948K, respectively, and slightly lower on the catalyst supported on Zr-Si – xerogel. Since  $X(C_3H_8)$  grows over the entire temperature range of DHP, with the high selectivity for propylene obtained, its yield also increases up to 873 K (Fig. 4b, curve 4) on the most active catalyst and up to 923 K on other samples (curves 1-3). At a higher reaction temperature,  $Y(C_3H_6)$  does not increase, that may be due to the formation of coke, the deposition of it on the surface of samples and the blocking by it of the active catalytic sites.

Sokolov *et al.*<sup>29,30</sup> state that during DHP process on the  $VO_x$ , supported on Al-Si acid oxide, the propylene yield increases with an increase in the amount of deposited carbon on a fresh support. It was concluded that coke creates sites of carbon phase on the Al-Si surface, which are involved in the conversion of propane. The total number of active sites of the catalyst increases and, as a result, the conversion of propane increases. Therefore, in spite of the gradual partial blocking by coke of the more active  $VO_x$  sites and the drop in

$S(C_3H_6)$ , the propylene yield remains high and almost constant when working in the reaction mixture for a long time. The presence and duration of activation by the carbon phase, according to Sokolov *et al.*,<sup>29</sup> should depend on the acid properties of the support and its available free surface. Similar processes are likely to occur with increasing temperature of the DHP reaction on the studied catalysts.

Since the amount of supported active sites of vanadium oxide on the studied catalysts is approximately equal, a large support area remains unoccupied by  $VO_x$  sites on a sample with a larger specific surface and it can participate in the formation of additional catalytically active sites of the carbon phases. Such an increase in the total number of active sites on a 10 %  $V_2O_5$ -Zr-Si catalyst with a larger surface area and pore volume will further increase the degree of propane conversion achieved on it during the DHP process. But this can also contribute to greater coke deposition, which blocks the more active catalytic sites of vanadium oxide. Therefore, it is likely, that with an increase in the DHP temperature the growth of  $Y(C_3H_8)$  on such a catalyst stops at a temperature lower by 50 K to compare with other samples (Fig. 4b).

Sokolov *et al.*<sup>29,30</sup> showed that the excellent ability of the catalysts to restore their initial activity after 2 h of oxidative regeneration is observed at 823 K.<sup>29, 30</sup> In our work, the regeneration of catalysts after DHP was carried out by their slow cooling in an air stream in an inertial reactor furnace from 923–948 K to room temperature. This treatment restored the initial color and structure of the catalysts and almost completely returned their catalytic activity.

It was shown,<sup>31</sup> that amorphous, homogeneous, containing 1 wt % Cr, Zr-Si xerogels, synthesized by thermal decomposition of thermolytic molecular precursors of alklocomplexes of elements, are much more active in DHP than xerogels based on aluminosilicate. Their use can significantly reduce the reaction temperature to obtain a high yield of propylene. In a reaction mixture containing 2 vol % of C<sub>3</sub>H<sub>8</sub>, at 723 K, on the Cr/Si/Zr/O catalyst, the value  $X(C_3H_6) > 35\%$  was achieved at  $S(C_3H_6) \sim 95\%$ , which is noted as one of the best values of these parameters reported in literature at such a low reaction temperature.<sup>31</sup>

A change in the structure obtained in this work of Zr-Si samples with supported of vanadium oxide also leads to a decrease in the temperature at which high  $Y(C_3H_6)$  values are obtained, but at more than 773 K (Fig. 4b). HTT of the catalyst hydrogel and subsequent decantation with ethanol successively decrease by ~50 K the temperature, at which approximately the same yields of propylene are obtained. As a result, on the final catalyst in the reaction mixture containing 7 vol% of C<sub>3</sub>H<sub>8</sub>, at 873 K the propylene yield reaches above 76 % at  $S(C_3H_6) \gg 96\%$  and  $X(C_3H_8) \gg 80\%$ , and these values of the catalytic parameters are higher than those published for industrial samples. It has been reported<sup>32</sup> that in the process of DHP, at the same operating temperature of above 873 K and atmospheric pressure, the Cr<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> and Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalysts show propane conversion of ~50 % and ~40 %, respectively; propylene selectivity is ~90 % and its yield is 45 and 36 %. Facing the manufacturability of the process for producing the investigated V<sub>2</sub>O<sub>5</sub>-Zr-Si catalyst, the relative cheapness of its composition, easiness of regeneration, and structural stability, it can be assumed, that in the future it can serve as a replacement for the depleted industrial catalysts of DHP processes.

