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*A.V. Redkina, N.V. Kravchenko, N.D. Konovalova, **V.V. Strelko*****INFLUENCE OF VANADIUM CONTENT ON STRUCTURE AND ACTIVITY OF V_2O_5 - ZrO_2 - SiO_2 CATALYST FOR PROPANE DEHYDROGENATION****Institute for Sorption and Problems of Endoecology, National Academy of Sciences of Ukraine, Kyiv, Ukraine**

In order to create alternative vanadium oxide-supported catalysts for the process of non-oxidative propane dehydrogenation to propylene, we studied the effect of the increased content of vanadium oxide in the V_2O_5 - ZrO_2 - SiO_2 composition on its structure and catalytic properties. Zirconium silicate hydrogel in the form of finished spherical granules with the SiO_2 content of more than 50% was prepared by direct sol-gel synthesis from zirconium oxychloride and sodium metasilicate using the droplet coagulation technology. Catalysts were fabricated by impregnation of hydrogel with an aqueous solution of vanadyl sulfate salt, hydrothermal treatment and calcination in air. By using scanning electron microscopy, X-ray diffraction analysis and low-temperature nitrogen adsorption/desorption method, we showed that amorphous samples with a developed mesoporous structure (with the pore diameter of ~6 nm and the specific surface area of ~300 m² g⁻¹) were formed when the content of the supporting V_2O_5 on zirconium silicate was 10, 20, 25, and 30 wt.%. In the course of temperature increase in the propane dehydrogenation reaction, the catalyst samples crystallized in the reaction mixture propane-inert gas with the formation of tetragonal zirconia. When the content of V_2O_5 was 25% or 30%, additional phases of reduced vanadium oxides and traces of the zirconium vanadate phase were formed. After the reaction, the specific surface area of the catalysts decreased significantly and the average pore size of the samples with 25% and 30% V_2O_5 increased to ~30 nm. The propylene yield reproducibly observed on the samples with 25% and 30% V_2O_5 was lower than that on the samples with 10% V_2O_5 ; however, it remained quite high, which was probably due to the expanded diameter of the pores and the appearance of additional ZrV_2O_7 sites that are active with respect to the dehydrogenation of light alkane.

Keywords: propane dehydrogenation, vanadium oxide, zirconium silicate, sol-gel synthesis, catalysis.

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Introduction

Vanadium oxides-supported alternative catalysts are currently considered as the most promising for dehydrogenation of light alkanes and, in particular, propane dehydrogenation (DHP) to propylene, which is the large-tonnage intermediate product of the chemical industry, and serves as the main raw material for the production of polypropylene, propylene oxide and acrylonitrile, polyurethane foam and many other products [1,2]. The need for pure propylene significantly exceeds its production volumes by traditional methods of thermal and catalytic cracking of petroleum distillation products. Therefore, the DHP processes are being developed

quickly, which is facilitated by the production of cheap shale gas containing significant amounts of propane [3,4]. The main manufacturing technologies of the dehydrogenation of light olefins and DHP processes are based on two following catalytic systems: Cr_2O_3/Al_2O_3 and $Pt-Sn/Al_2O_3$. It has been reported [4] that these catalysts at the operating temperature of >600°C and atmospheric pressure showed propane conversion of ~50% and ~40%, respectively; the propylene selectivity being ~90% and its yield being ~45% and 36% in the processes denominated Catofin and Oleflex, respectively. However, periodic oxidative regeneration of catalysts leads to a decrease in their activity and structural

stability due to the particle agglomeration (sintering); therefore, the catalysts must be replaced after 1–3 years of operation [3]. In addition, it was stressed that a high cost of Pt as well as serious pollution issues associated with Cr restrict a further development of the DHP processes, and many studies are aimed at developing new catalysts for propane dehydrogenation to overcome these shortcomings [1,2].

