Effect of Modification of Supported V_2O_5/SiO_2 Catalysts by Lanthanum on the State and Structural Peculiarities of Vanadium

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Abstract—Using the methods of diffuse reflectance electron spectroscopy, Raman spectroscopy and temperature-programmed reduction with hydrogen, the formation of surface phases in supported lanthanummodified V_2O_5/SiO_2 catalysts was studied. It is shown that the order of depositing the active component has a significant effect on the phase composition and catalytic properties of the samples in the reaction of propane oxidative dehydrogenation.

Keywords: supported vanadium catalysts, lanthanum oxide, oxidative dehydrogenation of propane, surface two-dimensional phases

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INTRODUCTION

Supported vanadium oxide systems attract much attention of researchers as catalysts for various redox reactions, including oxidative dehydrogenation of light hydrocarbons [1, 2], oxidation of methanol to formaldehyde [3–5], formaldehyde to formic acid [6], ethanol to acetaldehyde and acetic acid [6–8], and selective reduction of NO_x with ammonia [9–11]. The catalytic properties of such systems are determined by the presence of two-dimensional or three-dimensional vanadium oxide phases on the surface, the formation of which depends on the amount of the supported component, the nature of the support, and the nature of the vanadium precursor used for sample preparation [1, 3, 12–15].

The formation of two-dimensional VO_x phases on the surface, which most often attract the greatest interest for catalysis, occurs when the active component is supported within the monolayer [1, 2, 14, 15]. For most supports, the monolayer surface coverage of the VO_x phases corresponds to a surface density of 8–9 vanadium atoms per nm². An exception is silica, which, due to the low surface reactivity, is characterized by the formation of a three-dimensional V₂O₅ phase already at a surface density of ~3 vanadium atoms per nm².

The support affects both the maximum density of surface coverage by two-dimensional VO_x phases and their reactivity [1–3, 8, 14, 15]. For the majority of oxidative reactions on supported vanadium catalysts, a decrease in the activity is observed in the series of supports CeO₂ > ZrO₂ > TiO₂ > Al₂O₃ > SiO₂ [1–3, 14,

15]. The indicated dependence of the reactivity of supported vanadium catalysts on the support nature reflects the important role of the interaction of the active component with the support and the strength of the V–O bridging bond formed in the mechanism and kinetics of the oxidative reactions occurring on them. It is believed that the cations of the oxide support act as ligands in the second coordination sphere of vanadium and change the redox potential of the surface VO_x phases [1, 2].

For reactions proceeding via a consecutive mechanism with the formation of a more reactive target product as an intermediate, such as oxidative dehydrogenation of propane, the influence of support on the redox potential of the surface vanadium oxide phases affects not only their reactivity with respect to the activation of the starting reagent molecule, but also subsequent deep oxidation of the target product [1, 2]. In this regard, the most suitable supports for vanadium catalysts of the oxidative dehydrogenation of propane are Al₂O₃ and SiO₂, for which relatively high selectivities are observed for propane conversion up to 10% [1, 16].

Amorphous silica is one of the widely used inexpensive inert supports, having a high specific surface area S_{sp} and a developed porous structure that is controlled over a wide range. However, the probability of the formation of crystalline V₂O₅ characterized by the low selectivity in the oxidative dehydrogenation of light alkanes is higher on its surface than for Al₂O₃, TiO₂, Nb₂O₅, or ZrO₂, which leads to a drop in the selectivity to the target product at relatively low content of supported vanadium. This requires the devel-

opment of approaches to the formation of the active and selective surface of V_2O_5/SiO_2 catalysts with a high vanadium content.

Grant et al. [17, 18] showed that supporting vanadium on silica modified by sodium makes it possible to increase the coverage density of the support surface by two-dimensional VO_x phases without the formation of crystalline vanadium oxide up to 9 vanadium atoms per nm^2 . It was noted that the addition of sodium does not lead to significant changes in the catalytic activity and selectivity of catalysts at low sodium-to-vanadium molar ratios (Na : V < 0.25). This is due to the influence of the additive only on the formation of twodimensional vanadium oxide phases on the surface of silica and the absence of the effect of small amounts of sodium on the electronic structure of VO_x [17]. An increase in the amount of sodium in the sample leads to the formation of a crystalline sodium metavanadate characterized by low selectivity similar to V_2O_5 [17, 18]. At the same time, changes occurring in the first and second coordination spheres of vanadium in the surface vanadium oxide phases due to the formation of V–O–modifier bonds may affect their redox potential and catalytic properties [19-22]. In this regard, it is interesting to study additives that affect both the formation of two-dimensional vanadium oxide phases on the surface of silicon oxide and their redox potential.

