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# Relationship between the crystal structure, conductive and catalytic properties of perovskites $Bi_4Fe_{2x}V_{2-2x}O_{11-\delta}$

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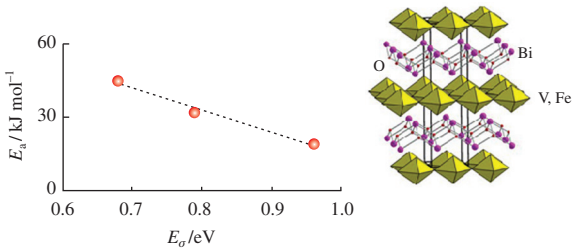
**The relationship between the crystal structure of bismuth vanadates $Bi_4V_{2-2x}Fe_{2x}O_{11-\delta}$, where $V^{5+}$ ions are partially replaced by $Fe^{3+}$ cations, and their conductive properties and catalytic activities in conversions of isobutanol was established. A correlation between concentration of Fe ions, activation energy of dehydrogenation, and conductance activation energy was revealed.**




Since their discovery in 1988, solid electrolytes (SELs) of the perovskite type have become the subject of significant attention of researchers due to their high oxide ion conductivity at relatively low temperatures. The perovskites are mixed metal oxides attracting much scientific and practical interest owing to their low price, adaptability, and thermal stability, which often depend on bulk and surface characteristics. These materials have been extensively explored for their electrical, magnetic and optical properties. They are employed in novel solar cells[1] and molten oxide membranes in separators of especially pure oxygen.[2] They are also promising candidates for the photocatalytic splitting of water.[3] SELs of a cage-lamellar framework structure are of considerable interest in the catalysis, since the scope of these materials can be expanded *via* variations in their composition introduced by a replacement of cations in the starting compound with reactive dopant ions. Complex perovskites based on bismuth vanadate $Bi_4V_2O_{11-\delta}$ belong to the SELs possessing the oxygen-ionic conductivity type.[4] The base oxide consists of alternating $(Bi_2O_2)_n^{n2+}$ and $(VO_3\square_{0.5})_n^{n2-}$ layers, wherein $Bi^{3+}$ cations are in tetrahedral coordination with oxygen, while $V^{5+}$ cations are in octahedral one. Anion vacancies (□) provide an oxygen migration in this structure. A replacement of vanadium by dopant ions affects the perovskite structural type and formation of structural defects responsible for oxygen mobility in the crystal lattice, resulting in the so-called BIMEVOX materials (or BIFEVOX if the doping metal is Fe). The high anionic conductivity of BIMEVOX oxides is related to a high vacancy concentration in the oxygen sublattice of vanadium layer and the occurrence of different coordination environments of vanadium cations.[5] This affects their transport properties as has been previously demonstrated by inflexions on the conductivity *vs.* temperature plot describing the structural changes and variations in the conductance activation energy.[6–8]

The present work was aimed at the establishment of relationship between the structural, conductive and catalytic properties of complex iron-containing bismuth vanadates $Bi_4Fe_{2x}V_{2-2x}O_{11-\delta}$.

Ceramic solid solutions $Bi_4Fe_{2x}V_{2-2x}O_{11-\delta}$, wherein $X_{Fe} = 0.04$ (**1**), 0.10 (**2**), 0.15 (**3**), were previously prepared by solid phase synthesis and characterized in detail.[9] The phase composition and crystal lattice parameters were determined by X-ray powder diffraction (XRD) analysis. Single-phase samples were obtained for the entire BIFEVOX series: sample **1** represented the monoclinic modification (α-phase), sample **2** was of the rhombic modification (β-phase), and sample **3** belonged to the tetragonal modification (γ-phase). The identity of crystal structures of the various modifications was confirmed by IR spectroscopy. The catalytic conversion of isobutanol was investigated in the temperature range of 200–400 °C.[†,10]

The mentioned metal concentrations in BIFEVOX samples **1** and **2** were confirmed by X-ray fluorescence spectroscopy (XFS), but in the case of sample **3**, the contents of vanadium and iron were 1.15 and 1.3 fold lower, respectively (Table 1). Taking into account that the elementary composition of catalyst surface and the element charges can vary, the XPS method was used. In the layer being analyzed with a thickness of no more than 4 nm, the surface was enriched with oxygen and bismuth as compared to the stoichiometric ratios of elements in $Bi_4V_2O_{11-\delta}$. The atomic ratio of bismuth and vanadium on the surface, $(Bi/V)_{surf}$, was 5, *i.e.*, 2.5 times higher than $(Bi/V)_{stoich} = 2$. After the catalysis, the content of vanadium on the surface did not change, whereas that of bismuth decreased [$(Bi/V)_{surf}$ was 3.4]. The $E_b$ value of Bi 4*f* line was 158.6 eV corresponding to the bismuth oxidation state of 3+, while that of V 2*p* was 516.6 eV for the original sample matching with the vanadium oxidation state of 5+ (Figure 1). In addition, the presence of doublet with energies of 516.4 and 516.0 eV after the catalysis suggests that the vanadium charge decreases and the $V^{4+}$ form is present. Thus, $VO_2$ is characterized by $E_b = 516$ eV, while the shoulder around 515 eV can be attributed to $V^{3+}$.[11,12]