It has been shown [5,6] that catalysts with vanadium oxide groups on porous silicate systems can operate for a long time in the stream in all DHP cycles as compared with industrial catalysts. In addition, they can be completely reduced by oxidative regeneration. Zirconia promoted by metals, which increases the number of anionic vacancies causing activation of propane, is also considered as an alternative type of catalyst capable of replacing spent DHP catalysts [7,8]. Zirconia is also considered the best catalytic supports, since it is chemically stable, has weak amphoteric properties and interacts well with transition metals, contributing to their finely dispersion on surface and inhibiting sintering. However, the support obtained by hydrolysis of $ZrOCl_2$ can change its surface area from $360 \text{ m}^2 \text{ g}^{-1}$ to $20 \text{ m}^2 \text{ g}^{-1}$ and morphology from microporous to mesoporous and macroporous ones when the temperature changes from 110 to 650°C [9]. This is explained by the diffusion of oxide particles, their growth and agglomeration, causing a change in the phase modification of ZrO_2 from amorphous to metastable tetragonal (t- ZrO_2) and monoclinic (m- ZrO_2) [9]. It is possible to reduce the diffusion of ZrO_2 particles and stabilize their state by creating a mixed ZrO_2 – SiO_2 oxide. The amorphous silica matrix does not allow ZrO_2 particles to grow to a critical size of the monoclinic phase and binary oxide remains amorphous up to a calcination temperature of 800°C at the SiO_2 content of more than 50 wt.% [10]. A layer of the active component dispersed on the ZrO_2 surface can also separate support particles from each other and suppress their surface diffusion. It was shown [11] that if the $Zr(OH)_4$ colloidal particles are coated with a solution of the active component before calcining, the resulting ZrO_2 catalysts will often have a large surface area, which gradually increases, reaches a maximum (when the content of the active component grows achieving the most dispersed state), and then slowly decreases with increasing loads.

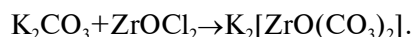
Earlier [12], we showed that the use of 10 wt.% supporting vanadium oxide on the hydrogel of spherically granular zirconium silicate and hydrothermal treatment of the samples before calcination resulted in a more than doubling of the

specific surface area of the V_2O_5 – ZrO_2 – SiO_2 catalyst as compared with the deposition of the same amount of V_2O_5 on the xerogel of the support. The volume and pore diameter of catalyst were also increased and the structure was changed from micro-mesoporous to uniformly mesoporous. This led to a significant increase in the propylene yield in DHP reaction, which exceeded the values obtained on industrial catalysts.

The goal of this work was to study the effect of the increased content of vanadium oxide in the compound of the spherically granulated V_2O_5 – ZrO_2 – SiO_2 composition on its structure and catalytic properties in order to develop vanadium oxide-supported alternative catalysts for the process of non-oxidative dehydrogenation of propane to propylene.

Materials and methods

To prepare nanostructured zirconium silicate, a previously developed method for its direct one-step sol-gel synthesis was used from available cheap salts of elements [12]. The method was supplemented with the use of coagulation in a drop, which allows obtaining ready-made and durable spherical granules of Zr–Si hydrogel. A solution of zirconium oxychloride was added to an excess of an aqueous solution of potassium carbonate to form metastable complex zirconium carbonate according to the following equation:



Its solution and the solution of water glass (sodium metasilicate) with the concentrations necessary to create the ratio of $Zr/Si=0.6$ were fed to a flow-mixing reactor where the mixed sol of zirconium oxyhydrate and silicic acid was formed as shown by the following equation:



The sol stream was directed to a column filled with two layers of liquids. The top layer was undecane, and the bottom was running tap water. During the passage of the undecane layer (1.0–1.5 m), the sol stream was break into separate droplets and it was turned into strong spherical granules of Zr–Si hydrogel for 3–5 seconds. They were transferred with water and first fell onto a sieve and then into a container, where they were washed with distilled water from alkalis, salts and traces of undecane, treated with a solution of NH_4OH and washed again with water until neutral value. Weighed portions of Zr–Si-silicate hydrogels without external

moisture were poured in terms of moisture capacity by VOSO_4 solutions with the concentrations necessary for applying 10, 20, 25, and 30 wt.% V_2O_5 . The samples were left for two days for flowing of diffusion process of the vanadium salt into the hydrogel spheres, then the excess water was drained, and the NH_4OH solution was poured into them to precipitate vanadium hydroxide in the pores of the support. Then, the samples were subjected to hydrothermal treatment in steel autoclaves at 250°C for 5 hours, after which they were dried at 130°C and calcined in air at 450°C during 5 hours with a gradual increase in temperature.

Analysis of the microstructure and elemental composition of the samples was carried out by scanning electron microscopy (SEM) using a JEOL JSM 7001F scanning electron microscope with an Oxford Instruments microanalyzer system.

Nitrogen adsorption isotherms of the samples were obtained according to the standard procedure after vacuum treatment at 150°C on an ASAP 2405N Micromeritics instrument. The pore size distribution was calculated by the theory of density functional (DFT).

