

Double perovskite $\text{Pr}_{2-x}\text{Bi}_x\text{Sr}_2\text{O}_6$ ($x = 0.533$) in ketonization of 1-butanol: Effect of water vapor addition

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ABSTRACT

An effective ketonization of 1-butanol mixed with water vapor over the catalyst $\text{Pr}_{1.467}\text{Bi}_{0.533}\text{Sr}_2\text{O}_{5.928}$ of monoclinically distorted perovskite structure is reported. The catalyst is characteristic of 1.2 at.% of oxygen vacancies, supposed to act as active centers of Lewis type, and of a high oxidative ability reflected by large change in the catalyst's effective valence factor ($V-3$). The ketonization performed without water addition is accompanied with total carbonization of 1-butanol, caused by the catalyst's oxygen, the latter easily releasable beginning from low temperatures. This negative effect is practically removable if the process is performed under the presence of water vapor. It is also found that water addition influences the formation of $\text{C}_3\text{H}_7\text{-CH=O}$ aldehyde and of $\text{C}_3\text{H}_7\text{-CO-C}_3\text{H}_7$ ketone. Nevertheless, water addition leads to a steady destruction of the catalyst's crystal structure because of CO_2 , appearing in course of the WGS process, and of its subsequent reaction with the structure component SrO to SrCO_3 . The catalyst is found easily reproducible by its re-oxidation in air at 850–900 °C.

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1. Introduction

A general rule concerning transformation of primary alcohols in heterogeneous reactions with dehydrogenating catalysts is that such reactions lead to appropriate aldehydes. However, if the catalysts possess certain oxidative ability, i.e. presence of some M-ions of comparatively high and variable valence (V_M), additionally supported by certain level of structure vacancies (the latter acting as active Lewis centers of anionic and/or cationic character [1,2]), then such transformation usually proceeds through several intermediates with symmetrical ketones as major product, containing $2n - 1$ carbon atoms in chains. Concerning aldehydes and esters, they undergo identical transformation [3,4]. However, if the raw material consists of a mixture of alcohols, aldehydes and/or esters, then the transformation leads to non-symmetric ketones, which are known to have several important applications [5–8]. Worth mentioning is condensation of the related compounds, i.e. the carboxylic acids, also resulting in non-symmetric ketones [9,10].

Considering the Fisher–Tropsch process, its recently observable renaissance is being directed towards an increased use of oxygenated products, the latter always accompanying the main products of the FT process, i.e. olefins and paraffins [11,12]. There is

a commercial interest to maximize significance of such selectivity, especially in the case of synthesis of higher alcohols [13–15].

The $\text{Pr}_{1.467}\text{Bi}_{0.533}\text{Sr}_2\text{O}_{5.928}$ sample tested in this work originates from terminal solid solution of the Bi/Pr substituted PrSrO_3 binary matrix of monoclinically distorted double perovskite structure [16], typical to a large group of $\text{REBiSr}_2\text{O}_6$ ternaries [17,18] (see dashed line in Fig. 1). As seen, domain of existence of the Pr-based analog of the $\text{RE}^{4+}\text{SrO}_3$ (Tb, Ce) family (in contrast to TbSrO_3), occurs to be slightly shifted from the 1:1 stoichiometry. A direct consequence of this deviation is the structure defectiveness of various kinds, such as anti-site atoms and oxygen vacancies, appearing vs. (x) in the Bi/Pr substituted representative of the family, thus making it more attractive from the point of view of eventual catalytic activity.

The exact composition found in [16] for the matrix phase PrSrO_3 corresponded to 55 at.% Pr. Easy to find out that this leads to the formula $\text{Pr}_{1.1}\text{Sr}_{0.9}\text{O}_3$, indicating the appearance of Pr ions within the structure positions of Sr. Consequently, analytical expression describing the solid solution based on this matrix is as follows:

$$[\text{Pr}_{(1-0.8x)}\text{Bi}_{0.8x}][\text{Sr}_{0.9+0.3x}\text{Pr}_{(0.1-0.3x)}]\text{O}_{0.9+3x+V(1.1-0.3x)/2}; (0 \leq x \leq 0.5),$$

where [] signs denote occupancy of the individual metal sublattices, i.e. Pr–, and Sr–, while the V factor reflects effective valence of the average metal ion $M = (\text{Pr}_{1.1(1-x)} + \text{Bi}_{0.8x})$.

