PHASE COMPOSITION AND OXIDATION DEGREE OF VANADIUM IN CATALYSTS FOR OXIDATIVE DEHYDROGENATION OF PROPANE

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Abstract: *The phase composition of vanadium and vanadium-antimony-containing samples of γ-Al$_2$O$_3$ and the degree of oxidation of vanadium in them were examined by XRD and EPR methods, respectively. The data of XRD and EPR spectroscopy show the formation of highly dispersed vanadium-oxygen and vanadium-antimony-oxygen structures on the surface of the support. It is shown that the EPR spectra of the studied samples are due to "isolated" vanadium ions with an oxidation state of +4 in non-stoichiometric vanadium-oxygen and vanadium-antimony-oxygen formations with a square pyramid local environment structure with a characteristic V=O double bond. The EPR spectra of two types of paramagnetic centers of vanadium, which differ in the distortion of the square-pyramidal structure of the local environment of the vanadium ion, were identified. It was established that the number of ions with an oxidation state of +4 in V,Sb-containing samples depends on the V/Sb ratio in them.*

Keywords: *oxidative dehydrogenation of propane, V,Sb-containing oxide catalysts, phase composition, EPR spectra.*

Introduction

Supported vanadium oxide systems draw attention of researchers as catalysts for various redox reactions, including oxidative dehydrogenation (OD) of light alkanes [1–3]. The catalytic properties of such systems are associated with the presence of VOx vanadium structures on the support surface, the composition, structure, and distribution of which are depend upon the amount of the supported component, the nature of the support, and the nature of the vanadium precursor used to prepare the samples [4–10]. A fairly wide range of OD catalysts is known [11–18], however, the search for an effective OD catalyst for C$_2$–C$_4$ alkane is still ongoing. Mixed oxides of vanadium and antimony are well known as active and selective catalysts for selective partial oxidation processes [19, 20]. V-Sb-O catalysts gave a good account of themselves in the selective oxidation of isobutene to methacrolein [21], methane to formaldehyde [22], propane to acrylic acid [23–25], and selective ammoxidation to acrylonitrile [26–29]. In mixed V–Sb–O oxide catalysts, during their formation, the SbOx and VOx structures react with the formation of the VSbO$_4$ rutile phase with cationic vacancies [30]. This mixed oxide phase can have different stoichiometry compositions [31, 32]. In V-Sb-O oxide catalysts, in addition to mixed V-Sb oxide phases, phases of amorphous antimony oxide (Sb$_2$O$_3$, α-Sb$_2$O$_4$) [33] and/or V$_2$O$_5$ may also be present. Studies into catalysts based on mixed oxide of vanadium and antimony by ion scattering spectroscopy showed that their surfaces were enriched with the surface structures of vanadium oxide [34]. Although there is a fairly wide range of studies of the physicochemical properties of mixed oxides of vanadium and antimony, the role of vanadium-.

antimony-containing structures in reactions of selective oxidative catalysis is still the subject of research.

This paper presents the results of research into samples of vanadium-, antimony-containing aluminum oxide by the method of electron paramagnetic resonance (EPR) in combination with the method of X-ray analysis in order to establish the phase composition and the effect of antimony on the degree of oxidation of vanadium in them.

Experimental part

Vanadium-containing samples were samples of γ-Al_2O_3 impregnated with a mixture of aqueous solutions of ammonium metavanadate and tartaric acid with a content of 15 wt.% vanadium in terms of ammonium metavanadate. Vanadium-antimony-containing samples were samples of γ-Al_2O_3 containing 15 wt.% vanadium oxide with different content of antimony trichloride $SbCl_3$ (1; 2; 2.7; 3.5 and 5 wt.%) dissolved in tartaric acid. Catalysts were prepared using γ-Al_2O_3 produced by the Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences (Russia) with a specific surface area of 85 m^2/g, ammonium metavanadate NH_4VO_3 (Qualikems, CAS No 7803-55-6, India) and antimony chloride $SbCl_3$ (Aldrich, Germany) as supports), dried at a temperature of 110°C and then subjected to stepwise calcination at 200^0, 400^0, 600^0C for 2 hours at each temperature. X-ray diffraction patterns and EPR spectra were recorded at room temperature using an X-ray diffractometer Phaser D2 X-ray diffractometer and an EMR spectrometer EMRmicro, Bruker, Germany, respectively.

