ACTIVITY OF $Bi_4V_{2-2x}Cu_{2x}O_{11-\Delta}$ IN THE TRANSFORMATION OF ISOBUTANOL AFTER PLASMA-CHEMICAL TREATMENT

Elena Povarova[1)], *Anna Pylinina*[1)], *Irina Mikhalenko*[1)], *Marina Safronenko*[1)]
[1)] *RUDN-university, Faculty of Science, Moscow, Russian Federation*

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[*] *Corresponding author: e-mail: povarova_ei@pfur.ru, Tel.: +7 916 459 1630, Department of Physical and colloidal chemistry, RUDN-University, 6 Miklukho-Maklaya str., Moscow, 117198, Russian Federation*

Abstract

The catalytic properties of plasma-chemically and thermally treated $Bi_4V_{2-2x}Cu_{2x}O_{11-\delta}$ with x= 0.00–0.16 (BICUVOX) in the transformation of isobutanol are studied. Plasma treatments lead to the total deactivation of the active sites of dehydration reaction, and the alcohol is converted with 100% selectivity into aldehyde. Activity of the dehydrogenation of alcohol after PCT increases in ~ 1.7 times on samples with x_{Cu}=0.04-0.06 (α.β phases) compared to the initial samples. Similar values which were found for the samples with x_{Cu}=0.0-0.06, including the double vanadate, suggests that PCT affects the ceramic matrix with Bi, O and V elements. Addition of small amounts of copper does not change this effect.

Keywords: new materials, nano-design, perovskite, plasma-chemical treatment

1 Introduction

Layered materials, with their structure consisting of stacked sheets, represent an interesting opportunity for developing new materials with a tailored nano-design, controlled accessibility to the sites and properties, tuneable pore size and volume, and high surface area. The use of layered materials (layered perovskite, anionic clays, pillared clays) in catalytic reactions is reviewed with emphasis on the possibilities offered from these catalysts to develop new processes for environmental protection, selective oxidation and refinery/biorefinery [1]. Of a great interest are bismuth vanadates belonging to the BIMEVOX family, for which oxygen-ionic conductivity is typical. In the crystal structure of bismuth vanadate $Bi_4V_2O_{11-\delta}$, cations Bi^{3+} are in tetrahedral coordination; V^{5+} cations, in octahedral coordination. Bismuth vanadates exist in several polymorphic modifications (α-, or monoclinic; β-, or orthorhombic; and γ-, or tetragonal). The tetragonal modification occupies a special place among bismuth vanadate polymorphic modifications due to its high transport characteristics. It is the γ-phase that has the highest conductivity and the lowest activation energy value [2, 3], since all oxygen atoms in vanadium octahedra are involved in the diffusion processes. In polymorphic perovskites, $\alpha \leftrightarrow \beta$ and $\beta \leftrightarrow \gamma$ phase transitions are observed as abrupt changes in the total conductivity with rising temperature. The catalytic activity of polymorphic copper-containing BICUVOX perovskites with the composition $Bi_4V_{2-2x}Cu_{2x}O_{11-\delta}$ (x =0.00–0.16) in isobutanol transformations was studied in [4].

Plasma-chemical treatment (PCT) allows us to obtain completely new materials with widely varied surface properties, while preserving most properties of the original materials. This

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advantage is used in the activation of catalysts and adsorbents. In some cases, plasma–chemical treatment (PCT) leads to a multifold increase in the activity of catalysts, due to changes in the nature of their active sites [5]. The aim of this work was to study the influence of PCT in oxygen on the catalytic activity of polymorphic copper-containing BICUVOX perovskites with the composition $Bi_4V_{2-2x}Cu_{2x}O_{11-\delta}$ (x=0.00–0.16) in isobutanol reactions.

2 Experimental materials and methods

Solid solutions of BICUVOX with the composition $Bi_4V_{2--2x}Cu_{2x}O_{11-\delta}$ where x = 0 (sample 1), 0.04 (2), 0.06 (3), 0.10 (4), and 0.16 (5) were prepared by solid state reaction method. Oxides of Bi^{3+} (high-purity grade), V^{5+} (analytical grade), and Cu^{2+} (analytical grade) preliminarily calcined at 600°C for 2 h were used as our initial substances. Stoichiometric mixtures of the initial oxides were homogenized in ethanol. The pelletized samples were annealed at: T_1 = 500°C (10 h), T_2 = 550°C (10 h), T_3 = 600°C (10 h), T_4 = 650°C (12 h), and T_5 = 800°C (3 h) followed by slow cooling to room temperature inside a muffle furnace with grinding after each annealing. The phase composition of samples at each synthesis step and the unit cell parameters of the resulting BICUVOX solid solutions were studied using powder X-ray diffraction (DRON-7, CuK_α radiation). X-ray diffraction patterns were recorded in a step scan mode in the range $2\theta = 12°–70°$ in steps of $\Delta 2\theta = 0.02°$. Unit cell parameters were refined by profile analysis for reflections with hkl = 200, 020, and 006 using Profitvz software [6]. IR-spectroscopic structural studies were carried out on Nicolet 6700 in the range 400–1200 cm^{-1} (attachment PIKE technologies GradiATR).