Oxides of rare-earth elements, in particular cerium and lanthanum oxides, are widely used as modifiers and promoters of various catalysts, including nickel oxide catalysts for the oxidative dehydrogenation of light hydrocarbons [23–29]. The interaction of the modifier with the support and/or the active component plays a major role in improving the properties of the modified samples. The use of cerium and lanthanum oxides as modifiers of supported vanadium oxide catalysts for the oxidative dehydrogenation of alkanes remains poorly studied.

In this work, the effect of lanthanum oxide modification on supported V_2O_5/SiO_2 catalysts with low surface densities of supported vanadium on the formation of surface 2D vanadium oxide phases in them, their structural features, and redox and catalytic properties in the oxidative dehydrogenation of propane was studied.

EXPERIMENTAL

Sample Preparation

A series of supported V₂O₅/SiO₂ catalysts modified with lanthanum oxide was prepared by consecutive incipient-wetness impregnation of the support with aqueous solutions of precursors. VOSO₄ (Reakhim, 99.0%) and La(NO₃)₃ · 6H₂O (Vekton, 99.0%) were taken as precursors. KSKG silica ($S_{sp} = 190 \text{ m}^2/\text{g}$, $V_{pore} = 0.61 \text{ cm}^3/\text{g}$) (Russia) hydrothermally treated to increase the pore size was used as a support. Hydrothermal treatment was carried out in an aqueous solution of ammonia followed by calcination at 900°C [30]. After each impregnation, the samples were calcined in air at 500°C for 2 h. Intermediate one-component V_2O_5/SiO_2 and La_2O_3/SiO_2 were used as reference catalysts. The nominal weight content of vanadium oxide in the samples was 0.059 g V_2O_5 per 1 g of SiO₂, which corresponds to the density of the coating of the surface of the support with vanadium of 0.25 monolayer or 2 vanadium atoms per nm² of the support. The molar ratio of V: La was 1 : 1 in all two-component samples. The use of coimpregnation for the preparation of catalysts was difficult due to the instability of the mixed solution of the precursors (precipitation and gas evolution were observed).

Study of Physicochemical Properties of Samples

The physicochemical properties of the synthesized samples were studied by a complex of methods: low-temperature nitrogen adsorption, X-ray diffraction (XRD), UV–Viz diffuse reflectance spectroscopy, Raman spectroscopy, infrared (IR) spectroscopy and temperature-programmed reduction with hydrogen (TPR-H₂).

The phase composition of the samples was studied by XRD on an XRD6000 diffractometer (Shimadzu, Japan) with monochromatic Cu K_{α} radiation ($\lambda =$ 1.54056 Å) in the range of angles $2\theta = 10^{\circ}-60^{\circ}$. The obtained diffraction patterns were analyzed using the PDF4 database.

UV–Viz diffuse reflectance spectra were obtained using an Evolution 600 spectrometer (ThermoScientific, USA). MgO was used as a standard. To record the spectra of dehydrated samples, they were kept in special hermetically sealed reactors with a valve at 200°C for 2 h in air and then for 1.5 min in vacuum (10–2 Torr). The reflection spectra of the studied samples were transferred to the absorption spectra using the Kubelka–Munk function:

$$F(R)=\frac{\left(1-R\right)^2}{2R},$$

where R is the reflection factor.

The Raman spectra of the synthesized samples were taken on a Raman confocal microscope (Renishaw, United Kingdom) with a wavelength of 532 nm and analyzed using the OMNIC program (Thermo Nicolet Corporation, USA).

