Yttria-Stabilized Zirconia as a High-Performance Catalyst for Ethanol to $n$-Butanol Guerbet Coupling

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ABSTRACT: It has been shown that yttria-stabilized zirconia is an effective catalyst for ethanol to $n$-butanol Guerbet coupling. The variation of the calcination temperature allows an improvement in the catalytic characteristics of this material via stabilization of the tetragonal phase of zirconia, having higher basicity than the monoclinic one. The treatment of yttria-stabilized zirconia at an optimal calcination temperature of 500 °C induces the increase in surface basicity required for the aldol condensation step, along with a decrease in surface acidity, which is responsible for the side reaction such as ethylene formation. The catalyst obtained significantly exceeds in selectivity and $n$-butanol yield than individual zirconia and other oxide systems which have been studied in this reaction.

1. INTRODUCTION

The valorization of bioethanol into value-added chemicals, such as $n$-butanol, has been of particular industrial interest over the last decades. $n$-Butanol is mainly used in the production of paints, solvents, and plasticizers and can be applied as a fuel additive or as a promising alternative to gasoline.2 The catalytic paints, solvents, and plasticizers and can be applied as a fuel additive served as a stabilizer for the tetragonal ZrO2.21 According to the Guerbet reaction mechanism, acidic and basic properties of the catalysts are equally important.11 In recent years, zirconium oxide and its stabilized forms have received attention as active catalysts in acid–base heterogeneous catalytic processes, including Guerbet condensation, due to the tunable bifunctional acid–base properties.12–15 However, it turned out that zirconia is not an effective catalyst for the ethanol-to-butanol conversion because dehydration to ethylene occurs much more readily than dehydrogenation to ethanal. It has been found that the presence of a strong Lewis base acidity of ZrO2 directs the alcohol conversion process toward the hydrocarbon formation.16 Partial neutralization of these sites by sodium additives14,17 or modification of ZrO2 with basic oxides18 increased the selectivity toward coupling products but decreased the productivity due to an increase in the surface coverage by adsorbed intermediates.17,18

Meanwhile, another possible tool for controlling the acid–base properties of zirconium oxide is the phase composition because it was shown that various crystalline modifications of zirconia differ in acid–base characteristics. It was found that tetragonal ZrO2 is characterized by higher basicity than the stable monoclinic phase.19 This leads to differences in the catalytic activity of ZrO2 with different phase compositions. In particular, we observed such an effect when studying the methanol carboxylation over zirconia catalysts calcined at different temperatures.20 It was also confirmed for the Guerbet coupling over ZrO2–CeO2 compositions, wherein the ceria additive served as a stabilizer for the tetragonal ZrO2.21

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Materials with the metastable phases of ZrO₂, which are stabilized by the addition of rare earth elements are well-known. Moreover, yttria is the most commonly used additive to stabilize the tetragonal or cubic phase of zirconia.²²,²³ Because of a number of valuable physical properties such as high strength and resilience; chemical stability; high melting point; and ionic, electrical, and optical properties, yttria-stabilized zirconia (YSZ) is an important engineering material used in various fields of industry, energy, engineering, electronics, and medicine.²⁴−²⁶

The catalytic properties of YSZ are caused by specific peculiarities of the electronic structure and are related to their redox and acid–base characteristics.²⁷,²⁸ The addition of ZrO₂, a substitution cation with a lower valence than Zr⁴⁺, causes the generation of oxygen vacancies to compensate the charge. Two Y³⁺ ions generate one vacancy on the anionic sublattice, which determines the conductivity of O₂⁻ ions. Because of this, YSZ is widely used as a catalyst and support in various processes, in particular, oxidation, hydrogenation, amination, isomerization, and so forth.²⁹ The efficiency of YSZ as a well-known material with an established production technology for bioethanol processing to higher alcohols can open up new prospects for the use of these materials in catalysis.