Thermal pre-treatment of the BICUVOX samples included their heat-treated in a helium flow at 703 K for 1 h, with an air flow of 1.1 l/h. The samples were cooled to the temperature of the catalyst activity experiment (523 K) in a flow of helium as well.

PCT was conducted in a glow discharge of oxygen in an evacuated flow apparatus using 50 Hz alternating current. The reactor design allowed temperature to be measured simultaneously with the treatment of the samples. Hollow water-cooled electrodes were placed outside the reaction zone. The samples were placed on a quartz pod, forming a 1 mm thick layer. The reactor’s flow mode promoted the removal of the reaction products, which were concentrated in a trap cooled with liquid nitrogen. The reactor was pumped down to 10^{-4} mm Hg residual pressure, the discharge current was 200 mA, and the voltage between the electrodes was 1.4 kV. Treatment was performed for 45 min at 433 K. A violet-rosy glow was observed inside the discharge. After conducting each experiment, the samples were cooled to ambient temperature in vacuum.

The composition of the surface layers of the samples was analyzed by means of X-ray photoelectronspectroscopy (XPS). The photoelectron spectra were recorded on a XSAM-800 instrument, using $AlK_{\alpha 1,2}$ radiation with an energy of 1486.6 eV; the C1s line (E_{bond}= 285 eV) of each sample was used as our internal standard. The accuracy of determining the E_{bond} was ±0.2 eV. The alcohol conversion in vapour phase was performed in a U-shaped continuous-flow microreactor at atmospheric pressure and 473–673 K with the use of 30 mg of the catalyst. Isobutanol diluted with He was fed to the reactor at a partial pressure of 760 Pa; the total flow rate was 1.1 $l^{-1}\cdot h^{-1}$. The reaction mixture was analyzed chromatographically (FID, helium as a carrier gas). Oxide catalysts exhibit catalytic activity due to their acidic properties, both Lewis and Bronsted type [7]. Adsorption of a weak base – pyridine – was used in order to determine the acidic centers [8] on the surface of $Bi_4V_{2--2x}Cu_{2x}O_{11-\delta}$. Pyridine adsorption was studied by spectrophotometry on a Specord, UV-VIS, SF-103 instrument. Sample weights of 10 mg were added to 0.3 μmol/L solutions of pyridine in octane. Spectra were recorded every 15 min for the first incubation hour, then after 24 h total incubation time and the equilibrium concentration of pyridine was determined by the spectral data.

3 Results and discussion

As shown by X-ray diffraction (**Fig. 1**), single-phase BICUVOX solid solutions over the entire range of the x values studied were obtained after annealing at 800C. The unit cell parameters calculated for the solid solutions are listed in **Table 1**. The change in the crystal lattice symmetry of BICUVOX with x growing is due to the entrance of aCu^{2+} cation, which has a greater radius than a V^{5+} or V^{4+}cation: $R_{CN6}(V^{5+}) = 0.68$ Å, $R_{CN6}(V^{4+}) = 0.72$ Å, and $R_{CN6}(Cu^{2+}) = 0.87$ Å (**Table 1**) [9-11]. The stabilization of the α phase in the series of the solid solutions studied occurs in the concentration range of $x \leq 0.04$. The crystal structure of the $x = 0.06$ solid solution sample is characterized by orthorhombic symmetry and belongs to the β phase. BICUVOX solid solutions having a tetragonal crystal lattice are formed in the range of $0.10 \leq x \leq 0.16$.