The redox characteristics of the samples were studied by the method of temperature programmed reduction by hydrogen (TPR-H₂) on a Chemisorb 2750 chemisorption analyzer (Micromeritics, USA) with a thermal conductivity detector. Before starting the experiments, all samples were subjected to oxidative treatment in a flow of air (20 mL/min) at a heating rate of 10°C/min to 500°C. All TPR-H₂ experiments were performed in the temperature range from 25 to

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Sample	Composition, wt %		$S = m^2/\sigma$	$V = am^3/a$	D nm
	V ₂ O ₅	La ₂ O ₃	$S_{\rm sp}$, III /g	V _{pore} , cm/g	$D_{\rm pore}, {\rm IIII}$
V ₂ O ₅ /SiO ₂	5.8	_	164	0.55	10.0
La ₂ O ₃ /V ₂ O ₅ -SiO ₂	5.2	10.2	151	0.50	10.0
La ₂ O ₃ /SiO ₂	—	10.7	168	0.54	9.7
V ₂ O ₅ /La ₂ O ₃ -SiO ₂	5.6	10.1	163	0.49	9.3

 Table 1. Designation composition, and textural characteristics of samples

Two-component catalysts La_2O_3/V_2O_5 -SiO₂ and V_2O_5/La_2O_3 -SiO₂ are obtained by impregnation of one-component samples V_2O_5/SiO_2 and La_2O_3/SiO_2 , respectively. Dashes mean that the corresponding oxides are not available in the sample composition.

800°C. The gas was supplied at a rate of 20 mL/min, the heating rate was 10°C/min. The water formed during the reduction was frozen before a detector in a special trap cooled by a mixture of liquid nitrogen and isopropyl alcohol.

Study of Catalytic Properties of Samples

The catalytic properties of the samples in the oxidative dehydrogenation of propane were studied in a flow-type reactor with a fixed catalyst bed in the temperature range from 500 to 600°C and atmospheric pressure. The analysis of products before and after the reactor was carried out on-line on a Crystal 5000.2 chromatograph (Chromatec, Russia). The reactor was a quartz tube with an inner diameter of 10 mm with a coaxially located pocket for a thermocouple with an outer diameter of 4 mm. The sample (0.20-0.25 g)fraction 0.25–0.5 mm, density 0.5–0.6 g/cm³) diluted with 1 cm^3 of quartz crumb (fraction 0.5-1.0 mm) was placed in the reactor. Before the experiment, the samples were subjected to oxidative treatment in a flow of air at 500°C for 30 min. A reaction mixture was 5 vol % C_3H_8 and 5 vol % O_2 in nitrogen. The temperature in the reactor was controlled by a thermocouple placed in the center of the catalyst bed.

The conversion of propane $X(C_3H_8)$ and selectivity to propylene $S(C_3H_6)$ were calculated by formulas:

$$\begin{aligned} X(C_{3}H_{8}) \\ &= \frac{3C_{C_{3}H_{6}} + 2C_{C_{2}H_{4}} + 2C_{C_{2}H_{6}} + C_{CO_{2}} + C_{CO}}{3C_{C_{3}H_{8}} + 3C_{C_{3}H_{6}} + 2C_{C_{2}H_{4}} + 2C_{C_{2}H_{6}} + C_{CO_{2}} + C_{CO}}{\times 100\%,} \\ &= \frac{S(C_{3}H_{6})}{3C_{C_{3}H_{6}} + 2C_{C_{2}H_{4}} + 2C_{C_{2}H_{6}} + C_{CO_{2}} + C_{CO}}{\times 100\%,} \end{aligned}$$

where $C_{C_3H_8}$, $C_{C_3H_6}$, $C_{C_2H_6}$, $C_{C_2H_4}$, C_{CO_2} , C_{CO} (in vol %) are the concentrations of components at the reactor outlet.

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The rate constants were determined using the firstorder equation for a plug flow reactor:

$$k = \frac{1}{t} \ln \frac{C^0}{C} = \frac{v}{V} \ln \frac{1}{1 - x}$$

where *t* is the contact time, s; C^0 is the initial concentration of the converted substance, vol %; *C* is the final concentration of the converted samples, vol %; *v* is the flow rate of the reaction mixture, cm³/s; *V* is the catalyst volume, cm³; *x* is the conversion in fractions of unity. When calculating the rate constant for the oxidation of propylene, k_2 , it was assumed that its initial concentration is determined by the conversion of propane, and the final concentration is determined by the selectivity of the oxidative dehydrogenation of propylene.

RESULTS AND DISCUSSION

Composition and Textural Characteristics of Samples

Table 1 shows the designations, composition, and textural characteristics of the synthesized samples. The content of supported components in the samples varies in the ranges of 5.1-5.8 wt % for V₂O₅ and 10.1-10.7 wt % for La₂O₃. A decrease in the content of vanadium oxide in La₂O₃/V₂O₅-SiO₂ compared with V₂O₅/SiO₂ and lanthanum oxide in V₂O₅/La₂O₃-SiO₂ compared with La₂O₃/SiO₂ is due to a change in the fraction of the corresponding component as a result of the introduction of the second component. Differences in the content of oxides of lanthanum and vanadium in two-component catalysts are associated with experimental errors in the course of sample preparation.