The calcination temperature is an important factor having an effect on the phase, structural, and acid–base characteristics of oxide catalysts,²⁰ which ultimately determines their catalytic properties. Therefore, the purpose of this work was to study the effect of the calcination temperature on acid–base and catalytic characteristics of YSZ for ethanol to n-butanol Guerbet coupling. The research objects in this work were ZrO₂–Y₂O₃ compositions calcined at temperatures 300−900 °C. The Y₂O₃ content in oxide compositions was 3.4 mol % because this concentration of the additive favors the crystallization of ZrO₂ mainly as a tetragonal phase.³¹,³²

2. RESULTS AND DISCUSSION

2.1. Structure Parameters and Phase Compositions. The X-ray diffraction (XRD) patterns of YSZ compositions are shown in Figure 1. For the YSZ 300 sample, no pronounced peaks in the XRD pattern was observed, indicating that this solid is amorphous and has too weak crystallinity to identify. Higher calcination temperatures cause the crystallization of zirconia. The increase in the calcination temperature up to 400 °C commonly results in the formation of the cubic phase of ZrO₂. However, the local structure determined by the radial distribution functions of the electronic density³³ for the YSZ-400 sample exhibits split coordination peaks corresponding to tetragonal distortion of the anion sublattice that was found in the YSZ-400 sample.³⁴ YSZ 500 and YSZ 700 compositions also contain only tetragonal ZrO₂. The increase in the calcination temperature of YSZ compositions up to 900 °C leads to a gradual transition from the metastable tetragonal phase of ZrO₂ to the stable monoclinic one.³⁵ Therefore, although the tetragonal phase predominates in the YSZ 900 sample, a certain amount of the monoclinic phase is also present.

Figure 2 shows the low-temperature nitrogen adsorption–desorption isotherms for YSZ compositions. According to the Brunauer classification,³⁶ all isotherms correspond to type IV. Capillary condensation in mesopores occurs at p/p₀ > 0.5 (0.5 for YSZ 400, 0.7 for YSZ 500 and 0.8 for YSZ 900). A sharp rise in isotherms at p/p₀ < 0.05 may be caused by the filling of micropores. All isotherms can be classified as type H1 accordingly to the shape of the hysteresis loop.³⁷ H1 isotherms are typical for uniformly packed agglomerates and close in size spherical particles. The corresponding pore size distribution curves for YSZ compositions are presented in Figure 3.

Table 1 represents some structural characteristics (specific area, Sₚₑₛ;c, average pore diameter, d_pores, and pore volume, Vₚ) and phase composition for the YSZ samples according to the Brunauer–Emmett–Teller (BET) and XRD data.
Table 1. Structural Characteristics and Phase Composition of YSZ Samples

| sample | $S_{BET}$ (BET), m$^2$/g | $d_{pore}$ nm | $V_p$ m$^3$/g | phase composition |
|--------|--------------------------|---------------|--------------|------------------|
| YSZ 300 | 209                      | 5.4           | 0.43         | A                |
| YSZ 400 | 160                      | 5.6           | 0.38         | T                |
| YSZ 500 | 93                       | 7.6           | 0.29         | T                |
| YSZ 700 | 43                       | 18.2          | 0.28         | T                |
| YSZ 900 | 21                       | 15.2          | 0.24         | T + M            |

"A"—amorphous; "T"—tetragonal; "M"—monoclinic phase of zirconia.

Heat treatment leads to significant changes in the parameters of the porous structure of ZrO$_2$: the specific surface area of the samples calculated by the BET method decreases from 209 to 21 m$^2$/g, which is probably due to the sintering of particles with increasing calcination temperature. Herewith, larger ZrO$_2$ particles form wider pores: the average pore diameter increases from 2.4 to 18.2 nm, and the total pore volume decreases from 0.43 to 0.24 cm$^3$/g. Within a temperature interval 500−700 °C, especially sharp change in the structure occurs. The average pore diameter for YSZ 300, YSZ 400, and YSZ 500 samples does not exceed 8 nm (Table 1), while for YSZ 700 and YSZ 900 samples, this value is 15−18 nm. Thus, an increase in the calcination temperature leads to the formation of larger pores and to a decrease in the specific surface.