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

The DHP reaction was carried out in a flowing quartz reactor 30 cm long and 0.7 cm in diameter,

using samples of the catalyst (0.85 g) with a volume of 1 cm^3 placed in the middle of the reactor. The flow rate of the working mixture containing 7 vol.% propane in argon was 18 mL min^{-1} and the contact time with the catalyst was 3.5 s. After holding samples in the reaction mixture for at least an hour at $250\text{--}300^\circ\text{C}$, the temperature of the reactor was increased by 25°C every 0.5 h to achieve 650°C . Propane and the products of reaction, propylene, methane, ethane and ethylene, contained in $v\text{ mL}$, were analyzed on a chromatographic column filled with silica gel using a flame ionization detector. The propane conversion was calculated as $X(\text{C}_3\text{H}_8)\% = 100 \cdot (v^{\text{in}}\text{C}_3\text{H}_8 - v^{\text{ou}}\text{C}_3\text{H}_8) / v^{\text{in}}\text{C}_3\text{H}_8$. When calculating the selectivities (S_i) of the formation of the reaction products in order to maintain the material balance with respect to carbon, the volumes of emitted gases (v_i) were multiplied by the coefficients of their volume change in relation to propane (α_i) which were equal to 1/3, 2/3, 2/3 and 1 for CH_4 , C_2H_4 , C_2H_6 and C_3H_6 , respectively. Then, we have: $S_i\% = 100 \cdot \alpha_i \cdot v_i / S_{\text{ai}} \cdot v_i$. The propylene yield was determined as $Y(\text{C}_3\text{H}_6)\% = X(\text{C}_3\text{H}_8) \cdot S(\text{C}_3\text{H}_6) / 100$.

Results and discussion

Tables 1 and 2 and Fig. 1 show the results of measuring the surface topography and structural parameters of the prepared catalysts.

SEM images (Table 1) show that spherical granules are well defined and have a size of $200\text{--}700\ \mu\text{m}$, the amount of zirconium dioxide in the

Table 1
SEM images and distribution of elements in the surface layer of granules of $\text{V}_2\text{O}_5\text{--ZrO}_2\text{--SiO}_2$ catalyst

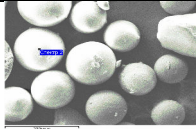
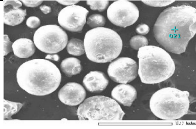
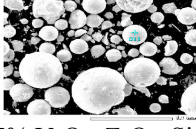
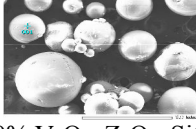
 10% $\text{V}_2\text{O}_5\text{--ZrO}_2\text{--SiO}_2$	Element	Wt.%	At.%	Compound, %	Formula	Ratio
	Si K	22.26	20.88	47.62	SiO_2	Zr/Si=0.43 Si/Zr=2.31 V/Si=0.14
	V K	5.63	2.91	10.06	V_2O_5	
	Zr L	31.33	9.05	42.32	ZrO_2	
	O	40.78	67.16			
 20% $\text{V}_2\text{O}_5\text{--ZrO}_2\text{--SiO}_2$	Element	Wt.%	At.%	Compound, %	Formula	Ratio
	Si K	19.84	18.63	42.66	SiO_2	Zr/Si=0.42 Si/Zr=2.37 V/Si=0.31
	V K	11.41	5.77	20.37	V_2O_5	
	Zr L	27.37	7.87	36.97	ZrO_2	
	O	41.28	67.72			
 25% $\text{V}_2\text{O}_5\text{--ZrO}_2\text{--SiO}_2$	Element	Wt.%	At.%	Compound, %	Formula	Ratio
	Si K	18.82	17.54	40.25	SiO_2	Zr/Si=0.42 Si/Zr=2.4 V/Si=0.42
	V K	14.26	7.32	25.25	V_2O_5	
	Zr L	25.54	7.32	34.5	ZrO_2	
	O	41.38	67.8		SiO_2	
 30% $\text{V}_2\text{O}_5\text{--ZrO}_2\text{--SiO}_2$	Element	Wt.%	At.%	Compound, %	Formula	Ratio
	Si K	17.41	16.23	37.25	SiO_2	Zr/Si=0.42 Si/Zr=2.38 V/Si=0.52
	V K	17.32	8.9	30.71	V_2O_5	
	Zr L	23.72	6.8	32.04	ZrO_2	
	O	41.55	68.06		SiO_2	

Table 2

Initial structural parameters of catalysts after hydrothermal treatment, drying and calcinations