The alcohol dehydrogenation at 400 °C proceeded on the surface of prepared samples with a selectivity of 74% towards isobutanal. The overall alcohol conversion $W_\Sigma$ and the product yields increased along with a growth in the content of $Fe^{III}$ cations, while the largest activity was characteristic of the γ-phase (Table 2, Figure 2).

[†] The catalytic experiments were carried out in a flow-through unit coupled with a chromatographic analyzer (helium as the nebulizer gas, a flame ionization detector, a column filled with Porapak Q).[10] A thin layer of the catalyst (30 mg) was placed on a porous glass filter of the microreactor. The bubbling mixture of alcohol vapor and helium was fed to the reactor at a rate of 1.1 dm$^3$ h$^{-1}$.[10] XPS (a XSAM-800 spectrometer) method was used to perform elemental analysis of the $Bi_4V_{1.7}Fe_{0.3}O_{11-\delta}$ surface before and after the catalysis. The BIFEVOX bulk composition was analyzed using a Clever C-31 X-ray fluorescent spectrometer.

**Table 1** Composition of $Bi_4V_{2-2x}Fe_{2x}O_{11-\delta}$.

| Element | XFS (wt%), $X_{Fe}$ = 0.04 (**1**) | | XFS (wt%), $X_{Fe}$ = 0.10 (**2**) | | XFS (wt%), $X_{Fe}$ = 0.15 (**3**) | | XPS (atom%), $X_{Fe}$ = 0.15 (**3**) | |
|---|---|---|---|---|---|---|---|---|
| | stoichiometric | calculated | stoichiometric | calculated | stoichiometric | calculated | before catalysis | after catalysis |
| O | – | – | – | – | – | – | 23.67 | 22.94 |
| V | 11.93 | 10.43 | 11.51 | 9.78 | 10.53 | 9.23 | 1.3 | 1.3 |
| Fe | 0.78 | 0.48 | 1.62 | 1.19 | 2.38 | 1.79 | – | – |
| Bi | 87.29 | 89.09 | 86.87 | 89.03 | 87.09 | 88.98 | 6.60 | 4.36 |
| Molecular formula | $Bi_4V_{1.92}Fe_{0.08}O_{11-\delta}$ | $Bi_{3.92}V_{2.20}Fe_{0.13}O_{11-\delta}$ | $Bi_4V_{1.8}Fe_{0.20}O_{11-\delta}$ | $Bi_{3.90}V_{2.11}Fe_{0.27}O_{11-\delta}$ | $Bi_4V_{1.7}Fe_{0.30}O_{11-\delta}$ | $Bi_{3.91}V_{1.94}Fe_{0.40}O_{11-\delta}$ | – | |

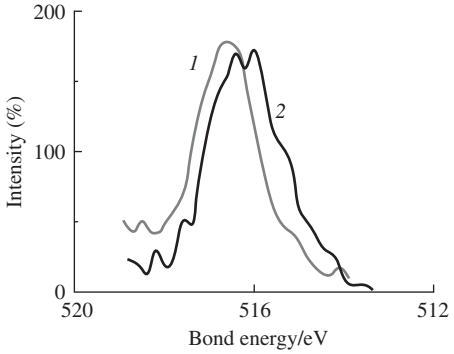



**Figure 1** XPS spectra of vanadium (*1*) before and (*2*) after the catalysis.

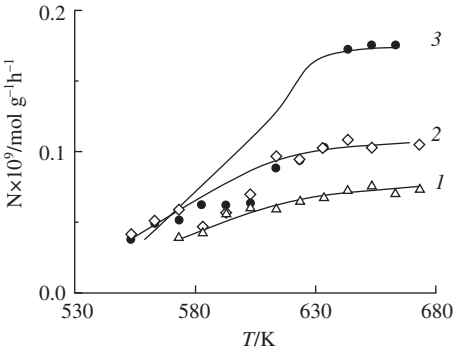



**Figure 2** Isobutanal yields at different temperatures for $Bi_4V_{2-2x}Fe_{2x}O_{11-\delta}$ samples, where $x$ is (*1*) 0.04 (**1**), (*2*) 0.10 (**2**), and (*3*) 0.15 (**3**).

