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Ethanol Conversion into 1,3-Butadiene by Lebedev Method over MTaSiBEA Zeolites (M= Ag, Cu, Zn)

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KEYWORDS: BEA zeolite, Tantalum, Copper, Silver, Zinc, Ethanol, 1,3-Butadiene

ABSTRACT:

Tantalum-containing SiBEA zeolite with isolated framework mononuclear Ta(V) doped with Ag, Cu and Zn were prepared and characterized by XRD, XPS, DR UV-VIS and FTIR (with pyridine, 2,6-di-tert-butylpyridine, pyrrole and deuterated chloroform). The conversion of ethanol as renewable raw material into 1,3-butadiene by Lebedev method over these zeolite catalysts was investigated.

The doping of TaSiBEA with Ag, Cu and Zn changes its catalytic properties in ethanol conversion into 1,3-butadiene as a result of modification of acid-base properties with formation

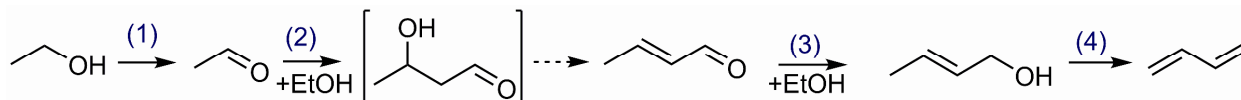
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3 of additional dehydrogenation sites. Such modification allows accelerating ethanol
4 dehydrogenation to acetaldehyde and subsequent steps of the ethanol-to-butadiene process.
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6 Ethanol conversion and butadiene selectivity over the catalysts increase in the order: TaSiBEA <
7
8 ZnTaSiBEA < AgTaSiBEA < CuTaSiBEA. Higher selectivity to butadiene (73 %) was achieved
9
10 over CuTaSiBEA (at 88% ethanol conversion, $T = 598 \text{ K}$, $\text{WHSV} = 0.5 \text{ h}^{-1}$).
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16 INTRODUCTION

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18 Production of chemicals from renewable raw materials, such as bio-ethanol obtained by
19 recycling of vegetable biomass, is a major focus in sustainable chemistry and technology.¹⁻³ The
20 interest of researchers is caused by the search for alternative non-fossil sources of hydrocarbons
21 and importance of CO_2 utilization. For example, straightforward calculations based on chemical
22 reactions show that 4 moles of CO_2 are recycled during biomass photosynthesis per 1 mole of
23 BD. Given the global demand for BD in 2015 (12 Mt)⁴, the replacement of petroleum-based
24 process by bio-ethanol one allows utilizing of 39 Mt of CO_2 per annum (details in the Supporting
25 Information).
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37 1,3-Butadiene (BD), the monomer of synthetic rubbers and polymers, is one of the most
38 important unsaturated hydrocarbons. There are two methods of BD production: Lebedev -
39 conversion of ethanol (EtOH) over one catalyst in one reactor, and Ostromisslensky - conversion
40 of a mixture of EtOH and acetaldehyde (AA), which is produced over a catalyst in the first
41 reactor and then converted to BD over another catalyst in the second reactor.⁵⁻⁷ These methods
42 are perspective for practical use as alternatives to BD production from petroleum.^{4,8,9}
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51 Analysis of economic and environmental aspects of realization of EtOH conversion into BD,
52 made by Cespi et al.⁴, indicates that Lebedev method is more perspective than Ostromisslensky
53 one.
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Scheme 1 shows an overall way of EtOH conversion into BD (Lebedev process)^{1,4,6}, including (1) AA formation from EtOH; (2) aldol condensation of AA to crotonaldehyde; (3) Meerwein–Ponndorf–Verley (MPV) reduction of crotonaldehyde with EtOH to crotyl alcohol and AA; and (4) dehydration of crotyl alcohol to 1,3-butadiene. BD selectivity of the process depends on the nature, strength and amount of acidic and basic sites on catalyst surface.^{10–12}



Scheme 1. Overall way of ethanol conversion into 1,3-butadiene by Lebedev method

Mixed acid-base binary oxide compositions, e.g. SiO₂ with MgO, ZrO₂ or Al₂O₃, modified with d-metal (Zn, Cu, Co, Mn, Fe, Ag) compounds, are traditional catalysts for Lebedev process.^{5,13–19}

It has been found recently,^{20–25} zeolite systems could be promising catalysts of the EtOH-to-BD process. Ivanova with colleagues²¹ have shown that material based on ZrBEA zeolite is more active in EtOH-to-BD process than Zr-loaded SiO₂ and ordered mesoporous silica because of higher amount of LAS on the catalyst surface. It should be pointed that catalysts based on ZrBEA prepared by the post-synthesis method of zirconium planting in the zeolite matrix have similar BD selectivity in EtOH conversion by Lebedev method as ZrBEA synthesized in a fluoride medium.²⁴

We have showed the conversion of EtOH and AA mixture into BD (Ostromisslensky process) proceeds with high selectivity (80 – 90 %) over tantalum-silicate zeolite (TaSiBEA) catalysts.²³ However, deficiency of active sites of EtOH dehydrogenation (step 1) may be the cause of observed low selectivity of BD formation in Lebedev process over TaSiBEA catalyst (12–29 %).

This work shows that high butadiene selectivity is achieved in ethanol conversion by Lebedev method over TaSiBEA zeolite modified with Ag, Cu and Zn. This approach allows combining

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2
3 the advantages of Lebedev (economic and environmental) and Ostromisslensky (high selectivity)
4 methods.
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9 EXPERIMENTAL DETAILS