Sample	Specific surface area, S_{BET} , $\text{m}^2 \text{g}^{-1}$	Total pore volume, V_{Σ} , $\text{cm}^3 \text{g}^{-1}$	Diameter pores, D_{DFT} , Å	Average pore diameter, Å
10% $\text{V}_2\text{O}_5\text{-ZrO}_2\text{-SiO}_2$	303.7	0.483	70.32	63.66
20% $\text{V}_2\text{O}_5\text{-ZrO}_2\text{-SiO}_2$	237.1	0.339	58.80	49.70
25% $\text{V}_2\text{O}_5\text{-ZrO}_2\text{-SiO}_2$	253.3	0.346	58.80	54.62
30% $\text{V}_2\text{O}_5\text{-ZrO}_2\text{-SiO}_2$	267.9	0.391	60.80	58.44

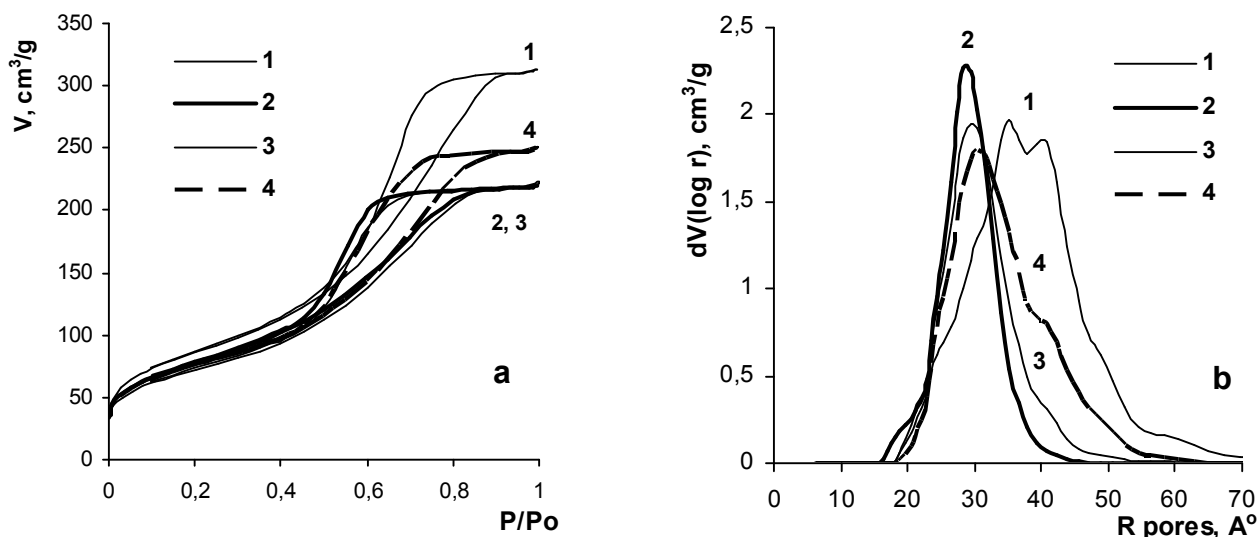


Fig. 1. Isotherms of low-temperature adsorption/desorption of nitrogen (a) and the pore size distribution (b) of freshly prepared $\text{V}_2\text{O}_5\text{-ZrO}_2\text{-SiO}_2$ catalysts with different content of V_2O_5 (wt. %): 1 – 10%, 2 – 20%, 3 – 25%, 4 – 30%

support structure is lower than it was in the synthesized sol, and the real Zr/Si ratio is about 0.42–0.43. Isotherms of N_2 adsorption/desorption of the samples under consideration belong to the IV type isotherms, which are typical of developed mesoporous systems (Fig. 1,a). An increase in the amount of V_2O_5 reduces the surface size and pore volume of the obtained catalysts; however, within the range of 20–30% V_2O_5 this leads to a small increase in these values (Table 2) and contributes to more ordered size distribution of the pores (Fig. 1,b). This may confirm the stabilizing effect of active phase on the structure of the ZrO_2 -based catalyst.

Catalytic tests (Fig. 2) show that an increase in the content of supporting V_2O_5 in Zr–Si hydrogel above 10 wt.% leads to a decrease in the yield of the formation of propylene on the prepared catalysts, but it remains quite high and almost independent of the concentration of V_2O_5 in the range of 20–30 wt.%. The selectivity of the propylene formation is high and almost independent of the content of V_2O_5 , the selectivity being decreased from 100% to ~90% with increasing the reaction temperature (Fig. 2,b).