## 4. Conclusions

Thus, the conducted research shows that at supporting the vanadium oxide on the spherically granulated zirconium silicate hydrogel, the obtained by direct sol-gel synthesis from the accessible salts of elements, a micro-mesoporous

catalyst is formed with a larger specific surface area and with a more uniform layer of the active component than when it is supported on Zr-Si xerogel. HTT of vanadium-zirconium silicate hydrogel and additional decantation with alcohol changes the catalyst structure to a developed mesoporous one, increases its surface area, volume and pore width. This helps to reduce the temperature of the DHP reaction on the V<sub>2</sub>O<sub>5</sub>-ZrO<sub>2</sub>-SiO<sub>2</sub> catalyst, at which a high yield of propylene is achieved, and allows to obtain large values of its yield, in comparison with industrial Cr<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> and Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalysts. This may also indicate that the role of the magnitude and acidity of the surface, volume, and pore structure are just as important for this gas-phase catalytic reaction as the nature and state of the active sites of the catalyst.

## References

- [1] Liu, G.; Zhao, Z.-J.; Wu, T.; Zeng, L.; Gong, J. Nature of the Active Sites of VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> Catalysts for Propane Dehydrogenation. *ACS Catal.* **2016**, *6*, 5207-5214. <https://doi.org/10.1021/acscatal.6b00893>
- [2] Rodemerck, U.; Stoyanova, M.; Kondratenko, E.V.; Linke D. Influence of the Kind of VO<sub>x</sub> Structures in VO<sub>x</sub>/MCM-41 on Activity, Selectivity and Stability in Dehydrogenation of Propane and Isobutane. *J. Catal.* **2017**, *352*, 256-263. <https://doi.org/10.1016/j.jcat.2017.05.022>
- [3] Zhao, J.-Z.; Wu, T.; Xiong, C.; Sun, G.; Mu, R.; Zeng, L.; Gong, J. Hydroxyl-Mediated Non-oxidative Propane Dehydrogenation over VO<sub>x</sub>/γ-Al<sub>2</sub>O<sub>3</sub> Catalysts with Improved Stability. *Angew. Chem. Int. Ed.* **2018**, *57*, 6791-6795. <https://doi.org/10.1002/ange.201800123>
- [4] Nawaz, Z. Light Alkane Dehydrogenation to Light Olefin Technologies: A Comprehensive Review. *Rev. Chem. Eng.* **2015**, *31*, 413-436. <https://doi.org/10.1515/revce-2015-0012>
- [5] 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**, *114* (20), 10613-10653. <https://doi.org/10.1021/cr5002436>
- [6] Pham, H.N.; Sattler, J.H.B.; Weckhuysen, B.M.; Datye, A.K. Role of Sn in the Regeneration of Pt/γ-Al<sub>2</sub>O<sub>3</sub> Light Alkane Dehydrogenation Catalysts. *ACS Catal.*, **2016**, *6*, 2257-2264. <https://doi.org/10.1021/acscatal.5b02917>
- [7] Sokolov, S.; Stoyanova, M.; Rodemerck, U.; Linke, D.; Kondratenko, E.V. Comparative Study of Propane Dehydrogenation Over V-, Cr-, and Pt-Based Catalysts: Time On-Stream Behavior and Origins of Deactivation. *J. Catal.* **2012**, *293*, 67-75. <https://doi.org/10.1016/j.jcat.2012.06.005>
- [8] Zazhigalov, V.A.; Konovalova, N.D.; Redkina, A.V.; Khomenko, K.N. Sravnitelnoe Issledovanie Degidrirovaniia Propana na VO<sub>x</sub>/MCM-41 i VO<sub>x</sub>/Ti-MCM-41 s Polucheniem Propilena i Vodoroda. *Ukr. Khim. Zh.* **2013**, *79* (11), 63-72.
- [9] Redkina, A.V.; Konovalova, N.D.; Khomenko, K.N. Degidrirovaniie Propana na V<sub>x</sub>O<sub>y</sub>/H-Ti-MCM-41. *Zh. Khim. Phys. ta Tekhnol. Poverkni*, **2014**, *5* (2), 174-189.
- [10] Cavani, F.; Ballarini, N.; Cericola, A. Oxidative Dehydrogenation of Ethane and Propane: How far from