2.2. FTIR Study. The Fourier transform infrared (FTIR) spectra for all YSZ compositions in the 4000−400 cm$^{-1}$ range are shown in Figure 4. The bands at 1638, 1617, and 1087 cm$^{-1}$ are attributed to bidentate carbonate or bidentate hydrocarbonate [band at 1243 cm$^{-1}$ −δ(OH)] that could be assigned to strongly adsorbed CO$_2$ as CO$_3^{2-}$/HCO$_3^−$ over strong basic sites. The ratio between CO$_3^{2-}$/HCO$_3^-$/ depends on the calcination temperature of the YSZ. The bands at 1384 cm$^{-1}$ with shoulder at 1350 cm$^{-1}$ could be attributed to vibration modes of monodentate carbonate species that may correspond to the carbon dioxide associated with weak basic sites. The intensity of these bands decreases with the increase of pretreatment temperature of YSZ powders.

2.3. Acid−Base Properties. Figure 5 shows the differential curves of ammonia and carbon dioxide quasi-equilibrium thermal desorption (QE-TD) results for YSZ samples, which demonstrate the energetic heterogeneity of the acid−base sites. Within the whole temperature interval of adsorption of probe substances, it is possible to distinguish several regions corresponding to adsorption on acid−base sites of various strength.

Because the desorption temperature of a probe substance in the quasi-equilibrium mode correlates with its adsorption heat, this parameter serves as an indirect characteristic of the strength of acid−base sites. The temperatures of maxima for the desorption peaks ($T_{des}^{\max}$) characterize the average strength of the acid−base sites of a certain type. The temperatures of total desorption ($T_{des}^{\text{total}}$) are related to the adsorption heat of the probe substance at zero coverage and characterize the limit strength of acid−base sites.

The results obtained show that the region of ammonia desorption from the surface of YSZ samples corresponds to lower temperatures than for carbon dioxide. This indicates a higher strength of the base sites, compared with acid ones. The data on the distribution of acid−base sites by strength are summarized in Table 2.

Both in the case of NH$_3$ and CO$_2$ adsorption, there is a certain portion of sites with $T_{des}^{\max}$ of probe substances below 50 °C. The adsorption region of probe substances for these super weak acid and base sites includes a temperature range up to 75 °C. Super weak acid sites are characteristic for YSZ samples with relatively low calcination temperatures (300−500 °C). The presence of super weak base sites was registered for all studied samples, with the exception of YSZ 700.

The adsorption of NH$_3$ on weak acid sites corresponds to a temperature range of 75−100 °C, and the adsorption of CO$_2$ on base weak sites corresponds to 75−125 °C. The ammonia adsorption on acid sites of medium strength observed at 100−150 °C and the carbon dioxide adsorption on the base sites of medium strength occurs in the range of 125−170 °C. The NH$_3$ adsorption region on strong acid sites corresponds to the temperatures of 150−200 °C, and the CO$_2$ adsorption region on strong base sites corresponds to the temperatures of 160 to 250 °C. Higher temperatures are related to the adsorption of probe substances over super acid and super base sites. Super acid sites are only observed for the YSZ 700 sample and super base ones only for the YSZ 500 sample.

The strong acidity of ZrO$_2$ is related to the acid Lewis sites representing the coordinatively unsaturated Zr$^{4+}$ particles and the strong basic properties of zirconia are assigned to the presence of O$^{2-}$ sites. Hydroxyl groups of zirconia having an amphoteric nature can possess both weak Brønsted acidity and weak basicity. Herewith, OH-groups of ZrO$_2$ can represent several types of basic sites of various strength, which form monodentate and bidentate hydrocarbonates upon adsorption of CO$_2$. The last type adsorbed complexes are very weak because they are destroyed easily with minimal heating.

In addition, CO$_2$ can form the adsorption complexes of media strength with acid−base pairs ( coordinatively unsaturated Zr$^{4+}$−O$^{2-}$). The main quantitative characteristics of acidity/basicity of samples, determined using the QE-TD method, are the acid/base capacity (mmol/g) and surface density (mmol/m$^2$) of the sites. The relevant data on the acid and basic characteristics of the samples are shown in Table 3.