Figure 1 shows the adsorption–desorption isotherms of nitrogen and the pore size distribution for the synthesized samples and the initial support. The adsorption–desorption isotherms of nitrogen for the prepared catalysts are similar to the isotherm of the initial support taking into account a change in the weight of samples as a result of consecutive deposition of lanthanum and vanadium oxides (Fig. 1a). For all samples, the adsorption–desorption isotherm shows a hysteresis loop of capillary condensation in the range of relative pressures of 0.7-0.95 with bending at ~0.86,



Fig. 1. (a) Nitrogen adsorption–desorption isotherms and (b) the pore size distribution of the prepared samples and the initial support.

which indicates the presence of mesopores in them. According to the data on the pore size distribution, the pore structure of the samples and the initial support is represented by pores with a size in the range of 4-20 nm. The observed changes in the pore size distribution indicate a uniform filling of pores in the support as the components are consecutively supported (Fig. 1b). Thus, the presented results indicate that the textural characteristics of the prepared catalysts are determined by the textural characteristics of the support. All samples have a high specific surface area of $151-168 \text{ m}^2/\text{g}$, a total pore volume of $0.49-0.55 \text{ cm}^3/\text{g}$, and an average pore diameter of ~10 nm (Table 1).

Figure 2 presents the XRD data. The X-ray diffraction pattern of the V_2O_5/SiO_2 sample is similar to the

X-ray diffraction pattern of initial SiO₂ (not shown in Fig. 2) and contains a wide halo in the range of $2\theta = 15^{\circ}-35^{\circ}$ due to the presence of amorphous silica in the sample. No reflection of the crystalline V₂O₅ phase was detected indicating the presence of vanadium in the sample as surface vanadium oxide phases or highly dispersed vanadium oxide, which is inaccessible for detection by the XRD method. Modification of the V₂O₅/SiO₂ sample with lanthanum oxide leads to the appearance of wide reflections on the pattern, which are related to the LaVO₄ phase with a monoclinic structure (the corresponding bar graph is shown in Fig. 2). The broadening of the LaVO₄ phase reflections indicates its high dispersion and/or defective-ness.

The XRD pattern of the La_2O_3/SiO_2 sample is characterized by the presence of wide halos: intense in the range $2\theta = 15^{\circ} - 35^{\circ}$ and weak in the range $2\theta =$ $36^{\circ}-55^{\circ}$. The reflections of crystalline phases of the La_2O_3 modifier or the products of its interaction with the support-lanthanum silicates-have not been identified on the XRD pattern. However, the broad peaks observed on the XRD pattern cannot be explained only by the amorphous phase of silicon oxide and are associated with the formation of amorphous lanthanum silicate on the support surface [31, 32]. The subsequent deposition of vanadium oxide does not lead to significant changes in the XRD pattern of the V_2O_5/La_2O_3 -SiO₂ sample, which indicates the presence of vanadium in the sample in the form of highly dispersed surface oxide phases.

Study of Samples by Raman Spectroscopy

Figure 3 shows the Raman spectra of hydrated samples at $123-1050 \text{ cm}^{-1}$. No bands were observed in the spectrum of the support (not presented) in the specified range. The spectrum of the V₂O₅/SiO₂ sample contains relatively narrow bands at 130 and 178 cm⁻¹ and wide bands at 250-380, 410-740, and 750-980 cm⁻¹. The bands at 130 and 178 cm⁻¹ are caused by lattice vibrations, and the bands at 250-380 and 450-740 cm⁻¹ belong to vibrations of V-O-V bonds in hydrated VO_x structures on the surface of silicon oxide [33]. The band at 750-980 cm⁻¹ corresponds to vibrations of the V-O-Si bonds in surface vanadium silicates [33].

