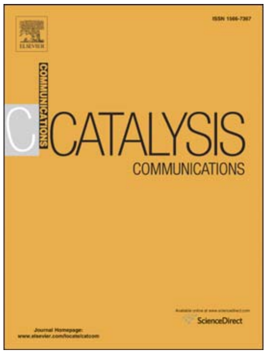

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High selectivity of TaSiBEA zeolite catalysts in 1,3-butadiene production from ethanol and acetaldehyde mixture

Pavlo I. Kyriienko[a,]*, Olga V. Larina[a], Sergiy O. Soloviev[a],
Svitlana M. Orlyk[a], Stanislaw Dzwigaj[b,c,]*

[a] L.V.Pisarzhevsky Institute of Physical Chemistry of the NAS of Ukraine,
31 Prosp. Nauky, 03028 Kyiv, Ukraine

[b] Sorbonne Universités, UPMC Univ Paris 06, UMR 7197, Laboratoire de Réactivité de Surface,
F-75005, Paris, France

[c] CNRS, UMR 7197, Laboratoire de Réactivité de Surface, F-75005, Paris, France

Figures: 4

Scheme: 1

Tables: 2

Keywords: tantalum, BEA, ethanol, 1,3-butadiene, catalysis

* Corresponding authors:

P.I. Kyriienko, E-mail address: pavlo_kyriienko@ukr.net, fax: +38 (044) 525 65 90.

S. Dzwigaj, E-mail address: stanislaw.dzwigaj@upmc.fr, fax: +33 01 44 27 60 33.

Abstract

New tantalum-silica based zeolite catalysts (TaSiBEA) were applied in this work for 1,3-butadiene production from ethanol. Tantalum incorporation into vacant T-atom sites of the SiBEA zeolites framework as mononuclear Ta(V) allowed preparing highly selective catalysts for ethanol/acetaldehyde mixture conversion into 1,3-butadiene, with selectivity to 1,3-butadiene of 80–90% at total conversion of the mixture of 45–30%. Effect of Ta content on activity of TaSiBEA zeolite catalysts and the ethanol/acetaldehyde molar ratio in selective production of 1,3-butadiene were demonstrated.

1. Introduction

1,3-Butadiene (BD) is the most important conjugated diene, being the basis of a variety of synthetic polymers [1–3]. BD can be produced from ethanol (EtOH) in two ways. In one-step process, using a variety of mixed metal oxide catalysts (ZnO-Al_2O_3, (ZnO, CuO)/MgO-SiO_2, etc.) [4–11], and in two-step process, using Ta_2O_5-silica [12–14] as well as ZrO_2-silica [15,16] catalysts in EtOH and acetaldehyde (AA) mixture conversion.

Scheme 1 shows an overall scheme of EtOH conversion into BD [1–3]. It involves multiple consecutive steps: (1) dehydrogenation; (2) aldol condensation; (3) crotonic condensation; (4) Meerwein–Ponndorf–Verley (MPV) reduction; and (5) dehydration. The key steps of the process are (2) [15] and (4) [4].

Angelici et al. [17] showed that the best MgO-SiO_2 catalyst for the one-step process is material composed of small amount of strong basic sites and higher amount of acidic and weak basic sites. It is well known that EtOH is preferably converted into 1-butanol on magnesium oxide with strong basic sites [18]. According to the works [16,19,20], the activity of zirconium-silica catalysts in EtOH to BD process is related to Lewis acidic sites (LAS). Obviously, the subtle ratio in acidic-basic sites of the catalysts is required to produce selectively BD from EtOH.

It was recently reported [19] that material based on ZrBEA zeolite is more active in EtOH to BD process than Zr-loaded SiO_2 and ordered mesoporous silica, probably because of higher amount of LAS on the catalyst surface. Ta/SBA-15 and Ta/KIT-6 show higher selectivity in transformation of EtOH and AA mixture into BD than Ta-containing conventional silica based catalysts and greatly improves efficiency of the process [13]. Thus, these literature results indicate that investigation of Ta-zeolite materials as catalysts for EtOH (or EtOH/AA mixture) conversion into BD seems to be very interesting. As shown earlier [21,22], TaSiBEA with isolated mononuclear Ta(V) possesses Lewis acidic-basic pairs which are required for both processes.

In this paper we report the remarkable selectivity achieved in production of BD from EtOH and AA over TaSiBEA zeolite catalysts with isolated mononuclear Ta(V). To the best of our knowledge, this is the first time that such catalytic properties of Ta-zeolite catalysts in this process have been reported.

2. Experimental

TaSiBEA zeolites were prepared by two-step postsynthesis method described earlier [21,22]. The method has allowed obtaining Ta(V)-single site BEA zeolite, as evidenced by XRD, FTIR and DR UV-vis (see Supplementary material (SM), section 2 and Figs. S1-S3). Analysis of acidic-basic properties of the zeolite catalysts was performed by adsorption of pyridine, pyrrole and deuterated chloroform ($CDCl_3$) followed by infrared spectroscopy. Catalytic activity tests were carried out in a fixed-bed flow reactor. EtOH or EtOH/AA mixtures with the molar ratios EtOH/AA of 2.2, 2.7 and 3.2 (17.4 mmol of EtOH or EtOH/AA through 1 g of a catalyst per 1 h) were fed into the catalytic reactor. Catalytic activity was characterized by total conversion of reagents (EtOH and AA), selectivity of products and BD yield.

Details of catalysts preparation method, catalyst characterization procedures and catalytic activity measurements are described elsewhere (see SM, section 1).