An increase in the calcination temperature leads to a decrease of the acid capacity, while the surface density of acid sites increases. Simultaneously, the strength of acid sites varies in a nonmonotonous way: the highest $T_{des}^{\text{total}}$ NH$_3$ is characteristic for YSZ 700 and the lowest for YSZ 300. For the base sites, both the capacity and surface density are also...
having no monotonous dependence with an increase in the calcination temperature. The YSZ 500 sample is the most basic in terms of base capacity, density, and strength of the basic sites. In general, for YSZ 300, YSZ 400, and YSZ 700 samples, the acidity is higher than the basicity, while for YSZ 500 and YSZ 900 samples, the base capacity exceeds the acid one. Between the YSZ 400 and YSZ 500 samples, there is a sharp increase in base capacity with a simultaneous decrease in acid capacity. As a result, the acid—base spectra for YSZ 400 and YSZ 500 differ significantly: the acidity of the YSZ 400 sample is 1.8 times higher than its basicity, while for the YSZ 400 sample the basicity is 1.6 times higher than the acidity.

As noted above, for all samples except YSZ 900, the strength of the base sites is not lower than the acid ones. The patterns of changes in the strength of acid/base sites with an increase in the calcination temperature of YSZ samples are depicted in Figure 6. Both on the acidity and basicity, the samples can be divided into two groups with a decrease in \( T_{\text{des}}^{\text{total}} \) for each of them. However, the “boundary position” in acidity and basicity is occupied by different samples: YSZ 700 has the highest strength of acid sites \( (T_{\text{des}}^{\text{total}} \text{NH}_3 = 250 \, ^\circ\text{C}) \), and YSZ 500 has the highest strength of the basic ones \( (T_{\text{des}}^{\text{total}} \text{CO}_2 = 325 \, ^\circ\text{C}) \).

Table 2. Temperatures of Desorption Peaks \( (T_{\text{des}}^{\text{max}}) \) and Total Desorption \( (T_{\text{des}}^{\text{total}}) \) of Probe Substances for YSZ

| sample  | \( T_{\text{des}}^{\text{max}} \text{NH}_3, \, ^\circ\text{C} \) | \( T_{\text{des}}^{\text{total}} \text{NH}_3, \, ^\circ\text{C} \) | \( T_{\text{des}}^{\text{max}} \text{CO}_2, \, ^\circ\text{C} \) | \( T_{\text{des}}^{\text{total}} \text{CO}_2, \, ^\circ\text{C} \) |
|---------|----------------|----------------|----------------|----------------|
| YSZ 300 | <50 115 170 180 | 50 105 155 195 | 225 200 180 190 | 325 280 260 225 |
| YSZ 400 | <50 110 160 190 | 170 125 180 210 | 200 180 150 140 | 300 270 240 225 |
| YSZ 500 | <50 85 130 135 | 150 110 190 200 | 250 140 225 245 | 325 280 265 250 |
| YSZ 700 | 160 230 250 200 | 60 115 150 140 | 250 225 200 190 | 325 280 265 250 |

Table 3. Acid—Base Characteristics of YSZ Compositions

| sample  | acidity | basicity |
|---------|---------|----------|
|         | acid capacity mmol NH\(_3\)/g | acid density \times 10\(^3\) mmol NH\(_3\)/m\(^2\) | base capacity mmol CO\(_2\)/g | base density \times 10\(^3\) mmol CO\(_2\)/m\(^2\) |
| YSZ 300 | 0.46    | 2.20     | 0.41     | 1.93    |
| YSZ 400 | 0.42    | 2.64     | 0.23     | 1.46    |
| YSZ 500 | 0.27    | 2.89     | 0.42     | 4.49    |
| YSZ 700 | 0.14    | 3.29     | 0.12     | 2.72    |
| YSZ 900 | 0.07    | 3.43     | 0.08     | 4.00    |

Figure 5. Differential QETD curves of ammonia (a) and carbon dioxide (b) for YSZ compositions.

Figure 6. Effect of the calcination temperature on the limit strength of acid and base sites of the YSZ compositions.
Table 4. Catalytic Characteristics of YSZ Compositions in the Guerbet Process[a]