Table 1 Unit cell parameters for $Bi_4V_{2-2x}Cu_xO_{11-\delta}$ solid solutions

X-ray diffraction						*XPS*			
Polymorph	x_{Cu}	*Parameters, Å*					*O1s*	*Bi4f*	*V2p*
		a	*b*	*c*	*V, Å*^{3}		*Initial surface*		
α	0.00	5.529	5.601	15.266	472.7	At, %	27.67	4.95	0.97
	0.04	5.535	5.594	15.357	475.6	$E_{bond,}$ eV	530.1	159.0	517.4
β	0.06	5.541	5.588	15.397	476.8		*After PCT*		
γ	0.10	5.541		15.386	472.4	At, %	34.06	17.57	3.24
	0.16	5.547		15.452	475.4	$E_{bond,}$ eV	530.0	158.7 155.6	516.8

The IR spectra (**Fig. 2**) of all synthesized samples contain abroad absorption band in the region of ~650–930 cm^{-1} associated with the valence vibrations of V–O bonds inVO_4 tetrahedra. The V–O valence vibrations inVO_6 octahedra also appear in the spectra of all of the synthesized solid solutions in the low-frequency region of ~550-450 cm^{-1}. In addition, the IR spectra of $0.00 \leq x \leq 0.04$ samples contain a low-intensity absorption band in the region of ~580–630 cm^{-1}, which corresponds to bond vibrations in VO_5 polyhedra. The presence of V^{5+} cations with CN = 5 in the vanadate layers of the BICUVOX crystal structure is characteristic of the α phase of the solid solutions, thereby verifying the stabilization of this phase in this concentration range at room temperature [12]. The disappearance of the absorption band in the region of~580-630 cm–1 and broadening of absorption bands at ~650-930 and ~450-550 cm^{-1} in the $x \geq 0.06$ sample are due to the increased concentration of Cu^{2+} cations, which have a lower oxidation number and a greater ionic radius than V^{5+} cations have. As x rises, the oxygen deficit increases in the vanadium sublattice of BICUVOX solid solutions. The consequence of these changes is the dominance of vanadium polyhedra with CN = 4 in the vanadate layers of $Bi_4V_{2-2x}Cu_{2x}O_{11-\delta}$ and the ordering of oxygen vacancies, which accompanies the formation of the oxygen-deficient tetragonal γ polymorph.

According to XPS spectroscopy, the surface of $Bi_4V_{1.88}Cu_{2\times0.16}O_{11-\delta}$has excess oxygen compared to the stoichiometry of $Bi_4V_2O_{11-\delta}$. The Bi/V atomic ratio on the surfaces is 5, i.e. 2.5 times higher compared to $(Bi/V)_{stoich}$ = 2, while the (O/V) ratio is 5 times higher. After PCT the abundance of the elements on the surface is increased, but their ratios become (Bi/V) = 2, which is in accord with stoichiometry, and (O/V) = 2, which I still elevated (table 1).The value of $E_{bondBi4f}$ = 158.7–159.0 eV corresponds tobismuth oxidation state +3. However, the spectrum for the sample subjected to PCT contains a clear "shoulder" with a maximum at 156 eV, which corresponds to the reduced form Bi^0. The value of $E_{bondV2p}$=517.4 eV of the starting sample is typical for V^{+5}. Its decrease after PCT to $E_{bondV2p}$=516.8 eV demonstrates the decrease of the charge of vanadium, i.e. the presence of V^{+4} [13]. All the spectra of O1s contain a peak with $E_{bondO1s}$=529.8–530.1 eV, corresponding to oxygen atoms in the oxide and to chemically adsorbed atomic oxygen.

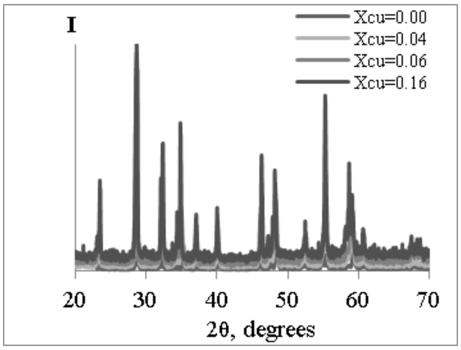

Fig. 1 X-ray diffraction patterns for $Bi_4V_{2-2x}Cu_xO_{11-x}$ samples after annealing at T = 800°C (10 h)

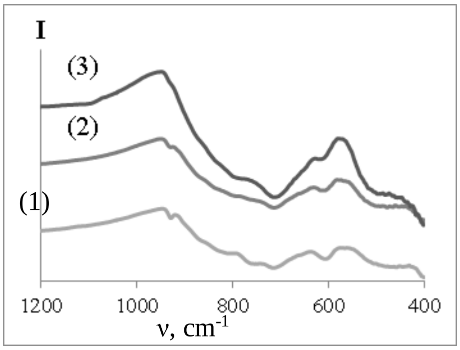

Fig. 2 IR absorption spectra for BICUVOX: x_{Cu}=0.00 (1); 0.04 (2); 0.06 (3)

Below are the results of experiments on the study of catalytic activity BICUVOX. On all samples with initial surface, where x_{Cu}=0.04 (1) 0.06 (2), and 0.16 (3), the main reaction is the dehydrogenation of an alcohol with a selectivity of isobutanal formation 83–100%. Isobutanol dehydration proceeds in parallel with the dehydrogenation reaction only on the sample with x_{Cu}= 0.16. Catalytic activity BICUVOX-perovskites increases with the copper increasing content and the highest catalytic activity is observed on superconductive tetragonal γ-phase (**Table 2**) [5].