After using the $\text{V}_2\text{O}_5\text{-ZrO}_2\text{-SiO}_2$ catalysts with different content of V_2O_5 , we observed a sharp change in the shape of the isotherms (Fig. 3), a decrease in the pore volume and an abrupt decrease in their specific surface area (Table 3). However, wider mesopores with diameters of ~160 and ~260 Å appear together with mesopores having diameters of 60–90 Å. Thus, the average mesopore diameter of the samples containing 30% V_2O_5 exceeds 300 Å.

Supporting vanadium oxides were previously studied and they showed the highest efficiency in the exothermic process of oxidative dehydrogenation of propane (ODHP) [13]. However, they exhibited low selectivity and yield towards propylene due to their further oxidation. Cavani et al. [13] showed that an increase in the yield of propylene can be achieved both in ODHP and in DHP by changing the porous structure of the catalysts and their chemical nature, which can initiate the additional passage 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 the catalysts can be more selective than in a

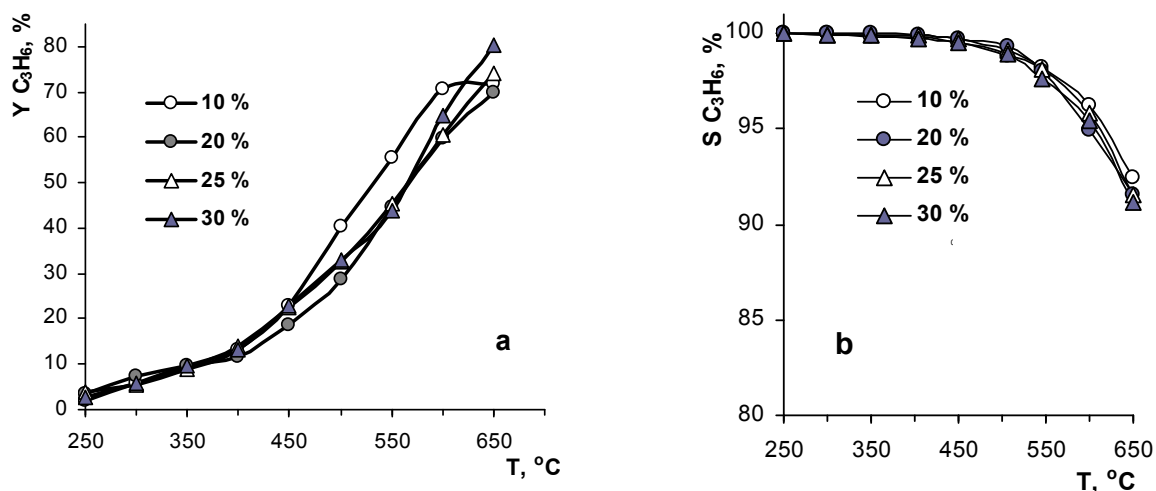


Fig. 2. The dependences of the yield (a) and selectivity (b) of the propylene formation on the temperature of reaction occurring on the V₂O₅-ZrO₂-SiO₂ catalysts with different content of V₂O₅