| catalyst | conversion, % | E  | BD  | DEE | C3+ | AA | Ac | EA | CA | n-BuOH | n-HeOH | other  | BuOH yield, % |
|----------|---------------|----|-----|-----|-----|----|----|----|----|-------|--------|--------|----------------|
| YSZ 300  | 9.0           | 24.8| 11.7| 1.8 | 3.5 | 6.3| 2.8| 8.6| 3.4| 20.2  | 2.0    | 14.9  | 1.8            |
| YSZ 400  | 24.7          | 6.2 | 3.0 | 0.3 | 2.6 | 3.1| 0.9| 3.2| 1.7| 63.9  | 2.3    | 12.8  | 15.8           |
| YSZ 500  | 24.2          | 5.3 | 2.7 | 0.3 | 2.0 | 3.1| 0.5| 4.6| 1.6| 69.2  | 1.1    | 9.8   | 16.8           |
| YSZ 700  | 9.7           | 8.9 | 3.6 | 0.4 | 0.2 | 6.5| 0.4| 4.0| 0.9| 70.2  | 0.6    | 4.3   | 6.8            |
| YSZ 900  | 2.5           | 30.0| 8.9 | 1.0 | 23.6| 9.0| 7.0| 2.8| 15.7| 1.8   | 8.4   | 0.4             |

[a] E—ethylene, BD—1,3-butadiene, DEE—diethyl ether, C3+—light alkenes, AA—acetaldehyde, Ac—acetone, EA—ethyl acetate, CA—crotonaldehyde, BuOH—n-butanol, n-HeOH—n-hexanol.

Thus, the strength of acid–base sites before and after maximum values of T_{\text{des}} NH_{3} and T_{\text{des}} CO_{2} gradually decreases.

2.4. Catalytic Performance. Studies have shown that YSZ is a sufficiently active catalyst for the vapor phase coupling of ethanol to n-butanol. Herewith, under conditions of our experiments, a number of products were formed: n-butanol, n-hexanol, ethylene, light alkenes, 1,3-butadiene, diethyl ether, acetaldehyde, acetone, ethyl acetate, and crotonaldehyde. The data on ethanol conversion, selectivity toward resulting products, and n-butanol yield at 300 °C are summarized in Table 4.

The ethanol conversion over YSZ catalysts reached 24.7%. The main reaction product was n-butanol, reaching 70% selectivity. The most selective (above 60%) catalysts towards n-butanol formation are samples containing exclusively the tetragonal ZrO_{2}. Both over the amorphous YSZ 300 sample and YSZ 900 sample with the monoclinic phase, a side reaction of the ethylene formation predominantly occurs, and therefore, the n-butanol selectivity is much lower (15–20%).

The dependence of n-butanol productivity on the calcination temperature of YSZ catalysts is represented by a volcano-shaped curve (Figure 7). This dependence shows that the medium YSZ calcination temperatures, when the tetragonal phase of zirconia is the most effectively stabilized, are necessary to obtain an effective catalyst for the Guerbet reaction. Long-term durability tests for the most active of the studied catalysts YSZ 500 were conducted and showed that YSZ 500 is fairly stable. During 12 h on the stream, EtOH conversion decreased from 24.2 to 23.8% whereas n-butanol selectivity slowly increased from 69.2 to 71.1%.

Direct correlations of acid–base characteristics and the catalytic activity of the YSZ samples have not been observed. However, comparison allows us to draw some qualitative conclusions about the effect of acidity and basicity on the n-butanol selectivity in the Guerbet process. The most active toward the n-butanol formation YSZ 400 and YSZ 500 catalysts are characterized by the presence of strong basic and relatively weak acid sites. Such a type of acid–base spectrum promotes the condensation of ethanol and does not contribute to the side reaction of EtOH dehydrogenation which is characteristic for zirconia catalysts. The YSZ 700 catalyst also has strong base sites and exhibits high selectivity for the target product. A small concentration of both acid and base sites leads to a low conversion and low mass productivity for n-butanol; although due to the less developed surface, this catalyst has higher specific productivity for BuOH than YSZ 400. The YSZ 500 catalyst is the most effective both in terms of mass and specific n-butanol productivity.

According to the data presented in Table 5, n-butanol selectivity and yield over the YSZ 500 catalyst under the study is sufficiently higher than over individual zirconia (more than 4 times) and most of the other oxide systems investigated by various authors under conditions comparable to our experiments. The higher BuOH yields than for YSZ 500 are achieved only over a Cu/HSACeO_{2} catalyst, when the process is carried out under pressure in a supercritical CO_{2} reactor. Consequently, YSZ can be considered as a promising catalyst for the production of higher alcohols from ethanol.