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11 **Catalysts preparation.** TaSiBEA, AgTaSiBEA, CuTaSiBEA and ZnTaSiBEA zeolites were
12 prepared by two-step postsynthesis method developed earlier by Dzwigaj et al. for incorporation
13 of vanadium atoms into BEA zeolite.²⁶ It consists in dealumination of a tetraethylammonium
14 BEA (TEABEA) (Si/Al = 17) by treatment in a 13 mol · L⁻¹ HNO₃ solution at 353 K for 4 h with
15 subsequent introduction of tantalum in resulting SiBEA (with Si/Al ratio of 1300) by stirring for
16 3 h at 353 K in 200 ml of isopropanol solution containing 1.1 × 10⁻³ mol·L⁻¹ Ta(OC₂H₅)₅ (Acros
17 Organic, 99.99 %). The obtained suspension (pH = 6.8) was stirred in evaporator under vacuum
18 of a water pump in air at 353 K for 1 h until isopropanol was evaporated. The resulting solids,
19 washed three times in distilled water and dried in air at 353 K for 24 h, were finally calcined at
20 773 K in flowing air for 3 h. The sample is white and contain 1.0 wt % of Ta and is labeled as
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37 Then 2 g of TaSiBEA was stirred under aerobic condition for 2 h at 298 K in 200 ml of i)
38 aqueous AgNO₃ solution (pH = 3.7) with concentration of 0.6 × 10⁻³ mol·L⁻¹ to obtain
39 AgTaSiBEA zeolite with 1.0 wt % of Ag, ii) aqueous Cu(NO₃)₂ × 3H₂O solution (pH = 3.7) with
40 concentration of 0.8 × 10⁻³ mol·L⁻¹ to obtain CuTaSiBEA zeolite with 1.0 wt % of Cu, and iii)
41 aqueous Zn(NO₃)₂ × 6H₂O solution (pH = 3.5) with concentration of 0.7 × 10⁻³ mol·L⁻¹ to obtain
42 ZnTaSiBEA zeolite with 1.0 wt % of Zn and Ta. The obtained suspensions were stirred in
43 evaporator under vacuum of a water pump for 2 h in air at 353 K until the water was evaporated
44 and calcined at 773 K in flowing air for 3 h. The resulting solids containing 1.0 wt % of each
45 metal were labeled as AgTaSiBEA, CuTaSiBEA and ZnTaSiBEA.
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3 AgSiBEA sample with 1.0 wt % of Ag, prepared according to the procedure described
4 previously²⁷, was mixed with TaSiBEA sample to obtain the mechanical mixture of AgSiBEA
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8 and TaSiBEA with the ratio of Ag/Ta equivalent to that in AgTaSiBEA sample.
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10 **Catalysts characterization.** The chemical analysis of the samples was performed with
11 inductively coupled plasma atom emission spectroscopy at the CNRS Centre of Chemical
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15 Analysis (Vernaison, France).
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17 XRD patterns of the powder samples were recorded using D8 Advance (Bruker AXS GmbH,
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20 Germany) diffractometer with monochromatized Cu-K α radiation (nickel filter, $\lambda = 0.15418$ nm).
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22 Diffuse reflectance (DR) UV-VIS spectra were recorded at ambient atmosphere on a Cary
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25 5000 (Varian, USA) spectrometer equipped with a double integrator with polytetrafluoroethylene
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27 as reference.
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29 The XP spectra were taken using an Omicron (ESCA+) X-ray photoelectron spectrometer.
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32 The base pressure in the experimental chamber was in the low 10^{-9} mbar range. The spectra were
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35 collected using a monochromatic Al K α ($h\nu = 1486.6$ eV) X-ray source with an accelerating
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38 voltage of 14 kV and a current intensity of 20 mA. The pass energy was 20 eV for the high
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41 resolution spectra and 100 eV for the surveys. Surface charging effects were compensated by
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44 referencing the BE (binding energy) to the C 1s line of residual carbon set at 284.7 eV BE.
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46 TEM micrographs were obtained on TEM-125 K (SELM) microscope operating at 100 kV.
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49 For TEM measurements samples were dispersed in acetone with ultrasound and deposited on Cu
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52 grid covered with carbon. Interplanar d_{hkl} spacings calculated from the diffraction ring pattern
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55 were compared with the ASTM data.
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57 Analysis of acid-base properties of the zeolite catalysts was performed by adsorption of
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60 pyridine, 2,6-di-tert-butylpyridine (DTBP), pyrrole and deuterated chloroform (CDCl₃) followed
by infrared spectroscopy. FTIR spectra were recorded on a Spectrum One FTIR spectrometer

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3 (Perkin Elmer, USA) accumulating 48 scans at a spectral resolution of 1 cm^{-1} . The samples after
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5 catalytic tests were pressed at $\sim 2 \text{ ton} \cdot \text{cm}^{-2}$ into thin wafers of ca. $12 \text{ mg} \cdot \text{cm}^{-2}$, and placed
6
7 inside IR cells. Before adsorption of pyridine, DTBP and pyrrole, the IR cell was connected to a
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9 vacuum-adsorption apparatus allowing a residual pressure below 10^{-3} Pa and the samples were
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11 outgassed at 673 K for 1 h. The spectra were recorded under ambient conditions after pyridine
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13 desorption at 423 and 523 K, after DTBP desorption at 353, 423 and 523 K and after pyrrole
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15 desorption at 338 K. Before adsorption of CDCl_3 the catalyst-containing IR cell was heated in a
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17 constant Ar flow ($\sim 60 \text{ mL} \cdot \text{min}^{-1}$). Once 723 K was reached, treatment lasted 1 h. Then, the
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19 samples were cooled to 323 K, and baselines were recorded. To carry the probe molecule to the
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21 IR cell Ar was passed through the CDCl_3 -containing gas bubbler for 30 min. After that, Ar was
22
23 passed through the IR cell for 30 min to avoid physical adsorbed CDCl_3 . The spectra of adsorbed
24
25 CDCl_3 were recorded. All measured spectra were recalculated to a “normalized” wafer weight.
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27 The height of each peak above the baseline was extracted from the experimental raw data.
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34 **Catalytic activity measurement.** Catalytic activity tests were carried out in a fixed-bed
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36 flow quartz reactor with inner diameter of 4 mm at 598–673 K and atmospheric pressure.
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38 Samples with grains of 0.25–0.5 mm were loaded into the reactor (0.25 g for TaSiBEA and
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40 MTaSiBEA, 0.5 g for the mixture of AgSiBEA and TaSiBEA). Argon was used as the carrier
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42 gas ($5\text{--}15 \text{ mL} \cdot \text{min}^{-1}$). Before the reaction samples were heated to 673 K under flowing argon,
43
44 and treatment lasted 1 h. EtOH were fed into the catalytic reactor by passing argon through
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46 temperature controlled bubbler (314 K) with 95% alcohol. Weight hourly space velocity
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48 (WHSV) was $0.5\text{--}1.5 \text{ g}_{\text{EtOH}} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$. The reagent and reaction products were analyzed on a gas
49
50 chromatograph (KristalLyuks 4000M, MetaChrome) equipped with a TCD detector and a packed
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52 column (10 % NiSO_4 on coal, $3 \text{ m} \times 3 \text{ mm}$) for CO, CO_2 , and a FID detector and a capillary
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54 column (HP-FFAP, $50 \text{ m} \times 0.32 \text{ mm}$) for organic compounds. Carbon balance was calculated as
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total carbon amount in the analyzed products, divided by the initial total amount of carbon, and it was generally higher than 95 %.