- Commercial Implementation? *Catal. Today*, **2007**, *127*, 113-131. <https://doi.org/10.1016/j.cattod.2007.05.009>
- [11] Otroshchenko, T.; Kondratenko, V.A.; Rodemerck, U.; Linke, D.; Kondratenko, E.V. ZrO<sub>2</sub>-Based Unconventional Catalysts for Non-Oxidative Propane Dehydrogenation: Factors Determining Catalytic Activity. *J. Catal.* **2017**, *348*, 282-290. <https://doi.org/10.1016/j.jcat.2017.02.016>
- [12] Otroshchenko, T.; Bulavchenko, O.; Thanh, H.V.; Rabeah, J.; Bentrup, U.; Matvienko, A.; Rodemerck, U.; Paul, B.; Kraehnert, R.; Linke, D. et al. Controlling Activity and Selectivity of Bare ZrO<sub>2</sub> in Non-Oxidative Propane Dehydrogenation. *Appl. Catal. A-Gen.* **2019**, *585*, 117189. <https://doi.org/10.1016/j.apcata.2019.117189>
- [13] Jeon, N.; Choe, H.; Jrong, B.; Yun, Y. Cu-Promoted Zirconia Catalysts for Non-Oxidative Propane Dehydrogenation. *Appl. Catal. A-Gen.* **2019**, *586*, 117211. <https://doi.org/10.1016/j.apcata.2019.117211>
- [14] Redkina, A.V.; Konovalova, N.D.; Kravchenko, N.V.; Strelko, V.V. Degidrirovannia Propana v Propilen na V<sub>2</sub>O<sub>5</sub>, Nanesennom na Micro-Mezoporistuiu Sistemu Oksidov ZrO<sub>2</sub>-SiO<sub>2</sub>-TiO<sub>2</sub>. *Ukr. Khim. Zh.*, **2018**, *84* (7), 43-59.
- [15] Redkina A.V., Konovalova N.D., Strelko V.V.: Sposib Oderzhannia Katalizatora Dehidruvannia Propanu v Propilen. Patent UA 131758 U, January 25, 2019.
- [16] Karakouliou, 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). *Micropor. Mesopor. Mater.* **2008**, *110*, 157-166. <https://doi.org/10.1016/j.micromeso.2007.10.027>
- [17] Selvam, P.; Dapurkar, S.E. The Effect of Vanadium Sources on the Synthesis and Catalytic Activity of VMCM-41. *J. Catal.* **2005**, *229*, 64-71. <https://doi.org/10.1016/j.jcat.2004.10.005>
- [18] Yamaguchi, T. Application of ZrO<sub>2</sub> as a Catalyst and a Catalyst Support. *Catal. Today* **1994**, *20*, 199-217. [https://doi.org/10.1016/0920-5861\(94\)80003-0](https://doi.org/10.1016/0920-5861(94)80003-0)
- [19] Cimino, A.; Cordischi, D.; De Rossi, S. Ferraris, G.; Gazzoli, D.; Indovina, V.; Minelli, G.; Occhiuzzi, M.; Valigi, M. Studies on Chromia/Zirconia Catalysts I. Preparation and Characterization of the System. *J. Catal.* **1991**, *127*, 744-760. [https://doi.org/10.1016/0021-9517\(91\)90196-B](https://doi.org/10.1016/0021-9517(91)90196-B)
- [20] Zhao, B.Y.; Xu, X.P.; Ma, H.R.; Sun, D.H.; Gao, J.M. Monolayer Dispersion of Oxides and Salts on Surface of ZrO<sub>2</sub> and Its Application in Preparation of ZrO<sub>2</sub>-Supported Catalysts with High Surface Areas. *Catal. Lett.* **1997**, *45*, 237-244. <https://doi.org/10.1023/A:1019048503124>
- [21] Tanabe, K.; Yamaguchi, T. Acid-Base Bifunctional Catalysis by ZrO<sub>2</sub> and Its Mixed Oxides. *Catal. Today*, **1994**, *20*, 185-197. [https://doi.org/10.1016/0920-5861\(94\)80002-2](https://doi.org/10.1016/0920-5861(94)80002-2)
- [22] Raju, V.; Jaenicke, S.; Chuah, G.-K. Effect of Hydrothermal Treatment and Silica on Thermal Stability and Oxygen Storage Capacity of Ceria-Zirconia. *Appl. Catal. B*, **2009**, *91*, 92-100. <https://doi.org/10.1016/j.apcatb.2009.05.010>