3. CONCLUSIONS

Our results show that YSZ is a sufficiently effective catalyst for ethanol to n-butanol Guerbet coupling. When studying YSZ, we obtained catalysts characterized by high selectivity (up to 70%) and a fairly high yield of n-butanol (up to 16.8%). The high activity of YSZ catalysts is primarily due to their acid–base bifunctionality and the phase composition, which consists of a ZrO_{2}–Y_{2}O_{3} solid solution with a crystalline structure corresponding to tetrahedral zirconia. The calcination temperature can be an effective tool for the improvement of the catalytic characteristics of this material by stabilizing the tetragonal zirconia phase, which is more basic than the monoclinic one. To obtain an effective YSZ catalyst for the Guerbet reaction, medium calcination temperatures (400–500 °C) are required. Such temperatures increase the strength of the base sites of catalysts necessary for the realization of the key stage of the process—aldol condensation. Simultaneously, there is a decrease in the strength and concentration of acid sites responsible for the occurrence of a side reaction of ethanol dehydration to ethylene. Accordingly, both at higher and lower calcination temperatures, the deficient basicity leads to a decrease in the rate of aldol condensation, which appears
as an increase in selectivity for acetaldehyde over YSZ 300 and YSZ 900 samples. Moreover, an increase in the strength of acid sites favors a side reaction of the ethylene formation.

Thereby, YSZ catalysts with medium calcination temperatures demonstrate sufficiently higher n-butanol selectivity and yield than individual zirconia and other oxide systems, which have been studied in this reaction by various authors. Given a quite wide market availability and the developed technologies for this material production, yttrium-stabilized zirconium oxide can be considered as a promising high-efficiency catalyst for ethanol to n-butanol processing.

## 4. EXPERIMENTAL SECTION

### 4.1. Catalysts Preparation

YSZ samples, containing 3.4 mol % Y₂O₃ were synthesized by coprecipitation of corresponding hydroxides from nitrates with aqueous ammonia at pH 9 followed by the microwave drying at 2450 MHz frequency. The resulting solids were calcined in the temperature range from 300 to 900 °C. The YSZ samples were marked corresponding to the calcination temperature.

### 4.2. Structure Characterization

XRD patterns of the powder samples were obtained using a HZG-4C diffractometer with monochromatized Cu Kα radiation (graphite filter). Data were collected over a diffraction angle range 2θ = 10°–70° with a step size of 0.05° at a scanning speed of 0.2° min⁻¹. This 2θ range allows us to index a tetragonal and monoclinic modifications of YSZ. Qualitative phase analysis and cell parameters have been carried out via JCPDS-ICDD database, and FullProf program. A low-temperature nitrogen adsorption isotherms were obtained by the volumetric method using a sorptometer Kelvin 1042 (Costech Microanalytical) at temperature −196 °C. The specific surface areas S_{spec} of the catalysts were determined by nitrogen adsorption values at monomolecular layer distribution on the surface of the samples.

### 4.3. FTIR Study

The FTIR absorption spectra of the YSZ powders were recorded using the transmission mode on a PerkinElmer Spectrum One Fourier IR spectrometer with a spectral resolution of 2 cm⁻¹. Three milligrams of the sample was dispersed in 100 mg of KBr and pressed at ~7 ton cm⁻² into thin wafers with a density of 15 mg/cm². Prior to the studies, the samples were treated for 1 h by heating at 400 °C under vacuum (10⁻⁷ mm Hg). The FTIR spectra were recorded at room temperature and atmospheric pressure in the wavenumber range of 4000–400 cm⁻¹ with a resolution of 1 cm⁻¹ and accumulating 12 scans.

### 4.4. Acidity and Basicity Measurement

The acid–base properties of YSZ samples were studied by the method of QEMD of NH₃ (acidity) and CO₂ (basicity). Prior to adsorption, the samples were heated in vacuum at a temperature determined by their calcination, until a constant weight was reached. The adsorption of test substances was carried out at room temperature until no uptake was observed, and the surplus was removed under vacuum. The weight was recorded with the stepwise temperature increase and evacuation. The concentration of acid–base sites was determined by the amount of probe substance adsorbed on the sample at 50 °C.