Catalytic activity was characterized by the conversion of EtOH (X), selectivity to products (S_i), BD yield (Y_{BD}) and BD productivity (P_{BD}):

$$X = \frac{n_{\text{EtOH}}^0 - n_{\text{EtOH}}}{n_{\text{EtOH}}^0} \cdot 100\%,$$

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

$$Y_{BD} = \frac{X \cdot S_{BD}}{100\%},$$

$$P_{BD} = \frac{Y_{BD} \cdot \text{WHSV} \cdot 0.587}{100\%},$$

where n_{EtOH}^0 is the initial amount of C moles of EtOH; n_{EtOH} and n_i are the amount of C moles of unreacted EtOH and product i in the stream of the reaction products, respectively; **0.587** is the maximum possible amount of BD (g) that can be produced from 1 g of EtOH.

Since the EtOH to BD process is characterized by carbonization and deposition of various polymerization products, a regeneration of catalyst was required after each operation cycle. The regeneration was carried out by heating the catalysts in an oxygen-containing flow (5 % O₂ in Ar, 30 ml/min) to 773 K, and treatment lasted 2 h. For each catalyst sample several cycles of catalysis were carried out, the original (initial) catalyst activity is restored after regeneration.

RESULTS AND DISCUSSION

Characterization of MTaSiBEA zeolites by XRD, DR UV-VIS and XPS. X-ray diffraction (XRD) patterns of as-prepared SiBEA, TaSiBEA and MTaSiBEA (M = Ag, Cu, Zn) (Fig. 1) are typical of BEA zeolite. It suggests that the doping of TaSiBEA with Ag, Cu and Zn does not significantly affect the zeolite crystallinity. The large increase of d_{302} spacing, calculated from

the corresponding 2θ value, from 3.920 Å (SiBEA; $2\theta = 22.68^\circ$) to 3.948 Å (TaSiBEA; $2\theta = 22.51^\circ$) is related to incorporation of tantalum into SiBEA. The zeolite matrix expansion occurs due to longer Ta–O bond length (1.90 Å for mononuclear Ta(V) species in BEA zeolite²⁸) than Si–O (1.60–1.65 Å in zeolites).²⁹ In the case of MTaSiBEA d_{302} spacing is changed from 3.920 Å (SiBEA; $2\theta = 22.68^\circ$) to 3.960 Å (AgTaSiBEA; $2\theta = 22.38^\circ$) and to 3.931 Å (CuTaSiBEA and ZnTaSiBEA; $2\theta = 22.61^\circ$), showing zeolites matrix expansion, in line with our earlier report.^{27,30–32}

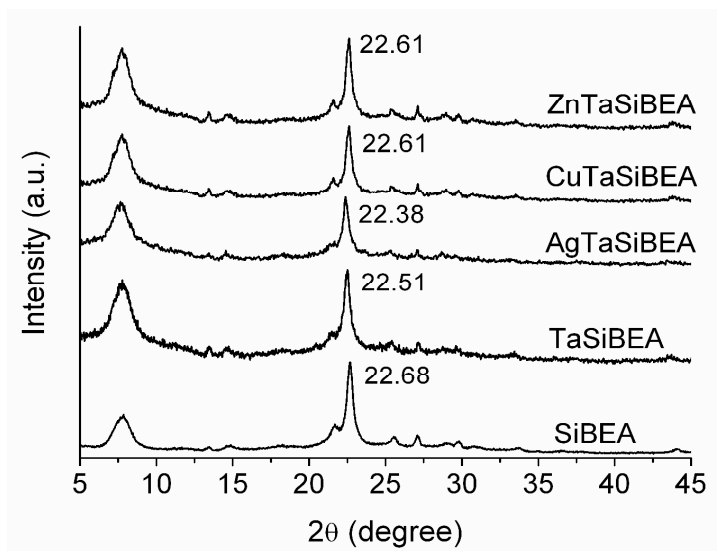


Figure 1. XRD patterns of as-prepared TaSiBEA, AgTaSiBEA, CuTaSiBEA and ZnTaSiBEA zeolites recorded at room temperature and ambient atmosphere.

DR UV-VIS spectra of SiBEA, TaSiBEA and MTaSiBEA zeolites after catalytic tests are shown in Fig. 2. The energy of oxygen-to-metal charge transfer (CT) which depends on the number oxygen atoms surrounding of the metal ion can be used to evaluate the coordination of tantalum, silver, copper and zinc in the samples.

In the spectrum of SiBEA absorption band at 208 nm are probably related to CT transitions in the BEA framework. For TaSiBEA the high-energy ligand-to-metal CT transition is centered at 216 nm, indicating the presence of mononuclear Ta(V) in the zeolite matrix.^{28,33,34}

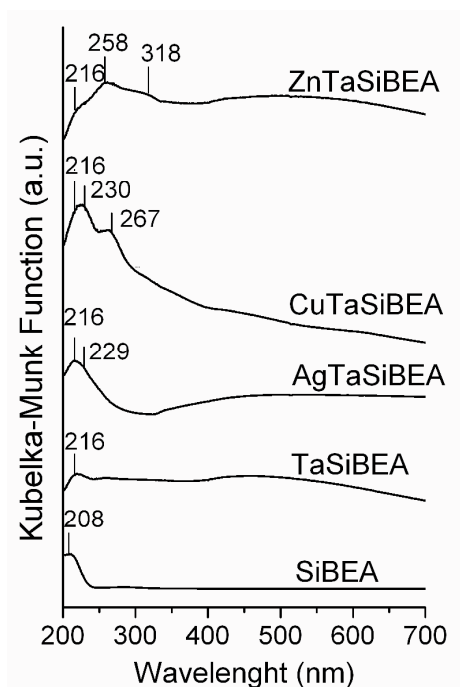


Figure 2. DR UV–VIS spectra of SiBEA, TaSiBEA, AgTaSiBEA, CuTaSiBEA and ZnTaSiBEA zeolites after catalytic tests recorded at room temperature and ambient atmosphere.

In the spectrum of AgTaSiBEA the bands at 216 and 229 nm are attributed to CT between $4d^{10}$ and $4d^95s^1$ levels of Ag(I) species and oxidized silver clusters ($Ag_n^{\delta+}$, where $n \leq 10$), respectively.^{27,35,36} Charge transfer in large Ag clusters or nanoparticles induces appearance of bands at higher wavelengths (above 350 nm), as was shown for Ag-MFI, Ag-BEA, Ag-MOR.³⁷ The absence of these bands suggests that these Ag species are not present in AgTaSiBEA. The band at 216 nm is more intensive on AgTaSiBEA spectrum compared to TaSiBEA, suggesting the superposition of the bands related to the presence of both isolated mononuclear Ta(V) and Ag(I) species.