- [23] He, X.; Zhang, H.; Li, Y.; Hong, C.Q.; Zhao, J.P. Preparation and Structural Characterization of SiO<sub>2</sub>-ZrO<sub>2</sub> Aerogels. *Key Eng. Mater.* **2007**, *336-338*, 2282-2285. <https://doi.org/10.4028/www.scientific.net/KEM.336-338.2282>
- [24] Sing, K.S.W.; Everett, D.H.; Haul, R.A.W.; Moscou, L.; Pierotti, R.A.; Rouquerol, J.; Siemieniewska, T. Reporting Physisorption Data for Gas/Solid Systems with Special Reference to the Determination of Surface Area and Porosity (Recommendations 1984). *Pure Appl. Chem.* **1985**, *57* (4), 603-619. <https://doi.org/10.1351/pac198254112201>
- [25] Li, M.; Feng, Z.; Xiong, G.; Ying, P.; Xin, Q.; Li, C. Phase Transformation in the Surface Region of Zirconia Detected by UV Raman Spectroscopy. *J. Phys. Chem. B*, **2001**, *105*, 8107-8111. <https://doi.org/10.1021/jp010526l>
- [26] 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**, *177*, 343-351. <https://doi.org/10.1006/jcat.1998.2143>
- [27] del Monte F., Larsen W., Mackenzie J.D. Stabilization of Tetragonal ZrO<sub>2</sub> in ZrO<sub>2</sub>-SiO<sub>2</sub> Binary Oxides. *J. Am. Chem. Soc.* **2000**, *83* (3), 628-634. <https://doi.org/10.1111/j.1151-2916.2000.tb01243.x>
- [28] Bosman, H.J.M.; Kruissink, E.C.; van der Spoel, J.; van den Brink, F. Characterization of the Acid Strength of SiO<sub>2</sub>-ZrO<sub>2</sub> Mixed Oxides. *J. Catal.* **1994**, *148*, 660-672. <https://doi.org/10.1006/jcat.1994.1253>
- [29] Sokolov, S.; Stoyanova, M.; Rodemerck, U.; Linke, D.; Kondratenko, E.V. Effect of Support on Selectivity and On-Stream Stability of Surface VO<sub>x</sub> Species in Non-Oxidative Propane Dehydrogenation. *Catal. Sci. Technol.* **2014**, *4*, 1323-1332. <https://doi.org/10.1039/C3CY01083J>
- [30] Sokolov, S.; Bychkov, V.Yu.; Stoyanova, M.; Rodemerck, U.; Bentrup, U.; Linke, D.; Tyulenin, Y.P.; Korchak, V.N.; Kondratenko, E.V. Effect of VO<sub>x</sub> Species and Support on Coke Formation and Catalyst Stability in Nonoxidative Propane Dehydrogenation. *ChemCatChem* **2015**, *7*, 1691-1700. <https://doi.org/10.1002/cctc.201500151>
- [31] Furdala, K.L.; Tilley, T.D. Thermolytic Molecular Precursor Routes to Cr/Si/Al/O and Cr/Si/Zr/O Catalysts for the Oxidative Dehydrogenation and Dehydrogenation of Propane. *J. Catal.* **2003**, *218*, 123-134. [https://doi.org/10.1016/S0021-9517\(03\)00141-6](https://doi.org/10.1016/S0021-9517(03)00141-6)
- [32] Maddah H.A. A Comparative Study between Propane Dehydrogenation (PDH) Technologies and Plants in Saudi Arabia. *Am. Sci. Res. J. Eng., Technol., Sci.* **2018**, *45*, 49-63.

Received: February 12, 2021 / Revised: February 22, 2021 / Accepted: October 12, 2021

### ВПЛИВ ПОРУВАТОЇ СТРУКТУРИ V<sub>2</sub>O<sub>5</sub>-ZrO<sub>2</sub>-SiO<sub>2</sub> КАТАЛІЗАТОРА НА РЕАКЦІЮ ДЕГІДРУВАННЯ ПРОПАНУ

**Анотація.** Сферично гранульований, аморфний, мезопоруватий каталізатор отримано нанесенням V<sub>2</sub>O<sub>5</sub> на синтезований прямим золь-гель способом гідрогель ZrO<sub>2</sub>-SiO<sub>2</sub> та ідентифікований методами СЕМ, РФА та адсорбції/десорбції N<sub>2</sub>. Показано, що його гідротермальне і спиртове оброблення підвищує питому поверхню, об'єм і ширину пор і приводить до збільшення виходу пропілену в реакції дегідрування пропану та зниження температури досягнення його високих значень.

**Ключові слова:** дегідрування пропану, пропілен, оксид ванадію, цирконій силікати.