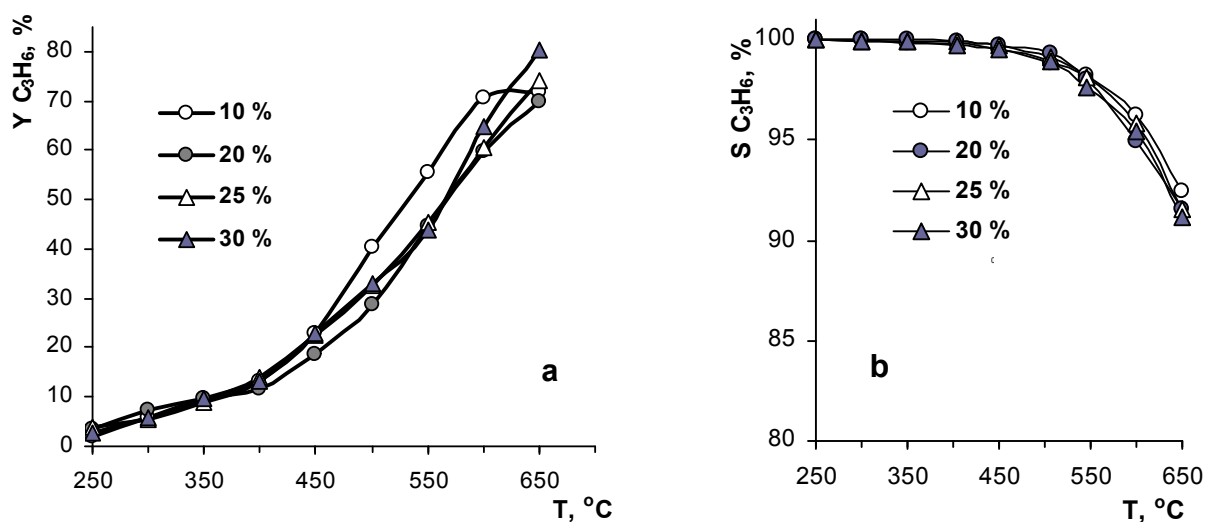


Fig. 3. Isotherms of low-temperature N₂ adsorption/desorption (a) and pore size distribution (b) for the V₂O₅-ZrO₂-SiO₂ catalysts after their using in DHP reaction. The content of V₂O₅ (wt.%): 1 – 10, 2 – 20, 3 – 25 and 4 – 30

Table 3

Structural parameters of catalysts after their use in the reaction of propane dehydrogenation

Sample	Specific surface area, S _{BET} , m ² g ⁻¹	Total pore volume, V _Σ , cm ³ g ⁻¹	Diameter pores, D _{DFT} , Å	Average pore diameter, Å
10% V ₂ O ₅ -ZrO ₂ -SiO ₂	140.2	0.314	81.44	89.44
20% V ₂ O ₅ -ZrO ₂ -SiO ₂	54.9	0.226	63.16	164.50
25% V ₂ O ₅ -ZrO ₂ -SiO ₂	35.8	0.213	70.32	273.80
30% V ₂ O ₅ -ZrO ₂ -SiO ₂	30.8	0.232	90.98	309.60

completely heterogeneous process [13]. For example, Liu et al. [2] explained the onset of the DHP reaction on VO_x/Al₂O₃ by the formation of propyl radicals associated with vanadium. Based on this, it can be assumed that a sufficiently high yield of propylene on V₂O₅-ZrO₂-SiO₂ catalysts with a high content

of vanadium, a low specific surface area, but a large mesopore diameter are associated with an increase in the contribution of high-temperature radical homogeneous reactions to the generic dehydrogenation process.

The temperature of 450°C for calcination of

the samples before the reaction was chosen because preliminary calcination of the catalyst at a relatively low temperature can significantly increase the size of its surface and its resistance to subsequent high firing temperatures [11]. This temperature is sufficient for the formation of the V_2O_5 phase and crystallization of amorphous ZrO_2 can begin at $450^\circ C$ [14], which is caused by the dissolution of vanadium in zirconium dioxide. Verification of this assumption showed that the prepared catalysts with 10–25% V_2O_5 that were calcinated in air at the temperature of 450 to $650^\circ C$ remained amorphous. The sample of 30% $V_2O_5-ZrO_2-SiO_2$ crystallized at $650^\circ C$ in air mainly with the formation of the ZrV_2O_7 and V_2O_5 phases having a very low specific surface area (1 and $3\text{ m}^2\text{ g}^{-1}$, respectively) (Fig. 4).

The XRD analysis of the catalysts preliminarily calcinated in air at $450^\circ C$ was also performed their

use in the DHP reaction. The results showed the presence of the tetragonal phase of zirconium oxide $t-ZrO_2$ in the samples, the intensity of the reflections of which increases with increasing vanadium content (Fig. 5). At the V_2O_5 content of 25%, the reflections from the monoclinic phase $m-ZrO_2$ and reduced vanadium oxides are observed; at the V_2O_5 content of 30%, the additional reflexes from the zirconium vanadate phase (ZrV_2O_7) appeared.

It is known [15] that a catalyst prepared by simple mixing of separately prepared ZrV_2O_7 and $\gamma-Al_2O_3$ phases exhibits high selectivity and activity in the process of non-oxidative dehydrogenation of light alkane, isobutene, on ZrV_2O_7 active sites. It can be assumed that the additional moderate formation of such active sites on the investigated $V_2O_5-ZrO_2-SiO_2$ catalysts with a high content of vanadium oxide in the reaction mixture of propane–