The iodometric titration applied to several samples of this system allowed to find out [16] the exact values for $V_{\text{Pr}} = 3.694$ and for $V_{\text{Bi}} = 4.565$, and to express the V parameter analytically as $V = (4.0634 - 0.4114x)/(1.1 - 0.3x)$. Thanks to this, the formula

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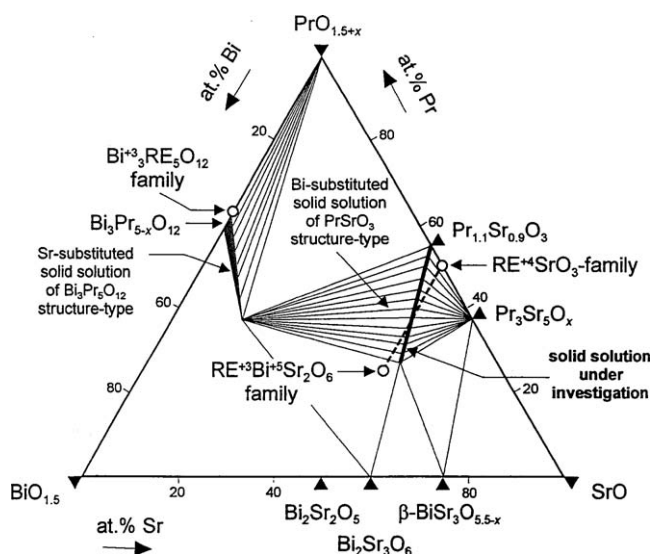
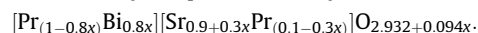


Fig. 1. Phase relations in the Bi-Pr-Sr-O system in air at 900 °C (reproduced from [16]).

given above for the Bi/Pr substituted solid solution could be substantially simplified, namely:



The main features, described in [16] for this solid solution are as follows:

- (i) the increasing character of the effective valence (V) variation vs. contribution of Bi in spite of the constant valence values of V_{Pr} and V_{Bi} ,
- (ii) the x -dependent variation of the structure defectiveness, resulting in vacancies on its oxygen sublattice, decreasing within the range ~ 2.27 – 0.7% with the increase in x .

The aim of this work was to verify if sample of the composition ensuring an intermediate level of the oxygen vacancies ($\sim 1.2\%$) and the pure occupancy of Sr-sublattice, i.e. the sample with $x = 1/3$, would occur catalytically active. Considering the structure defectiveness, such a sample would resemble much LaMnO_3 phase, recently proved to exhibit quite high catalytic activity in ketonization of 1-butanol [2]. In Fig. 1, this sample is located at the crossing point of the solid and dashed lines.

2. Experimental

To verify our expectation, sample of the composition $\text{Pr}_{0.733}\text{Bi}_{0.267}\text{SrO}_{2.964}$ has been taken for the tests. The preparation of this sample and its full crystallographic characterization are given in our previous reports [16,19]. The X-ray diffraction pattern of this selected composition is presented in Fig. 2.

The further parameters found in [16,19] for $\text{Pr}_{0.733}\text{Bi}_{0.267}\text{SrO}_{2.964}$ sample are as follows: space group $P12_1/n1$, lattice constants $a = 5.973 \text{ \AA}$, $b = 6.114 \text{ \AA}$, $c = 8.531 \text{ \AA}$, $\beta = 89.92^\circ$, densities $d_x = 6.22 \text{ g/cm}^3$, $d_m = 6.21 \text{ g/cm}^3$, and the effective valence of Bi and Pr ions $V = 3.92$, the latter being a direct measure of the phase oxidative ability ($V-3$).