The catalytic properties of the samples in the oxidative propane dehydrogenation (ODP) reaction were studied in a flow reactor with a fixed catalyst bed at 550°C and atmospheric pressure. Analysis of the products before and after the reactor was carried out in on-line mode on an LXM-80 chromatograph. Two chromatographic columns filled with Porapak QS and NaX molecular sieves were used for analysis. The reactor was a quartz tube with an inner diameter of 10 mm, into which ~0.2 g of a sample of a fraction of 0.25–0.5 mm was placed and diluted with quartz chips of a similar fraction. Before testing, the catalyst was calcined in a stream of air at 600°C for 1 hour. The propane/air reaction mixture contained 10 vol. % C_3H_8. Conditional contact time was changed by varying the volume of the catalyst and/or the space velocity of the reaction mixture. The propane conversion, as well as the selectivity for the formation of COx and C_3H_6, was calculated according to [11]. Note that, the γ-Al_2O_3 support samples used are not active in the oxidative dehydrogenation of propane and acquire this activity after the introduction of vanadium and antimony into them.

Results and discussion

Table 1 shows the results of testing samples of V-Sb-O/γ-Al_2O_3 containing 15% (wt.) vanadium and 1-5 wt.% antimony in the reaction of oxidative dehydrogenation of propane.

Table 1. Test results for V-Sb-O/γAl_2O_3 samples containing 15% (wt.) vanadium and 1-5 wt.% antimony in the reaction of oxidative dehydrogenation of propane (reaction conditions: T=550^{0}C, contact time - 4 s.)

Catalyst *	Conversion C_3H_8, %	Selectivity,%			Exit C_3H_6, %
		C_3H_6	C_1-C_3	CO_x	
1	11.5	11.6	6.6	81.8	1.33
2	12.6	11.7	5.6	82.7	1.47
3	14.3	12.0	7.2	81.8	1.72

| 4 | 12.9 | 12.2 | 5.4 | 82.6 | 1.57 |
| 5 | 12.7 | 13.0 | 6.1 | 82.9 | 1.65 |

* Samples of catalysts based on γ-Al$_2$O$_3$ containing (in wt.% in terms of ammonium metavanadate and antimony trichloride): 1 - 15% V and 1% Sb, 2 - 15% V and 2% Sb, 3 - 15% V and 2.7%Sb, 4 - 15%V and 3.5%Sb, 5 - 15% V and 5%Sb, respectively.

The data presented in Table 1 show that with the introduction of antimony into the composition of the vanadium-containing catalyst, the selectivity of the ODP reaction with respect to propylene and the yield of propylene increase. In this case, the maximum yield of propylene is found for a catalyst containing 2.7% antimony.

Figures 1 and 2 show X-ray diffraction patterns and EPR spectra, respectively, recorded at room temperature, of the following samples: a) 15% V/Al$_2$O$_3$ with vanadium deposited from a mixture of aqueous solutions of ammonium metavanadate and tartaric acid; b) on (a) a solution of 2.7% SbCl$_3$ in tartaric acid was added, c) on (a) solution of 5.0% SbCl$_3$ in tartaric acid was added, followed by drying at 110 °C and calcining in air at 600°C for 4 hours.
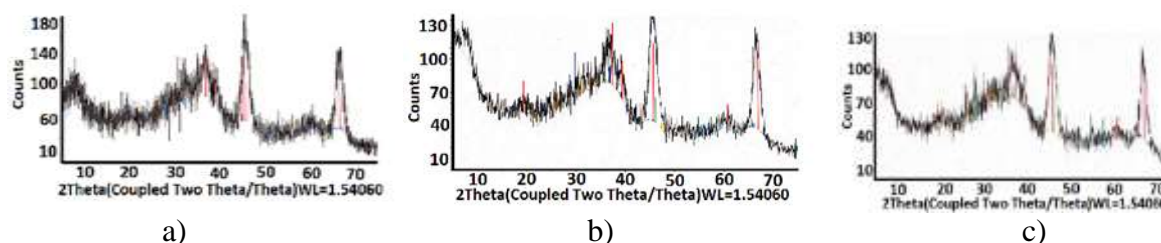

a)   b)   c)