Table 2 Catalytic activity of perovskites $Bi_4V_{2-2x}Cu_xO_{11-x}$ (BICUVOX) in isobutanol dehydrogenation

Sample	Phase	X_{Cu}	S_{623}, %	W_{623}, %	E_a, kJ/mol	$-\ln N_0$
Initial surface						
1	**β**	0.04	100	11	**60**	11.3
2	**β**	0.06	100	9	**58**	12.1
3	**γ**	0.16	81	58	**8**	15.7
After PCT in oxygen						
1*	**β**	0.04	100	28	**36**	14.6
2*	**β**	0.06	100	29	**50**	11.2
3*	**γ**	0.16	100	34	**62**	8.5

Plasma-chemical treatment (PCT) of all BICUVOX samples in oxygen, leads to the total deactivation of the active sites of dehydration reaction, and the alcohol is converted with 100% selectivity into aldehyde. Activity (conversion ***W*, *%***) of the dehydrogenation of alcohol after PCT increases ~ 1.7 times on α-phase samples compared to the initial samples (**Fig. 3**, **Table 2**). For high-conductivity γ-phase there is no activating plasma effect, on the contrary, the activity decreases after treatment.

During the catalyst in the repeated test the activity of γ-phase (sample 3*) is decreased by 15% by reducing the number of active sites with high adsorption heat, indicating instability of plasma effect and reaction medium effect on copper containing sites.

As opposed to initial samples with step-wise character of the Arrhenius dependences, the Arrhenius dependences on samples after PCT are linear (**Fig. 4**). Plasma treatment of BICUVOX in O_2 changes the experimental activation energy Ea of aldehyde formation which depends on a copper content (**Table 2**). As opposed to samples without PCT, values Eaincrease with increasing of x_{Cu}, therefore, the condition of copper sites after PCT changes, resulting a decrease in heat of adsorption of alcohol with the copper increasing content, where as before PCT Qa value increases (Ea decreases).

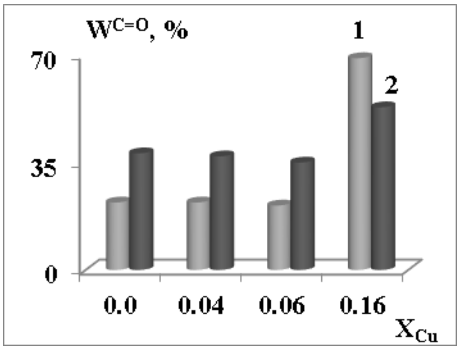

Fig. 3 Isobutanol conversion to aldehyde before (1-ligth) and after (2-dark) PCT in O_2 of $Bi_4V_{2-2x}Cu_{2x}O_{11-\delta}$ at $T=400^0C$

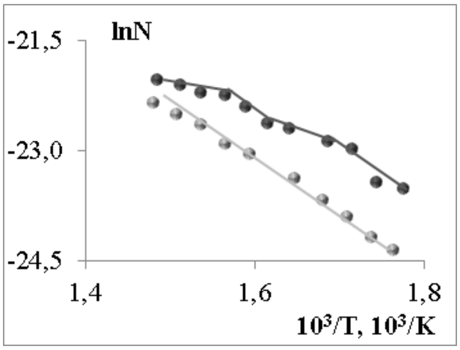

Fig. 4 Arrhenius dependences of the yields before (1-ligth) and after (2-dark) PCT in O_2 of $Bi_4V_{1.68}Cu_{0.32}O_{11-\delta}$

A change in the energy of the alcohol dehydrogenation reaction after PCT $\Delta Ea = Ea_{PCT} - Ea_{init}$ increases in the series of samples x_{Cu} = 0.04 (–24) → 0.06 (–8) → 0.16 (+54 kJ/mol) indicating the weakening of bond strength between the reagent and the active site on BICUVOX surface, with the greatest effect at the α-phase.Activation of theα-phase of the catalyst is caused by the appearance of centers with increased alcohol heat of adsorption (Q).The similarity of parameters measured for the α-phase samples including the double vanadate, shows that PCT mainly influences on the state of the structuring matrix containing bismuth, oxygen and vanadium. The presence of small amounts of copper does not alter this effect.