The modification of the V₂O₅/SiO₂ sample with lanthanum oxide leads to a significant change in the shape of the spectrum. The spectrum of La₂O₃/V₂O₅– SiO₂ contains bands at 857, 837, 821, ~785, 440, 373, 324, and 217 cm⁻¹, related to lanthanum orthovanadate LaVO₄ [34, 35], and bands at 146, 480, 513, 706, and 996 cm⁻¹ are characteristic of V₂O₅ [36, 37]. The broadening of bands indicates a high dispersion and imperfection of these phases. Considering the XRD data, it can be concluded that most of the vanadium is

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Fig. 2. XRD patterns of (1) V_2O_5/SiO_2 , (2) $La_2O_3/V_2O_5-SiO_2$, (3) La_2O_3/SiO_2 , (4) $V_2O_5/La_2O_3-SiO_2$ and bar graphs of expected crystalline phases V_2O_5 , La_2O_3 , $LaVO_4$, and La_2SiO_5 .

present in the sample as lanthanum orthovanadate, and vanadium oxide is the impurity phase.

In the spectrum of the La_2O_3/SiO_2 sample, only the signals at the noise level are visible. No bands corresponding to La-O bond vibrations are observed, the lanthanum oxide phase can thus be excluded. In the spectrum of V_2O_5/La_2O_3 -SiO₂, characteristic bands of the crystalline LaVO₄ and V₂O₅ were not detected [34–37]. Against the background of noise, wide bands at 400–980 cm⁻¹ are distinguishable and attributed to vibrations of V–O–V bonds in hydrated surface VO_x structures on the surface of silicon oxide and V-O-Si bonds in vanadium surface silicates [33]. However, the intensity of the corresponding bands, especially at 750-980 cm⁻¹, is lower than in the spectrum of the V_2O_5/SiO_2 sample, which may be due to the presence of lanthanum in the sample. The presence of lanthanum on the support surface can prevent the formation of V-O-Si bonds and contribute to the formation of $LaVO_x$ structures on the surface of silicon oxide.



Fig. 3. Raman spectra of hydrated samples: (1) La_2O_3/SiO_2 ; (2) $V_2O_5/La_2O_3-SiO_2$; (3) V_2O_5/SiO_2 ; and (4) $La_2O_3/V_2O_5-SiO_2$.

Study of Samples by UV–Viz Diffuse Reflectance Spectroscopy

Figure 4 shows the electronic spectra of hydrated and dehydrated samples at 200-900 nm. In the spectrum of La_2O_3/SiO_2 , there is a weak band at 200–280 nm, which does not make a significant contribution to the spectra of vanadium-containing samples. In the spectra of all vanadium-containing samples, the metalligand V(V) charge transfer bands (CTB) were detected at 200-600 nm [38, 39]. Low-intensity bands at 700–900 nm in the spectra of V_2O_5/SiO_2 and La_2O_3/V_2O_5 -SiO₂ are caused by d-d transitions in V(IV), which is present as impurity in samples as a result of partial V(V) reduction. Bands caused by d-dtransitions in V(IV) are not observed in the spectrum of V_2O_5/La_2O_3 -SiO₂, which indicates the stabilization of vanadium(V) in it. The profile of CTB V(V), which depends on the local environment of vanadium, is different in the spectra of the samples and is determined by the method of catalyst preparation and the conditions for obtaining spectra.

The spectrum of the initial (hydrated) V_2O_5/SiO_2 sample is characterized by intense absorption at 200– 600 nm with a pronounced band at ~400 nm associated with vanadium in VO₆ and/or VO₅ (Fig. 4a). Dehydration of the sample leads to a decrease in the intensity of this band, with the band at 270 nm, which is characteristic of vanadium in isolated VO₄ tetrahedra, becoming pronounced. Absorption bands remain at 350–600 nm, which may be due to CTB in VO₆/VO₅ in the surface structures present in the sample due to



Fig. 4. UV–Viz diffuse reflectance spectra of (a) hydrated and (b) dehydrated samples, and samples (c) V_2O_5/SiO_2 and (d) $V_2O_5/La_2O_3-SiO_2$ after dehydration (black spectrum) and further interaction with moist air (grey spectra). On parts (b) and (d) of this figure, an arrow show an increase in the intensity of the band at 400 nm with time due to the interaction with moist air.