Fig. 1. X-ray diffraction patterns of samples calcined at 600 °C: a) 15% V/Al$_2$O$_3$ with vanadium deposited from a mixture of aqueous solutions of ammonium metavanadate and tartaric acid, b) on (a) a solution of 2.7% SbCl$_3$ in tartaric acid was added; c) on (a) a solution of 5.0% SbCl$_3$ in tartaric acid was added.
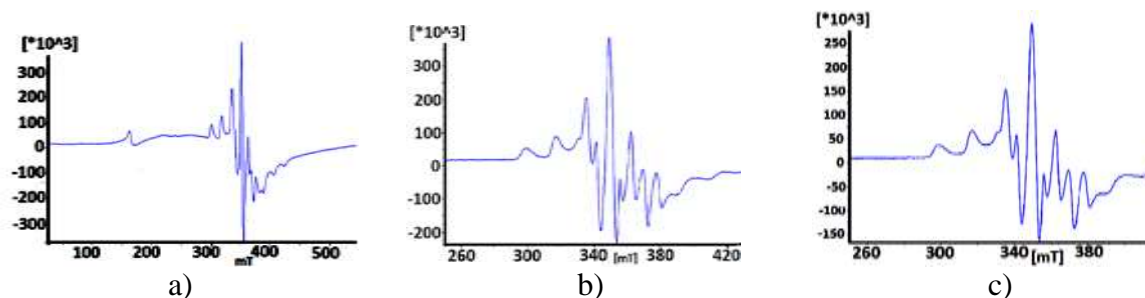

a)   b)   c)

Fig. 2. EPR spectra recorded at room temperature of samples calcined at 600 °C: a) V-15% / γ-Al$_2$O$_3$ and b, c) γ-Al$_2$O$_3$ -containing: b) 15% V-2.7% Sb, c) 15 %V, 5.0%SbCl$_3$

The X-ray diffraction patterns of these samples show phases characteristic of γ-Al$_2$O$_3$ (PDF 41-1426) and VO$_x$ (V$_2$O$_5$ - PDF#10-0425; VO$_2$ - PDF#44-0252; V$_6$O$_{13}$ - PDF #71-2235) structures. Depending on the oxygen partial pressure and temperature, VO$_2$, V$_6$O$_{13}$ and V$_2$O$_5$ can be obtained as pure or mixed phases. Reduction of V$_2$O$_5$ in a hydrogen atmosphere at 400°C for 10 min. led to its reduction to V$_2$O$_3$.

During the subsequent admission of air into the system at the same temperature, the V$_2$O$_3$ phase was oxidized to VO$_2$. Studies demonstrated that through sequential redox procedures, a controlled redox cycle V$_2$O$_3$ ↔ VO$_2$ can be achieved. The XRD results show that VOx is present either as an amorphous phase or in a highly dispersed form on the support surface.

The results of EPR studies suggest that the changes in the content of vanadium+4 ions in the VSbO/Al₂O₃ catalysts as compared to the VOx/Al₂O₃ catalyst were due to the interaction between the particles of SbOx and VOx oxides. The introduction of antimony reduces the redox properties of VOx structures while the introduction of ~3% antimony into the composition of VOx/Al₂O₃ is useful not only for improving catalytic activity, but also for obtaining catalysts that work stably in a continuous mode for 10 hours. The stable and increased activity of VOx/Al₂O₃ catalysts with the introduction of antimony is mainly due to the formation of $(-V - Sb - O-)_n$ structures and easy transfer of oxygen from the volume of antimony oxide. In the diffraction patterns of the VSbO/Al₂O₃ catalysts, in addition to the γ-Al₂O₃ carrier phase, weak reflections were found, most likely belonging to the SbO_x (Sb_2O_3, α -Sb_2O_4) structures [33] and the nonstoichiometric, defective $V_{1-x}Sb_xO_4$ phase [30], which exhibits a characteristic EPR spectrum from V^{4+} ions.

In the process of calcination at 600°C in an air flow of samples, which were ammonium metavanadate deposited from an aqueous solution on aluminum oxide by impregnation at room temperature, the ammonium metavanadate decomposes to form vanadium(V) oxide, releasing ammonia and water ($2NH_4VO_3 \rightarrow 2NH_3 + V_2O_5 + H_2O$). Calcination at 600°C of samples obtained by impregnation of aluminum oxide at room temperature with a mixture of aqueous solutions of ammonium metavanadate NH_4VO_3 and tartaric acid HOOC-CH(OH)-CH(OH)-COOH and then dried at 110°C, was accompanied by the formation of vanadium(V) oxide, evolution of ammonia, water, oxides of nitrogen and carbon.