The total number of the acidic centers of the surface, determined by pyridine adsorption is decreased in 1.5 times after PCT compared to the initial surface. When the copper content in the samples is increased, Ap_y tends to grow, which is in accord with the increase of the pre-exponential factor (**Table 3**). Compared to the starting BICUVOX samples, samples after PCT in oxygen have more acidic centers on the surface, which adsorb pyridine at a high rate W_0 and their activity does not depend on x_{Cu}.

Table 3 Surface acidity parameters for BICUVOX tested by pyridine adsorption (equilibrium absorption A_{Py}, *µmol/g* and adsorption rates for two acidic center types W, µmol/g×min) for the initial surface (I) and after PCT (II) in comparing with pre-exponential factor logarithm for isobutanol conversion to isobutanal

X_{Cu}	A_{Py},		W_0		W		lnN_0	
	I	II	I	II	I	II	I	II
0.04	1.00	0.57	no	13.6	no	0.001	− 11.4	− 14.6
0.06	0.90	0.62		13.0		0.005	− 11.9	− 11.2
0.16	0.91	0.71		13.4		0.007	− 19.2	− 8.5

4 Conclusion

Plasma treatment of BICUVOX activates such perovskite catalysts only in case of α.β phases. Similar values of isobutanol conversion which were found for the α,β-phase samples, including the double vanadate, suggests that PCT affects the ceramic matrix with Bi, O and V elements. Addition of small amounts of copper does not change this effect. For γ-phase, where reaction goes on copper sites with strong bond energy with isobutanol. Their role of such active centres is weakened some after PCT due to enrichment of γ-BICUVOX surface by Bi, O and V. Thus, PCT in O_2 of the α-phase sample forms sites strongly attached to the surface of perovskite, therefore we observed activating effect of plasma.

References

[1] G. Centi, S. Perathoner: Catalysis by layered materials: A review Microporous and Mesoporous Materials, Vol. 107, 2008, p. 3 – 15, DOI: 10.1016/j.micromeso.2007.03.011

[2] F. Abraham, Jc. Boivin, G. Mairesse, G. Nowogrocki: Solid State Ionics, Vol. 40–41, 1990, p. 934-937, DOI: 10.1016/0167-2738(90)90157-M

[3] M.H. Paydar, A.M. Hadian, G. Fafilek: Journal of the European Ceramic Society, Vol. 21, Issues 10–11, 2001, p. 1821-1824, DOI: 10.1016/S0955-2219(01)00123-6

[4] E.I. Povarova, A.I. Pylinina, I.I. Mikhalenko: Russian Journal of Physical Chemistry A, Vol. 87, No.4, 2013, p. 560–564, DOI: 10.1134/S0036024413040237

[5] A.I. Pylinina, E.I. Povarova, I.I. Mikhalenko, T.V. Yagodovskaya: Russian Journal of Physical Chemistry A, Vol.87, No. 6, 2013, p. 929–934, DOI: 10.1134/S0036024413060216

[6] V. V. Zhurov, S. A. Ivanov: Acta Crystallographica Section A, Vol. 55, part 6, 1999, p. 923-930, DOI: 10.1107/S0108768199009374

[7] O. V. Krylov: *Heterogeneous catalysis*, first ed., Akademkniga, Moscow, 2004.

[8] A.I. Pylinina, M. N. Chernyshova, N. N. Lobanov, S. V. Savilov, E. M. Kasatkin: Theoretical and Experimental Chemistry. Vol .53, No. 1, 2017, p. 47-52, DOI: 10.1007/s11237-017-9500-3

[9] F. Abrahams, F. Krok: Journal of Materials Chemistry. Vol. 12, 2002, p. 3351-3362, DOI: 10.1039/b203992n

[10] R. D. Shannon, C. T. Prewitt: Acta Crystallographica Section B, Vol. 25, 1969, p. 925-946, DOI: 10.1107/S0567740869003220

[11] R. D. Shannon: Acta Crystallographica Section A, Vol. 32, 1976, p. 751-767, DOI: 10.1107/S0567739476001551

[12] F. Abraham, M.F. Debreuile-Gresse, G. Mouresse, G. Nowogrocki: Solid State Ionics, Vol. 28-30, part 1, 1988, p. 529-532, DOI: 10.1016/S0167-2738(88)80096-1

[13] J. Su et al.: Journal of Physical Chemistry C, Vol. 115, No. 16, 2011, p. 8064-8071, DOI: 10.1021/jp200274k

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