the rapid hydration during the study or in microcrystalline V_2O_5 . The absence of characteristic bands of V_2O_5 in the Raman spectrum allows us to assign bands at 350–600 nm in the UV–Viz diffuse reflectance spectrum of the dehydrated sample to CTB in VO_6/VO_5 in the surface structures. The subsequent interaction of the sample with moist air leads to a reverse increase in the intensity of the band in the region of 400 nm, which indicates that the hydration– dehydration process is reversible (Fig. 4b). A change in the spectrum due to the hydration–dehydration of the sample indicates the primarily formation of surface vanadium oxide structures accessible for interaction with water in V_2O_5/SiO_2 [38]. The modification of V_2O_5/SiO_2 by lanthanum oxide leads to a significant change in the UV–Viz diffuse reflectance spectra. The spectra of the hydrated and dehydrated La₂O₃/V₂O₅–SiO₂ sample are almost identical and characterized by an intense band at 270 nm caused by V(V) in isolated VO₄ tetrahedrons, and also by a relatively weak absorption at 350–550 nm associated with the CTB V(V) in VO₆/VO₅. The constancy of the spectrum during dehydration–hydration indicates the presence of vanadium in it in stable crystalline phases, which agrees with the XRD and Raman spectroscopy data confirming the formation of the microcrystalline phases of lanthanum orthovanadate LaVO₄ and vanadium oxide V₂O₅.

The spectrum of the initial V_2O_5/La_2O_3 -SiO₂ sample is also characterized by an intense band at 270 nm, caused by vanadium(V) in isolated VO_4 tetrahedra, with a shoulder at 400 nm associated with CTB V(V) in VO_6 . The dehydration of the sample leads to the complete disappearance of the band at 400 nm, but, during the subsequent interaction of the sample with moist air, this band appears again in the spectrum (Fig. 4d), which indicates the presence of vanadium in the dehydrated sample only in isolated VO₄ tetrahedrons, part of which remains accessible for interaction with water. The intense band at 270 nm in the spectrum of the hydrated sample indicates the partial stabilization of vanadium in isolated VO₄ tetrahedra, which may be due to the presence of lanthanum in the second coordination sphere of vanadium. However, according to Raman spectroscopic data, the formation of the lanthanum orthovanadate phase LaVO₄ does not occur in the sample. Thus, a change in the local structure of vanadium during the interaction with water indicates the formation of some surface twodimensional LaVO_x structures rather than stable threedimensional phases in the V_2O_5/La_2O_3 -SiO₂ sample.

Study of Samples by $TPR-H_2$

Figure 5 shows the TPR-H₂ profiles of the studied catalysts. The profiles of all samples are characterized by two peaks of hydrogen consumption at temperatures above 450°C. The TPR-H₂ profile of the V_2O_5/SiO_2 sample contains a relatively intense asymmetric peak with a maximum at 613°C and a shoulder at 550°C, as well as a small peak with a maximum at 886°C. The low-temperature peak can be attributed to the reduction of surface VO_x phases [39, 40], while the hightemperature peak may be due to the reduction of vanadium from surface vanadium silicate according to the Raman spectroscopy data. In general, the amount of hydrogen consumed during the reduction of the V_2O_5/SiO_2 sample is low compared with other catalysts, which, according to UV-Viz diffuse reflectance spectroscopy, may be due to the presence of a relatively large amount of vanadium(IV) in the sample.

The TPR-H₂ profile of the La₂O₃/V₂O₅–SiO₂ sample exhibits an intense peak at 662°C and a less intense peak at 770°C, which are determined by the reduction of the dispersed crystalline phases of lanthanum orthovanadate LaVO₄ and V₂O₅ [41–44]. In general, the amount of hydrogen consumed during the reduction of La₂O₃/V₂O₅–SiO₂ is higher than that during the reduction of V₂O₅/SiO₂, which is probably due to the stabilization of vanadium(V) in the crystal-line phases of V₂O₅ and LaVO₄.

The TPR-H₂ profile of the V_2O_5/La_2O_3 -SiO₂ sample is characterized by two peaks of hydrogen consumption with maxima at 613 and 717°C. The temperature of the maximum of the first peak is similar to



Fig. 5. TPR-H₂ profiles of samples.

that of the hydrogen consumption peak on the V_2O_5/SiO_2 profile. In this regard, this peak can be attributed to the reduction of vanadium from surface $LaVO_x$ structures available for hydration. In contrast to V_2O_5/SiO_2 , for the $V_2O_5/La_2O_3-SiO_2$ sample, the shoulder profile at 550°C is not observed on the reduction profile, which indicates the absence of readily reducible VO_{x} forms in it. The peak with the maximum at 717°C corresponds to the reduction of vanadium from surface LaVO_x structures with lanthanum in the second coordination sphere, which are not available for hydration. The amount of hydrogen consumed in the reduction of V_2O_5/La_2O_3 -SiO₂ is higher than in the reduction of V_2O_5 -SiO₂ and La₂O₃/V₂O₅-SiO₂ samples, which is consistent with the UV–Viz diffuse reflectance spectroscopic data on the absence of vanadium(IV) in this sample and provides evidence of further stabilization of vanadium(V) in the resulting surface $LaVO_x$ phases.