The EPR spectra of these samples contain signals characteristic of vanadyl ions VO^{2+}. The data of EPR measurements unambiguously indicate the presence of "isolated" vanadium ions with an oxidation state of +4 in the samples. The formation of vanadium ions with an oxidation state of +4 during calcination in this case is, most probably,

due to the formation of nonstoichiometric vanadium structures with anion defects on the aluminum oxide surface: $V^{5+}_{2-x}V^{4+}_xO_{5-x}$/ γ-Al₂O₃, where x< 1. For samples of V,Sb-containing samples obtained by impregnation of aluminum oxide samples at room temperature with a mixture of aqueous-acid solutions of ammonium metavanadate and antimony trichloride, followed by drying at 110°C and further calcination at 600°C in air, the X-ray diffraction patterns mainly revealed the γ-Al₂O₃ phase. The lines characteristic of vanadium-oxygen V_6O_{13} and vanadium-antimony-oxygen $Sb(VO_3)_3$ structures were rather weakly manifested.

The calcination of these samples at 600°C leads to the decomposition of these structures with the formation of two phases - α-Sb_2O_4 and $VSbO_4$. In the X-ray diffraction patterns of V, Sb-containing alumina (Fig. 1,b,c) against the background of the γ-Al₂O₃ phase, reflections from vanadium and antimony and V/Sb phases appear very weakly, due to the low content of antimony and the highly dispersed state vanadium structures. For catalysts with a vanadium content of <5%, only peaks characteristic of the gamma modification of alumina appeared. For catalysts with a vanadium content of >5%, X-ray diffraction patterns showed weak, broadened peaks in the range of 20–35°, which were due to vanadate-like structures dispersed on the aluminum oxide surface [4–6]. The EPR spectra of vanadium-containing samples contained signals characteristic of VO^{2+} ions, which differed only in the intensity of these signals. For these samples, EPR spectra were found, characterized by a hyperfine structure due to the interaction of the unpaired $3d^1$ electron of VO^{2+} ions with the spin of the ^{51}V nucleus (I = 7/2) and belonging to "isolated" ions $(VO)^{2+}$ with distorted octahedral coordination and a "strong" bond V =O. The values of the magnetic resonance parameters of the EPR spectra of these samples are given in Table. 2.

The overall intensity of the EPR spectrum was measured and compared with the intensity of the standard - polycrystalline $VOSO_4$.

Table 2. Values of the magnetic resonance parameters of the EPR spectra of the studied samples

*Samples	g-factor		Hyper-fine structure constant, in mT		**Ration V^{4+}/V^{5+}
	$g\parallel$	$g\perp$	$A\parallel$	$A\perp$	
V-15%/Al$_2$O$_3$	1.934 1.963	1.998	19.4	10.2	0.092
V-15%-Sb-2.7% /Al$_2$O$_3$	1.933 1.964	1.998	19.8	9.9	0.0821
V-15%-Sb-5%/Al$_2$O$_3$	1935 1.958	1.995	19.9	10.3	0.0793

*The weights of the studied samples were ~30 mg. To estimate the number of paramagnetic centers in the samples, polycrystalline VOSbO$_4$ •5H$_2$O was used as a standard. ** - the ratio of the number of VO^{2+} ions recorded by the EPR spectra to the total number of vanadium ions in the sample.

This calculation showed that approximately 10% of the vanadium ions in these samples were in the +4 oxidation state. The XRD results show that the VOx particles were present either as an amorphous or highly dispersed phase on the carrier surface. In general, the changes observed in the EPR spectra and X-ray diffraction patterns of the studied samples with an increase in the antimony content are due to the transformations of the surface vanadium oxide phases VOx. It ought to be noted that the intensity of the EPR signals from V^{4+} ions in the V$_2$O$_5$/Al$_2$O$_3$ sample was higher than in the V-Sb containing samples, which was due to a decrease in the ability of vanadium to reduce when vanadium samples were modified with antimony.

Note that changes in the phase composition of the surface of supported VOx/γ-Al$_2$O$_3$ catalysts by the introduction of antimony and a decrease in the amount of V^{4+} ions affected their catalytic properties. In general, the results of EPR studies indicate that changes in the first and second coordination spheres of vanadium in surface vanadium oxide structures are due to the formation of -O -V-O-Sb-O-V-O- structures with the introduction of antimony into the samples.