In the spectrum of CuTaSiBEA the bands at the range of 216–267 nm could be attributed to CT transitions between O^{2-} and isolated mononuclear Ta^{5+} and Cu^{2+} species and oxidized copper clusters.^{28,30,31,33,34} The absence of the bands in the range of 300–600 nm (Fig. 2) assigned to the

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3 $O^{2-} \rightarrow Cu^{2+}$ CT and/or d-d transitions of octacoordinated Cu(II) indicates the absence of any bulk
4 metal oxides on the surface of CuTaSiBEA.³⁸
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8 The appearance of absorption bands below 230 nm are generally considered as the
9 distinguishing proof of zinc atoms incorporation into zeolite framework by isomorphous
10 substitution, in agreement with earlier report.³⁹ Pure ZnO gives broad adsorption band at about
11 360 nm, assigned to the $O^{2-} \rightarrow Zn^{2+}$ CT transition between oxygen and zinc in oxide.⁴⁰ The
12 bands in the range of 216-360 nm on the spectrum of ZnTaSiBEA (Fig. 2) are attributed to
13 mononuclear Ta(V) species (216 nm)^{28,33,34}, isolated mononuclear framework Zn(II) (258 nm)³⁹
14 and polynuclear zinc oxide present in the extra-framework position (318 nm).⁴⁰
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24 XPS was used to determine the valence state of tantalum, silver, copper, and zinc in
25 MTaSiBEA catalysts before and after catalytic tests. The results of curve-fitting of the obtained
26 XP spectra are presented in Table 1 (the XP spectra are shown on Figs S1-S3).
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31 The XP spectra of MTaSiBEA (Figs S1a, S2a and S3a) in the Ta $4f_{5/2}$ and $4f_{7/2}$ range show
32 two intensive signals at about 29.1-29.2 and 24.8-25.2 eV, respectively, characteristic of Ta(V)
33 species well dispersed in zeolite matrix.⁴¹ Fig. S1b shows the Ag $3d_{3/2}$ (374.6 eV) and $3d_{5/2}$
34 (368.65 eV) bands, indicating that Ag^+ and $Ag_n^{\delta+}$ are main silver species in AgTaSiBEA.^{42,43} In
35 the case of CuTaSiBEA (Fig. S2b), the bands at 953.3 eV in the $2p_{1/2}$ range and 933.3 eV in the
36 $2p_{3/2}$ range are characteristic of well dispersed Cu(II) strongly interacting with BEA zeolite
37 matrix.^{31,44}
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48 Two intensive bands at 1045.5 eV and 1022.5 eV were observed on the XP spectrum of
49 ZnTaSiBEA in the Zn $2p_{1/2}$ and Zn $2p_{3/2}$ ranges (Fig. S3b), which may be attributed to dispersed
50 Zn(II) species present in the zeolite structure.⁴⁵ The BE of the peak in the Zn $2p_{3/2}$ range of
51 1022.5 eV strongly suggest that zinc is present in ZnTaSiBEA in the framework position, in
52 agreement with earlier report on framework zinc substituted zeolites.⁴⁶
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BEs of Ta 4f_{5/2} and 4f_{7/2}, Ag 3d_{3/2} and 3d_{5/2}, Cu 2p_{1/2} and 2p_{3/2}, Zn 2p_{1/2} and Zn 2p_{3/2} for spent-MTaSiBEA differ slightly (max 0.3 eV) from fresh samples (Table 1). Insignificant changes of valence state of tantalum, silver, copper and zinc in the catalysts suggest the stability of Ta(IV), Ag(I), Cu(II) and Zn(II) species in MTaSiBEA framework after EtOH-to-BD catalytic runs.

Table 1. XPS results for MTaSiBEA zeolites

Catalysts	Binding energy (eV)			
<i>AgTaSiBEA</i>	<i>Ag 3d_{3/2}</i>	<i>Ag 3d_{5/2}</i>	<i>Ta 4f_{5/2}</i>	<i>Ta 4f_{7/2}</i>
fresh	374.6	368.6	29.2	25.2
spent	374.5	368.5	29.0	24.9
<i>CuTaSiBEA</i>	<i>Cu 2p_{1/2}</i>	<i>Cu 2p_{3/2}</i>	<i>Ta 4f_{5/2}</i>	<i>Ta 4f_{7/2}</i>
fresh	953.3	933.5	29.1	24.8
spent	953.1	933.3	28.9	24.7
<i>ZnTaSiBEA</i>	<i>Zn 2p_{1/2}</i>	<i>Zn 2p_{3/2}</i>	<i>Ta 4f_{5/2}</i>	<i>Ta 4f_{7/2}</i>
fresh	1045.5	1022.5	29.2	25.0
spent	1045.5	1022.4	29.0	24.9

Under reaction conditions (603 K, presence of H₂, EtOH, AA) reduction of extra-framework oxidized species might have been expected.^{27,47} However, XPS and DR-UV-VIS results for spent-samples demonstrate the presence of highly dispersed mononuclear Ta(V), Ag(I), Cu(II) and Zn(II). Apparently, these species are easily oxidized in air at ambient conditions during the replacement into XPS/DR-UV-VIS chambers and/or species strongly bonded or incorporated in the framework are not reduced in the reaction conditions. Moreover, reduction of zinc oxide occurs at temperatures above 823 K.⁴⁸

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3 On the TEM images of MTaSiBEA calcined at 773 K (Supporting Information, Fig. S4) no
4 bulk metal oxides and/or metal particles of tantalum, silver, copper and zinc are seen. No clear
5 ring diffraction patterns of tantalum, silver, copper and zinc are visible which may indicate high
6 dispersion of tantalum, silver, copper and zinc in the zeolites. The interplanar d_{hkl} spacings for
7 the most contrast electron diffraction rings are equal to 3.948 Å for TaSiBEA, 3.960 Å for
8 AgTaSiBEA and 3.931 Å for CuTaSiBEA and ZnTaSiBEA can be attributed to the (302) plane
9 BEA zeolite that consist with the XRD results.

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11 Thus, using the SiBEA zeolite as carrier allows stabilization of the tantalum, silver, copper and
12 zinc as highly dispersed mononuclear Ta(V), Ag(I), Cu(II), and Zn(II) species.