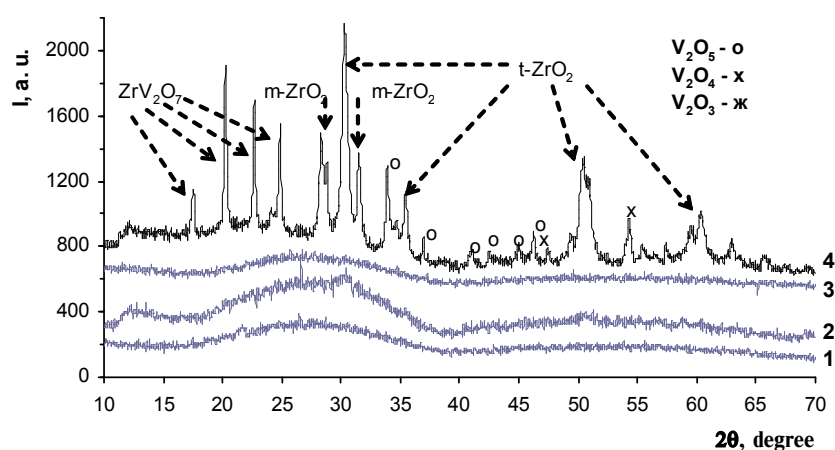


Fig. 4. X-ray diffraction patterns of the 25% $V_2O_5-ZrO_2-SiO_2$ (1 and 2) and 30% $V_2O_5-ZrO_2-SiO_2$ (3 and 4) catalysts after their calcination in air at the temperature of $450^\circ C$ (1 and 3) and $650^\circ C$ (2 and 4)

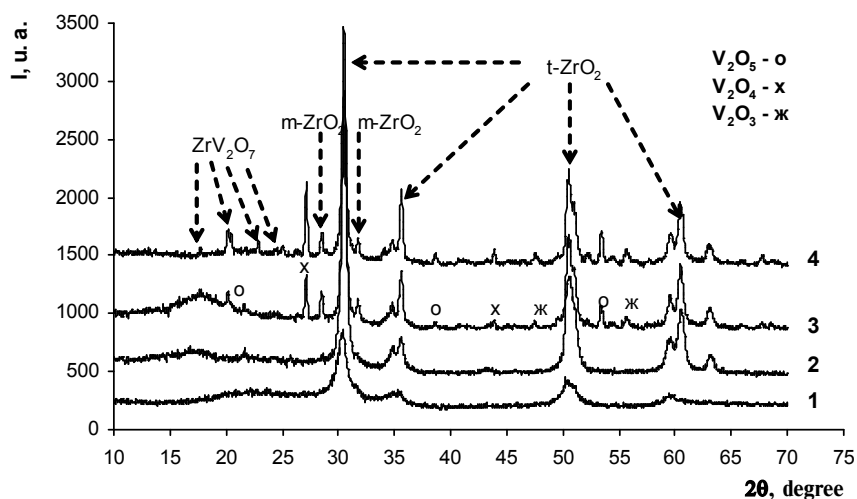


Fig. 5. X-ray diffraction patterns of $V_2O_5-ZrO_2-SiO_2$ catalysts after their use in the DHP reaction. The content of V_2O_5 (wt.%): 1 – 10, 2 – 20, 3 – 25 and 4 – 30

inert gas can provide an increase in the degree of propane conversion and, accordingly, maintain a high propylene yield, despite a significant decrease in the specific surface area of the catalysts.

After using in the DHP reaction, the catalysts were regenerated by slow cooling in a stream of compressed air in an inertial reactor furnace from 650°C to room temperature. This treatment returned the original color and external structure of the catalysts; and the catalysts almost completely restored their catalytic activity. Consecutive carrying out five cycles of operation on the 30% V₂O₅-ZrO₂-SiO₂ catalyst in the used reaction mixture and the subsequent regeneration described above resulted in a decrease in the propylene yield from ~65% (Fig. 2) to ~55%. These values of Y(C₃H₆) are higher than those given in ref. [4] for industrial catalysts.

Conclusions

The effects of an increased amount of vanadium (10, 20, 25 and 30% of V₂O₅) introduced into a spherically granulated zirconium silicate hydrogel on the structure and activity of the obtained catalysts in the propane dehydrogenation reaction were studied. It was shown that catalysts is amorphous after their preparation and calcination in air, their specific surface area was ~300 m² g⁻¹. The catalysts crystallized and showed a developed and close mesoporous structure with an average pore diameter and mesopore of ~6 nm in the reaction mixture (propane-inert gas) at increasing reaction temperature. The specific surface area of the catalysts was significantly reduced and the average pore size of the samples with 25% and 30% of V₂O₅ was increased to ~30 nm. The propylene yield reproducibly observed on these samples was lower than in the case of 10% V₂O₅-ZrO₂-SiO₂; however, it remained quite high, which was possibly due to the expanded diameter of their pores and the appearance of additional ZrV₂O₇ sites that were active towards the dehydrogenation of light alkane.