### 4.5. Catalytic Experiments

Catalytic properties of YSZ samples were tested at 300 °C and atmospheric pressure. Samples with grains of 1–2 mm were loaded into the fixed-bed flow quartz reactor with an inner diameter of 4 mm. The temperature of the experiments was chosen as optimum based on the results of previous studies. Ethanol (azeotrope mixture with 4% of water) was introduced to the evaporator via a syringe infusion pump. Ar was used as a carrier gas at a flow rate of 0.17 cm³/s to achieve a weight hourly space velocity of the reagent WHSV = 0.2 h⁻¹. Before the catalytic tests, samples were treated for 1 h in an Ar flow at 200 °C and then cooled down to the experiment temperature. The reagents and reaction products were analyzed using a gas chromatograph (KristalLyuks 4000M, Metachrome) equipped with a TCD detector and a packed column (10% NiSO₄ on coal, 3 m x 3 mm) for CO and CO₂ and a FID detector and a capillary column (HP-FFAP, 50 m x 0.32 mm) for organic compounds.

Catalytic properties of YSZ compositions were characterized by EtOH conversion (X) and selectivity toward resulting products (Sᵢ).

\[
X \, (\%) = \frac{n_{\text{EtOH}}^0 - n_{\text{EtOH}}}{n_{\text{EtOH}}^0} \cdot 100
\]

\[
S_i \, (\%) = \frac{n_i}{n_{\text{EtOH}}^0 - n_{\text{EtOH}}} \cdot 100
\]

where \(n_{\text{EtOH}}^0\) is the initial amount of C moles of EtOH; \(n_{\text{EtOH}}\) and \(n_i\) are the amount of C moles of unreacted EtOH and product \(i\) in the stream of the reaction products, respectively.

The activity of catalysts in the n-butanol formation was characterized by the \(n\)-BuOH yield, \(Y_{\text{BuOH}}\) (%) and \(n\)-BuOH productivity, \(r_{\text{BuOH}}\) (mol/(g·h)).

### Table 5. Overview of the Heterogeneous Catalysts for the EtOH to n-BuOH Vapor Phase Guerbet Condensation in a Flow Reactor

| catalyst        | T (°C) | P (MPa) | WHSV (g mol⁻¹ h⁻¹) | conversion (%) | selectivity (%) | yield (%) | ref |
|-----------------|-------|--------|--------------------|----------------|----------------|-----------|-----|
| ZrO₂–CeO₂       | 300   | 0.1    | 1.97               | 9.9            | 19.9           | 2.0       | 21  |
| ZrO₂–CeO₂       | 300   | 0.1    | 13.3               | 13.3           | 31.6           | 4.2       | 21  |
| HAP (Sr/P = 1.70) | 300   | 0.1    | 11.3               | 11.3           | 86.4           | 9.7       | 47  |
| Mg₆Fe₂Al₅O₁₄     | 350   | 0.1    | 80.0               | 80.0           | 14.0           | 11.2      | 48  |
| HAP (Ca/P = 1.64) | 300   | 0.1    | 14.7               | 14.7           | 76.3           | 11.2      | 7   |
| Mg₆Al₅O₁₄        | 350   | 0.1    | 34.0               | 34.0           | 37.0           | 12.6      | 9   |
| YSZ 500         | 300   | 0.1    | 24.2               | 24.2           | 69.2           | 16.8      | our results |
| Cu/HSACeO₂       | 260   | 10     | 67.0               | 67.0           | 44.8           | 30.0      | 46  |

“GHSV—alcohols gas-hourly space velocity in std (25 °C, 101 kPa), inert gas excluded; WHSV—weight hourly space velocity is the weight of feed flowing per unit of weight of the catalyst per hour; LHSV—liquid hourly space velocity is the volume of the feed flowing per unit of volume of the catalyst per hour; W/F—the contact time is expressed as the ratio of catalyst weight to total flow rate.

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$Y_{\text{BuOH}} (%) = \frac{X - S_{\text{BuOH}}}{100}$

$r_{\text{BuOH}} = \frac{Y_{\text{BuOH}} \times WHSL}{M \times 3600 \times 10^{-3}}$

where $M$ is the molecular weight of butanol (74.12 g/mol).

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**Notes**

The authors declare no competing financial interest.

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