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14 **FTIR characterization of acid-base sites by pyridine, DTBP, pyrrole and CDCl_3**
15 **adsorption.** FTIR spectra of pyridine adsorbed on TaSiBEA and MTaSiBEA are presented in
16 Fig. 3. The bands at 1611-1613, 1599-1600 and 1446-1454 cm^{-1} correspond to pyridine
17 interacting with Lewis acidic sites (LAS), formed by incorporated metal ions, in line with earlier
18 data for tantalum,^{28,34,49} silver²⁷ and copper³⁰ in SiBEA, and zinc in MFI.^{40,50} The intensity of
19 these bands for SiBEA²⁷ is much lower. Thus, additional LAS are formed upon incorporation of
20 Ta, Ag, Cu and Zn ions in the zeolite framework.

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22 In Cu- and Zn-containing zeolites spectra bands of adsorbed pyridine are more intensive than
23 for Ag-containing (at 523 and 623 K), which may indicate formation of higher amount of strong
24 LAS after copper and zinc incorporation.

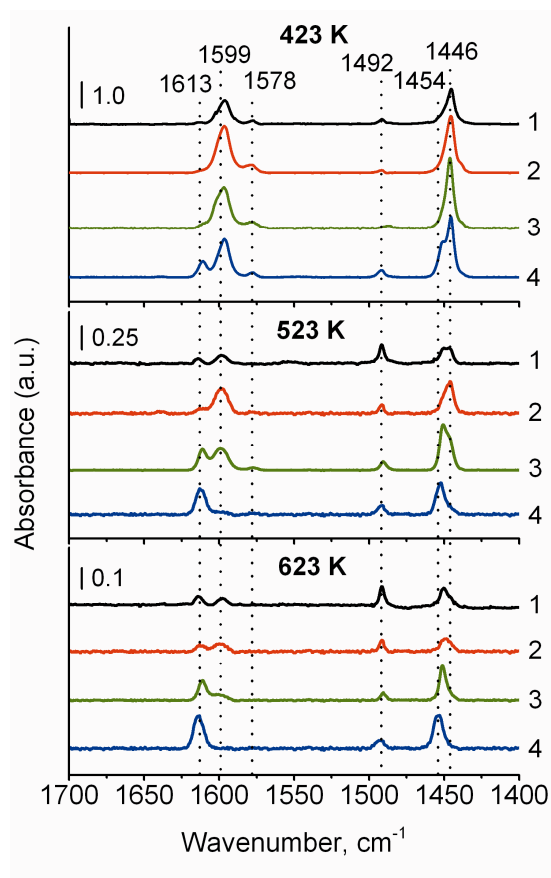


Figure 3. FTIR spectra of adsorbed pyridine on as-prepared TaSiBEA (1), AgTaSiBEA (2), CuTaSiBEA (3) and ZnTaSiBEA (4) catalysts after desorption at different temperatures.

Bands of pyridinium ions formed on Brønsted acidic sites (BAS) were not observed (1638 and 1545 cm^{-1}). Therefore, DTBP as stronger base than pyridine has been used to establish presence of weak BAS (Fig. 4). The bands at 1614 and 1530 cm^{-1} are assigned to protonated DTBP adsorbed on BAS.^{34,51,52} The intensity of these bands is slightly higher for ZnTaSiBEA than for TaSiBEA indicating higher amount of BAS.

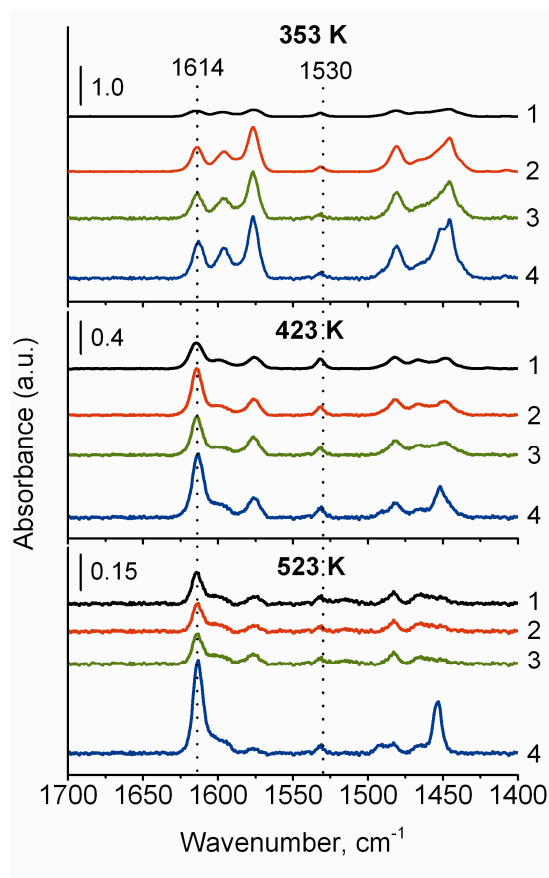


Figure 4. FTIR spectra of adsorbed DTBP on as-prepared TaSiBEA (1), AgTaSiBEA (2), CuTaSiBEA (3) and ZnTaSiBEA (4) catalysts after desorption at different temperatures.

Pyrrole and CDCl_3 were used as probe molecules for identification of basic sites on the surface of TaSiBEA, AgTaSiBEA, CuTaSiBEA and ZnTaSiBEA zeolites (Fig. 5). The bands at 1534, 1470, 1420 and 1379 cm^{-1} are attributed to pyrrole ring-stretching vibrations, in line with earlier reports.^{53,54} The band at 3545 cm^{-1} corresponding to strongly perturbed OH vibrations of pyrrole, as well as bands at 3480 cm^{-1} combined with 1490 cm^{-1} indicates the presence of pyrrole species adsorbed on acidic sites.^{53,54} The intensity of the band at 3480 cm^{-1} is high for CuTaSiBEA and ZnTaSiBEA. It is likely that copper- and zinc-containing acidic sites are stronger, in line with the FTIR data with pyridine adsorption (Fig. 3). The shoulder at 3390 cm^{-1} in the spectra of

TaSiBEA and MTaSiBEA zeolites indicates the presence of weak basic sites, in line with previous report.⁵³