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ВПЛИВ ВМІСТУ ВАНАДІЮ НА СТРУКТУРУ І АКТИВНІСТЬ $V_2O_5-ZrO_2-SiO_2$ КАТАЛІЗАТОРА ДЕГІДРУВАННЯ ПРОПАНУ

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З метою створення альтернативних нанесених оксидованадієвих каталізаторів для процесу неокислювального дегідрування пропану в пропілен, проведено вивчення впливу підвищеного вмісту оксиду ванадію в складі $V_2O_5-ZrO_2-SiO_2$ композиції на її структуру та каталітичні властивості. Гідрогель цирконій силікату, у вигляді готових сферичних гранул, з вмістом $SiO_2 > 50\%$, отримували методом прямого зольгель синтезу з цирконій оксихлориду і натрій метасилікату з використанням технології коагуляції в краплі. Каталізатори готували методом просочення гідрогелю водним розчином солі ванадій сульфату, гідротермальним обробленням і прожарюванням на повітрі. Методами сканувальної електронної мікроскопії, рентгенівського фазового аналізу та низькотемпературної адсорбції/десорбції азоту було показано, що при нанесенні 10, 20, 25 і 30 мас.% V_2O_5 на цирконій силікат утворюються аморфні зразки з розвиненою мезопоруватою структурою, з діаметром пор ~ 6 нм і величиною питомої поверхні ~ 300 м²/г. У процесі підвищення температури реакції дегідрування пропану в реакційній суміші пропан-інертний газ зразки каталізаторів кристалізувалися з утворенням тетрагонального цирконій діоксиду, а при вмісті 25 і 30% V_2O_5 – з додатковим формуванням фаз відновленого ванадій оксиду і слідів фази цирконій ванадату. Після протікання реакції питома поверхня каталізаторів істотно знизилася, а середній розмір пор зразків з 25 і 30% V_2O_5 збільшився до ~ 30 нм. Вихід пропілену, відтворено одержуваний на цих зразках, був нижчий, ніж на 10% $V_2O_5-ZrO_2-SiO_2$, але він залишався досить високим, що можливо пов'язано з розширеним діаметром їх пор і з виникненням додаткових центрів ZrV_2O_7 , активних в дегідруванні легких алканів.

Ключові слова: дегідрування пропану, оксид ванадію, цирконій силікат, золь-гель синтез, каталіз.

INFLUENCE OF VANADIUM CONTENT ON STRUCTURE AND ACTIVITY OF $V_2O_5-ZrO_2-SiO_2$ CATALYST FOR PROPANE DEHYDROGENATION

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In order to create alternative vanadium oxide-supported catalysts for the process of non-oxidative propane dehydrogenation to propylene, we studied the effect of the increased content of vanadium oxide in the $V_2O_5-ZrO_2-SiO_2$ composition on its structure and catalytic properties. Zirconium silicate hydrogel in the form of finished spherical granules with the SiO_2 content of more than 50% was prepared by direct sol-gel synthesis from zirconium oxychloride and sodium metasilicate using the droplet coagulation technology. Catalysts were fabricated by impregnation of hydrogel with an aqueous solution of vanadyl sulfate salt, hydrothermal treatment and calcination in air. By using scanning electron microscopy, X-ray diffraction analysis and low-temperature nitrogen adsorption/desorption method, we showed that amorphous samples with a developed mesoporous structure (with the pore diameter of ~ 6 nm and the specific surface area of ~ 300 m² g⁻¹) were formed when the content of the supporting V_2O_5 on zirconium silicate was 10, 20, 25, and 30 wt.%. In the course of temperature increase in the propane dehydrogenation reaction, the catalyst samples crystallized in the reaction mixture propane-inert gas with the formation of tetragonal zirconia. When the content of V_2O_5 was 25% or 30%, additional phases of reduced vanadium oxides and traces of the zirconium vanadate phase were formed. After the reaction, the specific surface area of the catalysts decreased significantly and the average pore size of the samples with 25% and 30% V_2O_5 increased to ~ 30 nm. The propylene yield reproducibly observed on the samples with 25% and 30% V_2O_5 was lower than that on the samples with 10% V_2O_5 ; however, it remained quite high, which was probably due to the expanded diameter of the pores and the appearance of additional ZrV_2O_7 sites that are active with respect to the dehydrogenation of light alkane.

Keywords: propane dehydrogenation; vanadium oxide; zirconium silicate; sol-gel synthesis; catalysis.

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