Conclusion

The phase composition of vanadium and vanadium-antimony-containing samples of γ-Al$_2$O$_3$ and the degree of oxidation of vanadium in them were studied by XRD and EPR methods, respectively. X-ray diffraction patterns showed that the synthesized samples were gamma alumina with highly dispersed vanadium-oxygen and vanadium-antimony-oxygen structures on the carrier surface. It revealed that the EPR spectra of the studied samples were due to "isolated" vanadium ions with an oxidation state of +4 in nonstoichiometric vanadium-oxygen and vanadium-antimony-oxygen structures with a square-pyramidal structure of the local environment of vanadyl (VO)$^{2+}$ ions with a characteristic "silt" bond V=O. It is assumed that the increased activity and selectivity of the supported V, Sb-containing catalyst in the target reaction is due to the Sb-V-O structures. These structures are formed as a result of the interaction of VOx and SbOx particles, although it should be noted that SbOx structures are not active in the oxidative dehydrogenation of alkane.

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ФАЗОВЫЙ СОСТАВ И СТЕПЕНЬ ОКИСЛЕНИЯ ВАНАДИЯ В КАТАЛИЗАТОРАХ ОКИСЛИТЕЛЬНОГО ДЕГИДРИРОВАНИЯ ПРОПАНА

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Аннотация: Методами РФА и ЭПР исследованы, соответственно, фазовый состав ванадий, ванадий-сурьма-содержащих образцов γ-Al_2O_3 и степень окисления ванадия в них. Данные РФА и ЭПР спектроскопии указывают на формирование высокодиспергированных ванадий-кислород и ванадий- сурьма-кислородных структур на поверхности носителя катализаторов. Показано, что спектры ЭПР исследованных образцов обусловлены «изолированными» ионами ванадия со степенью окисления +4 в нестехиометрических ванадий-кислород и ванадий- сурьма-кислородных образованиях с квадратно-пирамидальной структурой локального окружения с характерной двойной связью V=O. Идентифицированы спектры ЭПР двух типов парамагнитных центров ванадия, различающихся искажением квадратно-пирамидального строения локального окружения иона ванадия. Установлено, что количество ионов со степенью окисления +4 в V,Sb – содержащих образцах зависит от соотношения V/Sb в них.

Ключевые слова: окислительное дегидрирование пропана, V,Sb –содержашие оксидные катализаторы, фазовый состав, ЭПР спектры

PROPANIN OKSİDLƏŞDİRİCİ DEHİDROGENLƏŞMƏ KATALİZATORLARININ FAZA TƏRKİBİ VƏ ONLARDA VANADİUMUN OKSİDLƏŞMƏ DƏRƏCƏSİ

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Xülasə: Tərkibində vanadium və vanadium-sürmə olan γ-Al_2O_3 nümunələrinin faza tərkibi və onlarda vanadiumun oksidləşmə dərəcəsi müvafiq olaraq RFA və EPR metodlarının istifadəsi ilə tədqiq edilmişdir. Müəyyən edilmişdir ki, qeyd olunan metodla sintez olunmuş katalizatorların daşıcıyısı səthində yüksək dispersli vanadium-oksigen, vanadium–sürmə-oksigen quruluşları əmələ gəlir. Göstərilmişdir ki, tədqiq olunan nümunələrin EPR spektrləri qeyri-stexiometrik vanadium-oksigen və vanadium-sürmə-oksigen birləşmələrində ikiqat V=O rabitəli, lokal sahəsi kvadrat piramida quruluşlu və oksidləşmə dərəcəsi +4 olan "izolə olunmuş" vanadium ionlarına xasdır. EPR spektrlər əsasında lokal sahəsinin kvadrat-piramidal quruluşunun pozulma dərəcəsinə görə fərqlənən iki növ paramaqnit vanadium mərkəzləri müəyyən edilmişdir. Müəyyən edilmişdir ki, tərkibində V, Sb olan nümunələrdə oksidləşmə dərəcəsi +4 olan ionların miqdarı V/Sb nisbətindən asılıdır.

Açar sözlər: propanın oksidləşdirici dehidrogenləşməsi, V, Sb tərkibli oksid katalizatorları, faza tərkibi, EPR spektrləri.