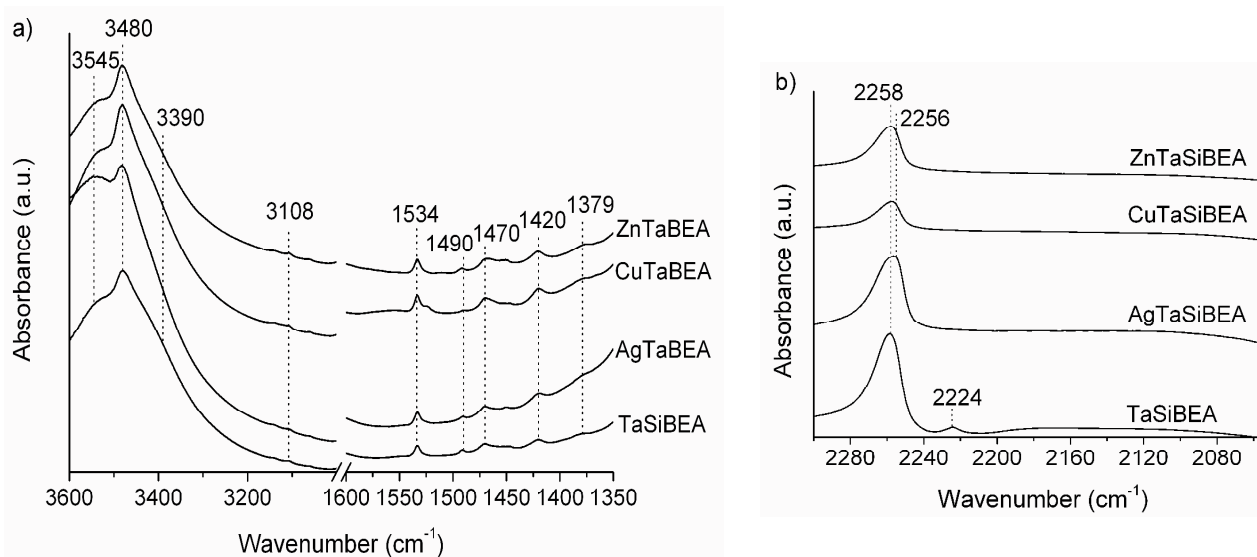


Figure 5. FTIR spectra of adsorbed pyrrole after desorption at 338 K (a) and adsorbed CDCl₃ after desorption at 323 K (b) on as-prepared TaSiBEA and MTaSiBEA catalysts.

FTIR spectra of CDCl₃ adsorbed on TaSiBEA and MTaSiBEA are presented in Fig. 5-b. The bands at 2558 and 2224 cm⁻¹ in the spectra of TaSiBEA are attributed to weak and medium basic sites.⁵⁵ In the spectra of the MTaSiBEA samples only one band at 2256 cm⁻¹ is present. It suggests that incorporation of Ag, Cu or Zn into TaSiBEA leads to elimination of medium basic sites and simultaneous decreasing of the number of weak basic sites. The similar phenomenon was earlier observed for CuO/SiO₂-MgO system.⁵⁵ Intensity of the band at 2258–2256 cm⁻¹ depends on the kind of the metal introduced in the TaSiBEA zeolite. This band is less intense on the spectra of CuTaSiBEA and ZnTaSiBEA indicating the lower number of weak basic sites for CuTaSiBEA and ZnTaSiBEA. These data falls into line the results of FTIR spectroscopy of adsorbed pyridine and pyrrole.

Thus, the TaSiBEA and MTaSiBEA zeolites possess weak Brønsted acidic, Lewis acidic and basic sites, formed by incorporation of Ta, Ag, Cu and Zn into framework of BEA zeolite.²³

Catalytic properties of MTaSiBEA zeolites. The main products of ethanol conversion on TaSiBEA and MTaSiBEA are BD, AA, ethylene and diethyl ether (DEE) (Table 2). The formation of propylene, ethylene, ethyl acetate and other products are also observed (Table S1 in Supplementary materials). EtOH conversion over TaSiBEA does not exceed 13.3 %, and BD selectivity – 16.4 %.²³ The introduction of Ag, Cu and Zn in TaSiBEA zeolite entails substantial increase in EtOH conversion and selectivity to BD. The highest values are observed over CuTaSiBEA with EtOH conversion of 87.9 and BD selectivity of 72.6 %.

The selectivity of EtOH conversion into BD in the presence of AgTaSiBEA (Table 2) is relatively high (62.6 %). It is comparable to the value observed in the presence of Ag/ZrBEA catalysts prepared by direct and postsynthetic methods.^{21,24} However, significant amount of unreacted AA remains among the reaction products, probably, because of insufficient number of acidic and basic sites with strength required for accelerate AA conversion through aldol condensation (step 2 in Scheme 1).

Table 2. Catalytic performance of TaSiBEA and MTaSiBEA zeolites in EtOH conversion^a

Catalysts	EtOH conversion (%)	Product selectivity (C mol%)						BD yield (C mol%)
		BD	AA	croton aldehyde	ethylene	diethyl ether	other	
TaSiBEA ^b	13.3	16.4	33.0	0.1	28.3	20.8	1.4	2.2
AgTaSiBEA	82.9	62.6	23.9	0.4	7.6	0.9	4.6	51.9
CuTaSiBEA	87.9	72.6	15.0	0.2	2.7	1.0	8.5	63.8
ZnTaSiBEA	51.7	42.8	22.7	0.2	17.1	13.0	4.2	22.1
AgSiBEA+ TaSiBEA	58.3	46.0	16.2	0.1	11.9	22.1	3.7	26.8

^a T = 598 K, WHSV = 0.5 g_{EtOH}·g_{cat}⁻¹·h⁻¹, time-on-stream = 3.5 h, ^b the data of report²³