Study of Catalytic Properties of Samples

Figure 6 presents the results of catalytic studies of vanadium-containing samples in the reaction of oxidative dehydrogenation of propane. According to the data obtained in the presence of all catalysts, propane conversion was low (less than 2%) in the temperature range of $500-600^{\circ}$ C, which is associated with a low content of vanadium in them (Fig. 6a). V₂O₅/SiO₂ is the most active. The reaction rate for it at 500° C is comparable to that for a similar sample in the works by Grant et al. [17, 18]. Samples modified by lanthanum oxide are characterized by the lower activity, while the formation of crystalline phases in the La₂O₃/V₂O₅–SiO₂ sample leads to a stronger decrease in the activity, which is consistent with the lower reactivity of the samples in reduction by hydrogen. For all samples, an



Fig. 6. Dependences of the reaction rate and propane conversion on temperature for various catalysts (a); the dependences of the selectivity to propylene, the rate constants of the consecutive conversion of propane and their ratio of the composition of the catalyst at 600° C (b).

increase in activity with increasing temperature is observed.

Figure 6b shows the selectivity to propylene for the studied catalysts at 600°C. Due to the 1.3–1.8-times differences in propane conversion for the samples, a correct comparison of the obtained selectivity values is not possible. To analyze the contribution of the non-selective propane conversion, the rate constants of consecutive transformations were determined:

$$C_3H_8 \xrightarrow{k_1} C_3H_6 \xrightarrow{k_2} CO_3$$

The contribution of direct oxidation of propane to the products of deep oxidation was neglected [1]. The values of the corresponding rate constants and their ratios k_2/k_1 are presented in Fig. 6b. The value of k_2/k_1 decreases in the series $La_2O_3/V_2O_5-SiO_2 \gg$ $V_2O_5/SiO_2 > V_2O_5/La_2O_3-SiO_2$, which corresponds to an increase in the propylene selectivity. The comparison of the rate constants and k_2/k_1 shows that the formation of the crystalline phases LaVO₄ and V₂O₅ in the sample La_2O_3/V_2O_5 -SiO₂ leads not only to a noticeable decrease in its activity, but also to decrease in selectivity for propylene. The formation of the surface LaVO_x phases in the V_2O_5/La_2O_3 -SiO₂ catalyst is accompanied by an increase in the propylene selectivity against a moderate decrease in the activity as compared to unmodified V_2O_5/SiO_2 . This may be due to the absence of highly active, but not selective sites. which are characterized by the lowest reduction temperatures according to TPR-H₂, on the surface of the V_2O_5/La_2O_3 -SiO₂ sample.

CONCLUSIONS

The results of studying the modification of V_2O_5/SiO_2 catalysts by lanthanum oxide at low surface densities of vanadium showed that the composition and structure of the deposited phases formed in the modified samples as well as their catalytic properties are determined by the order of introduction of the supported components. The modification of the supported V_2O_5/SiO_2 catalyst contributes to the formation of microcrystalline $LaVO_4$ and V_2O_5 phases in the sample, which leads to a deterioration of the catalytic properties (a noticeable decrease in the activity and selectivity of the sample) compared with the unmodified catalyst. The deposition of vanadium oxide on the preliminarily modified La2O3/SiO2 support contributes to the formation of surface LaVO_x phases in the modified sample, which is accompanied by an increase in the selectivity to propylene against the moderate decrease in the activity compared to the unmodified sample. Taking account of the relatively high La/V molar ratio in the studied catalysts, we should expect further improvement of the catalytic properties of the samples obtained by depositing vanadium oxide on the preliminarily modified La₂O₃/SiO₂ support with decreasing the La/V molar ratio partly as a result of an increase in the surface density of vanadium.

Thus, it is shown that the introduction of lanthanum into supported V_2O_5/SiO_2 catalysts by modifying the support surface can be considered as a promising approach to the formation of active and selective vanadium oxide catalysts supported on silica characterized by a high density of the support surface coating by twodimensional VO_x phases.

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