Transformation of 1-butanol in the gas phase at the atmospheric pressure was used as a model reaction. The experiments on ketonization of 1-butanol were carried out in a typical flow installation. About 2 cm^3 of $\text{Pr}_{0.733}\text{Bi}_{0.267}\text{SrO}_{2.964}$ sample, mixed with $\sim 1 \text{ cm}^3$ of SiO_2 , both of 0.6 – 1.2 mm granulation, was placed in a quartz tube and installed in a vertical pipe furnace Thermolyne F21100. Liquid 1-butanol, water and butyraldehyde were sub-

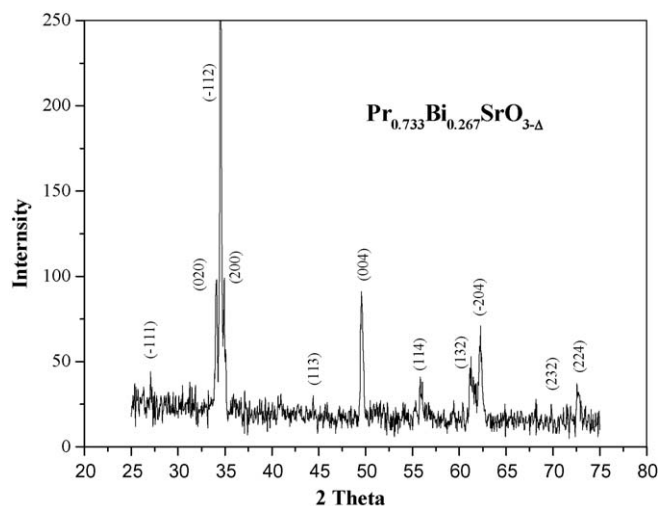


Fig. 2. X-ray diffraction diagram of the $\text{Pr}_{0.733}\text{Bi}_{0.267}\text{SrO}_{2.964}$ catalyst used in catalytic transformation of 1-butanol.

jected for dispersion using an infusion pump (Medipan 610-2) with a total speed of $\sim 3 \text{ cm}^3/\text{h}$. The upper part of the reactor served as an evaporator as well as a mixer. No carrier gas was used.

The reactions were performed as a function of step-by-step fixed temperature, within the range 200 – $460 \text{ }^\circ\text{C}$. With some exceptions, one cycle of the experiment lasted $\sim 7 \text{ h}$. Since the preliminary tests showed very strong carbonization of the 1-butanol, further tests were performed with water vapor addition. So, on reaching $300 \text{ }^\circ\text{C}$, composition of the stream passing over the catalyst was changed from $3 \text{ cm}^3/\text{h H}_2\text{O}$ to $2 \text{ cm}^3/\text{h H}_2\text{O} + 1 \text{ cm}^3/\text{h 1-butanol}$. Tests with some smaller quantities of water, performed exceptionally at a temperature of $460 \text{ }^\circ\text{C}$, were also done to see any effect on the process of 1-butanol conversion.

The chromatographic analysis of the resulting products (INCO-505 gas chromatograph, 5% Apiezon L on Chromosorb W, TCD) was repeatedly made within each new cycle of fixed temperature, after 0.5 h of its duration.

Considering the catalyst itself, its state was also analyzed, precisely after the catalysis and after re-oxidation in air at $850 \text{ }^\circ\text{C}$ for 36 h . The analysis comprised: X-ray diffraction (DRON diffractometer with Fe filtered $\text{CoK}\alpha$ radiation) to determine eventual phase composition variation, gravimetry, to find out its real weight gain or loss (Δm), and iodometric titration [20], to evaluate appropriate change in the catalyst's oxidative ability ($V-3$). In addition, textural properties of the catalyst were analyzed to recognize variation of its specific surface and porosity. The latter were determined using liquid N_2 volumetric equipment Autosorb 1 of Quantachrom at 77 K .

3. Results and discussion

As we expected (by a great similarity to the LaMnO_3 type catalyst [2]), the $\text{Pr}_{0.733}\text{Bi}_{0.267}\text{SrO}_{2.964}$ sample appeared quite active in the ketonization of 1-butanol. As seen in Fig. 3, at $460 \text{ }^\circ\text{C}$ it offers the highest selectivity ($\sim 44\%$) to ketone. Considering conversion and its yield from 1-butanol, they are also quite high, reaching at this temperature $\sim 50\%$ and $\sim 20\%$, respectively (Fig. 4).

In this respect, the parameters of 1-butanol transformation obtainable with the $\text{Pr}_{0.733}\text{Bi}_{0.267}\text{SrO}_{2.964}$ catalyst are indeed comparable (if not to say higher, despite the presence of water) to those found in the case of stoichiometric LaMnO_3 , reported in [2] for somewhat lower temperature range.

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