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3 It should be mentioned that in the presence of AgSiBEA catalyst (obtained by the method
4 described in earlier report²⁷) EtOH conversion proceeds with predominantly formation of AA
5 (97 % selectivity). Over mechanical mixture of AgSiBEA + TaSiBEA 46 % selectivity to BD
6 was achieved. The much higher value of selectivity to BD in the presence of AgTaSiBEA
7 catalyst than for mixture of AgSiBEA + TaSiBEA may be caused by proximity localization of
8 the active sites of EtOH dehydrogenation (step 1) and the subsequent steps (2–4).
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17 In the presence of ZnTaSiBEA 51.7 % EtOH conversion occurs with 42.8 % BD selectivity
18 (Table 2). The significant amount of ethylene and DEE was observed in the reaction products
19 (total selectivity of 30 %). This phenomenon may be caused by higher number of BAS and LAS
20 (Figs. 3 and 4), accelerating side reaction of EtOH dehydration.
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27 Let us consider the origin of different effect of the dopants (Ag, Cu, Zn) on the activity and
28 selectivity of TaSiBEA. The main role of Ag, Cu and Zn in the MTaSiBEA catalysts consists in
29 the formation of sites of EtOH dehydrogenation and modification of acid-base characteristics of
30 the zeolites. The mechanism of alcohol dehydrogenation over silica- and alumina-supported
31 silver catalysts includes: 1) the activation of ethanol with formation of hydrogen-bonded surface
32 complex on silica/alumina surface, 2) C—H bond cleavage on Ag sites and proton abstraction on
33 silica/alumina acid-base sites (rate-determining step), and 3) desorption of H₂ and acetaldehyde,
34 with regeneration of the active sites.^{56,57} Acid-base properties of the support and nature of silver
35 species affect the dehydrogenation process.^{56,57}
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48 As was previously shown over Ag/SiO₂ and Cu/SiO₂ EtOH is mainly converted to AA,²² and
49 over ZnO/SiO₂ – to ethylene with selectivity of 35 %.¹⁸ The rate of ethanol dehydrogenation in
50 the presence of Cu species is higher than on ZnO,⁵⁸ because dehydrogenation pathways over
51 metallic copper and zinc oxide are different. Moreover, probability of ethanol dehydration to
52 ethylene over ZnO is higher than over Cu species.⁵⁹ Apparently, appropriate ratio of acid-base
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3 and redox characteristics of the catalyst is achieved by the doping of TaSiBEA with copper, and,
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5 thereby, higher yield of BD is achieved over CuTaSiBEA.
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8 We have previously shown that high BD selectivity is maintained after repeated operation
9 cycles on TaSiBEA.²³ EtOH conversion, BD yield and selectivity to products as a function of
10 time-on-stream for MTaSiBEA catalysts are presented in Fig. 6. The values of EtOH conversion
11 and BD yield noticeably reduce with time in the presence of MTaSiBEA catalysts. Higher
12 stability in time of the EtOH conversion, selectivity and yield of BD are observed in the case of
13 CuTaSiBEA catalyst among the studied samples (Fig. 6). It seems that the active sites formed
14 upon the doping of TaSiBEA with copper are more stable in the process of EtOH conversion into
15 BD. The similar results were observed in the EtOH-to-AA process over the Ag/SiO₂ and
16 Cu/SiO₂ catalysts.²² Stable performance of the copper-containing catalyst in this process was
17 also demonstrated in the earlier report.⁶⁰
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31 Tables 3 and Fig. 7 summarize the effect of WHSV on EtOH conversion over CuTaSiBEA.
32 Increasing of WHSV results in substantial decrease in EtOH conversion, selectivity to BD, and,
33 as a result, BD productivity in the process. Moreover, the amount of unreacted AA as well as
34 EtOH dehydration products (ethylene and DEE) increases significantly (side products are shown
35 in Table S2). Similar dependence of selectivity to products in EtOH conversion on the contact
36 time was observed for others catalytic systems.^{13,61,62}
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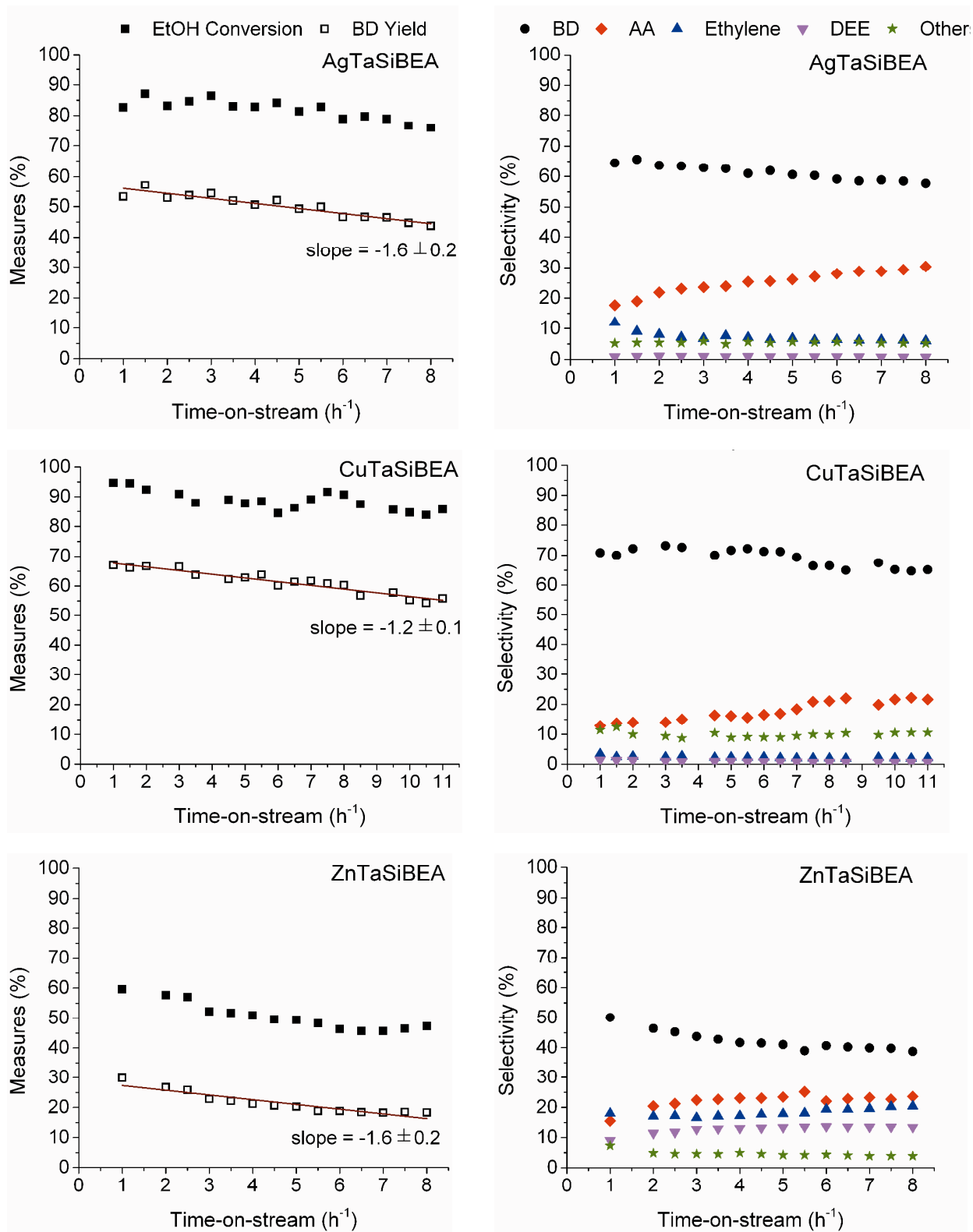


Figure 6. EtOH conversion, BD yield and selectivity to products over MTaSiBEA catalysts as function of time-on-stream ($T = 598 \text{ K}$, $\text{WHSV} = 0.5 \text{ g}_{\text{EtOH}} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$).