As one can see from Table 2, the apparent activation energies $E_a^{C=O}$ are lower than the $E_a^{C=C}$ values by a factor of ~3.5 and increase linearly with raising the $Fe^{3+}$ content. Hence, the catalytically active center contains $Fe^{III}$ ions, while the nature and number of these centers are different in both reactions. It is known[13] that the formation of aldehyde proceeds *via* an alkoxide moiety, while the limiting step involves the reduction and reoxidation of catalytically active dopant ion with a change in the oxidation state. Therefore, incorporation of $Fe^{3+}$ ions favors the formation of complex Fe–O–V centers followed by partial reduction of vanadium cations ($Fe^{2+}$–O–$V^{5+}$ ⇔ $Fe^{3+}$–O–$V^{4+}$) according to the XPS data. In the case of dehydratation reaction, the abrupt increase in $E_a^{C=C}$ values indicates that the heat $Q$ of isobutanol adsorption decreases in the series of samples **1** > **2** > **3** according to the Brønsted–Polanyi–Semenov relationship ($E_a = E_a^0 - \alpha Q$).[14] Hence, the olefin is formed *via* a strong chemisorbed complex on acid–base centers that also contain $Fe^{III}$ ions.[13]

Figure 2 shows the dependence of aldehyde yield on temperature. The plots are nonmonotonic and resemble the conductivity *vs.* temperature plot.[15] It should be noted that similar plots of the yields of isobutanol transformation products were reported for copper-containing vanadates $Bi_4V_{2-2x}Cu_{2x}O_{11-\delta}$.[16] The curve shape in systems of this type may result from a change in the conductive properties of SELs along with an increase in temperature, *i.e.*, a decrease in the conductance activation energy $E_{a,\sigma}$ upon transitions α → β → γ. The increase in the $X_{Fe}$ content in $Bi_4V_{2-2x}Fe_{2x}O_{11-\delta}$ materials leads to the decreased coordination number of ions in the $V^V$ sublattice and growth in the number of oxygen vacancies, which leads consequently to the increased total charge of dopant ion, raises the chemical potential of electrons, and hinders their release. This is important for redox reactions since it limits the reoxidation step for the reactive ion as indicated by the increased activation energy of dyhydrogenation reaction.[17] Thus, the acquired data indicate that there is a correlation between the content of the dopant ion, conductance activation energy $E_{a,\sigma}$ and activation energy of alcohol dehydrogenation $E_a^{C=O}$ (Figure 3).

**Table 2** Catalytic activity of $Bi_4V_{2-2x}Fe_{2x}O_{11-\delta}$ in the conversion of isobutanol.[a]

| Sample | Phase | $X_{Fe}$ | Isobutanol conversion, 400 °C | | $E_{a,\sigma}$/eV | Activation energies | |
|---|---|---|---|---|---|---|---|
| | | | $W_\Sigma$(%) | $S_{c=o}$(%) | | $E_a^{C=O}$/kJ mol$^{-1}$ | $E_a^{C=C}$/kJ mol$^{-1}$ |
| **1** | α | 0.04 | 15 | 74 | 0.96 | 19 | 66 |
| **2** | β | 0.10 | 21 | 76 | 0.79 | 32 | 103 |
| **3** | γ | 0.15 | 30 | 78 | 0.68 | 45 | 169 |

[a] $W_\Sigma$ is the overall conversion, $S_{c=o}$ is the selectivity, $E_{a,\sigma}$ is the conductance activation energy, and $E_a$ is the activation energy of reactions.

In conclusion, the iron-containing bismuth vanadates BIFEVOX have been proved to serve as efficient catalysts of isobutanol dehydrogenation due to the high activity of BIFEVOX tetragonal phase. The dependence of ionic dopant content on the activation energy of dehydrogenation and on the activation energy of conductivity has been established.

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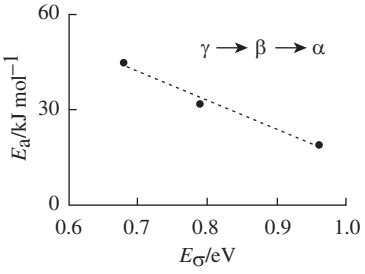


**Figure 3** Activation energy of isobutanol dehydrogenation *vs.* the conductance activation energy of $Bi_4V_{2-2x}Fe_{2x}O_{11-\delta}$.

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