Table 3. Effect of WHSV on EtOH conversion over CuTaSiBEA catalyst^a

WHSV ($\text{g}_{\text{EtOH}} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$)	EtOH conversion (%)	Product selectivity (C mol%)						BD yield (C mol %)	BD productivity ($\text{g}_{\text{BD}} \text{g}_{\text{cat}}^{-1} \text{h}^{-1}$)
		BD	AA	croton aldehyde	ethylene	diethyl ether	other		
0.5	87.9	72.6	15.0	0.2	2.7	1.0	8.5	63.8	0.19
1	52.1	52.5	23.4	0.3	6.4	9.8	7.6	27.4	0.16
1.5	30.1	44.8	28.8	0.1	12	8.4	5.9	13.5	0.12

^a T = 598 K, time-on-stream = 3.5 h.

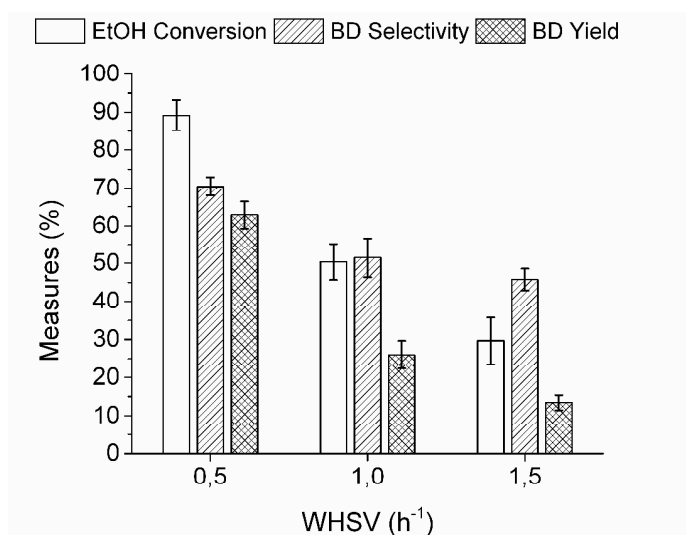


Figure 7. EtOH conversion, BD selectivity and yield over CuTaSiBEA catalyst as function of WHSV (T = 598 K). The bars represent average measures for range of 1–9 h time-on-stream.

Raise of the reaction temperature from 598 to 673 K significantly increases EtOH conversion from 30 to 65 % (Fig. 8), but selectivity to desired product (BD) is markedly reduced from 45 to 27 %. Thus, the high selectivity and yield of BD over MTaSiBEA are achieved only under definite range of parameters for process proceeding.

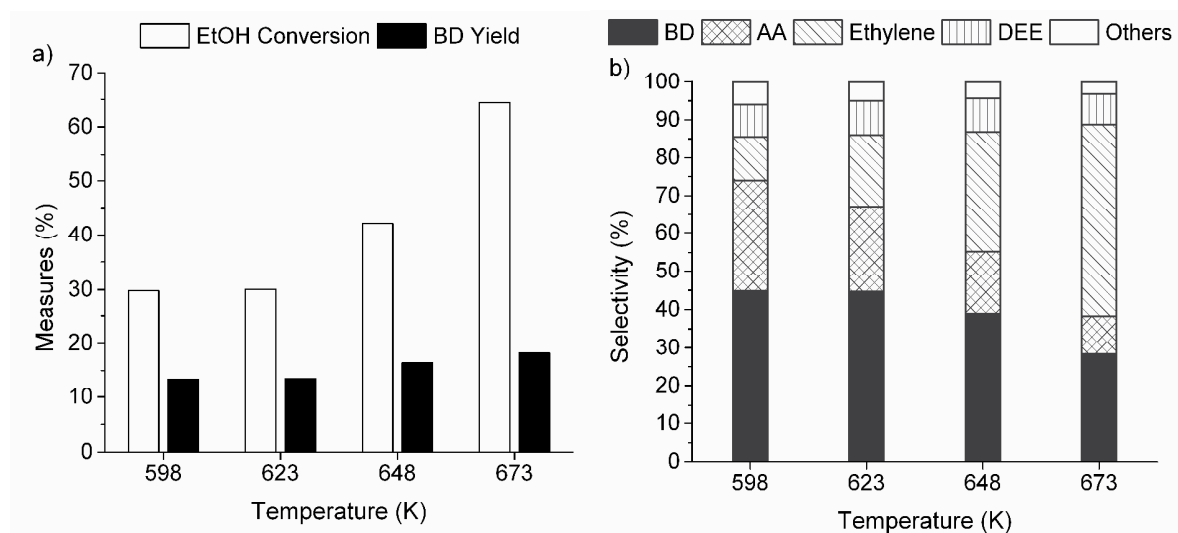


Figure 8. EtOH conversion, BD yield (a) and product selectivities (b) over CuTaSiBEA as function of temperature (WHSV=1.5 $\text{g}_{\text{EtOH}}\cdot\text{g}_{\text{cat}}^{-1}\cdot\text{h}^{-1}$).

CONCLUSIONS

The doping of tantalum-siliceous zeolite (TaSiBEA) with Ag, Cu and Zn changes its catalytic properties in ethanol conversion into 1,3-butadiene by Lebedev method as a result of modification of acid-base properties with formation of additional dehydrogenation sites.

Such modification allows accelerating ethanol dehydrogenation to acetaldehyde and subsequent steps of the ethanol-to-butadiene process.

Ethanol conversion and butadiene selectivity over MTaSiBEA increase in the order: TaSiBEA < ZnTaSiBEA < AgTaSiBEA < CuTaSiBEA.

Higher selectivity to BD (73 %) was achieved over CuTaSiBEA (at 88% ethanol conversion, T = 598 K, WHSV = 0.5 h^{-1}), suggesting that this zeolite material could be a promising catalyst for Lebedev process.

ASSOCIATED CONTENT

Supporting Information. The details of the calculations of the amount of recycled CO₂ in 1,3-butadiene production from biomass, XP spectra, TEM images and diffraction patterns, additional catalytic results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Ethanol Conversion into 1,3-Butadiene by Lebedev

Method over MTaSiBEA Zeolites (M= Ag, Cu, Zn)

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Synopsis

Doping of TaSiBEA with Ag, Cu or Zn allows increasing selectivity of the bioethanol-to-butadiene process through proceeding easier ethanol dehydrogenation.