3. Results and discussion

3.1. FTIR characterization of acidic-basic sites: pyridine, pyrrole and $CDCl_3$ adsorption

FTIR spectra of $Ta_{1.0}$SiBEA and $Ta_{3.0}$SiBEA after pyridine adsorption are presented in Fig. 1. The bands at 1613, 1598, 1492 and 1445-1450 cm^{-1} correspond to pyridine interacting with LAS, in line with earlier data [22,23]. Intensity of absorption bands attributed to LAS for $Ta_{3.0}$SiBEA is higher than that for $Ta_{1.0}$SiBEA. The intensity of these bands for SiBEA is much lower [24]. Thus, it proves that upon incorporation of Ta ions in the vacant T-atom sites of SiBEA the additional LAS are formed in framework of the zeolite. Absence of the bands at 1638 and 1545 cm^{-1} in FTIR spectra of SiBEA [24] and TaSiBEA (Fig. 1) suggests that Brønsted acidic sites are not present in SiBEA and are not created upon incorporation of Ta ions in framework of SiBEA zeolite.

It is well known that pyrrole being an amphoteric molecule can react with either basic sites or acidic ones. FTIR spectra of $Ta_{1.0}$SiBEA after pyrrole adsorption are presented in Fig. 2. The bands at 1534, 1470, 1421 and 1379 cm^{-1} are attributed to the ring-stretching vibrations of pyrrole [25,26]. The band at 3480 cm^{-1} combined with the band at 1490 cm^{-1} indicated the presence of the pyrrole species interacting with acidic sites [25,26]. The weak shoulder at ca. 3390 cm^{-1} in the spectra of TaSiBEA could suggest the presence of basic sites, in agreement with earlier work [25].

FTIR spectra of $Ta_{1.0}$SiBEA after $CDCl_3$ adsorption are presented in Fig. 3. The bands at 2558 and 2224 cm^{-1} are attributed to weak and medium basic sites [17]. The bands attributed to strong basic sites are absent for TaSiBEA.

Thus, the FTIR investigations of TaSiBEA have shown that these catalysts possess both Lewis acidic and basic sites with a predominance of the former ones.

3.3. Catalytic properties of TaSiBEA

Results of the catalytic activity of TaSiBEA catalysts in conversion of EtOH/AA mixture into BD are presented in Table 1. Stability of BD selectivity and yield over $Ta_{1.0}$SiBEA and $Ta_{3.0}$SiBEA at 598 K and 623 K as a function of time-on-stream are presented in Fig. S4 (see SM). The high BD selectivity is maintained after repeated operation cycles, as well as the stability of the zeolite structure according to XRD and FTIR data (see SM, section 3).

Incorporation of Ta into the BEA framework has allowed preparing catalysts with remarkable selectivity in production of BD from EtOH/AA mixture. The highest selectivity to BD (87.3–90.3%) for the TaSiBEA zeolite catalysts is observed at the EtOH/AA molar ratio of 2.2 (Table 1). At higher molar ratio of EtOH/AA selectivity to BD is lower, but total conversion of the mixture, as well as BD yield, increases. If only EtOH is present in the feed high selectivity and yield of BD are not observed (Fig. 4). The major products at such conditions are AA, ethylene and diethyl ether (DEE) (Table 2).

EtOH dehydrogenation to AA and dehydration to ethylene/DEE are suggested occurring on Ta(V)-containing sites, which posses redox [27] and acidic-basic properties [22,23]. However, in Ta(V)-containing zeolite catalysts the acidic-basic properties predominant over redox one as reported earlier [22]. Substantial amount of AA obtained in step (1) from EtOH (Table 2) indicates that bridged oxygen of Ta-O-Si is basic site. Nevertheless, amount of the dehydration products is higher than AA. Consequently, it suggests that acidic properties of Ta(V)-containing zeolite catalyst prevail its basic properties, in line with the FTIR data of adsorbed pyridine, pyrrole and $CDCl_3$ (Figs. 1-3).

Increasing BD selectivity in the presence of AA in the feed (Fig. 4) is result of acceleration of the key step (2). Aldol condensation (2) competes against EtOH dehydration to ethylene/DEE for acidic Ta(V)-containing sites. Increasing EtOH content (with simultaneous decreasing of AA) in the feed contributes accelerating the EtOH dehydration and leads to decrease in BD selectivity. However, increasing EtOH content in the feed promotes more complete MPV reduction of crotonaldehyde as evidenced by decrease in amount of crotonaldehyde in the reaction products (Table 1).

The effect of temperature on the conversion of EtOH or EtOH/AA mixture over TaSiBEA catalysts is shown in Fig. 4. In both cases, BD yield increases with temperature, because EtOH-to-BD process is endothermic with an enthalpy of 102-109 $kJ\cdot mol^{-1}$ [2]. If only EtOH is present in the feed selectivity to BD increases with temperature, and in the case of EtOH/AA mixture conversion selectivity to BD decreases. Such changing of BD selectivity is likely to be explained by kinetic factors, related to the activity of the catalyst, in line with results of thermodynamic analysis for one- and two-step EtOH-to-BD processes [2].

It is important to mention here that increase of the content of Ta atoms in the zeolite matrix from 1 to 3 wt % does not provide proportional increase of BD yield in the conversion of

EtOH or EtOH/AA mixture. This may be due to the different accessibility of Ta(V)-containing sites being active in the process.

It was recently shown [20] that isolated tetrahedral Zr(IV) species linked with four (closed site) or three (open site) silicon atoms in framework of ZrBEA zeolite constitute LAS. The open sites of ZrBEA are more efficient in the process of BD production, which can be related to the higher acidic strength and better steric accessibility of such sites. The same may be true for the TaSiBEA catalysts with different contents of tantalum. The number of space-available LAS in $Ta_{3.0}$SiBEA is not significantly greater than in $Ta_{1.0}$SiBEA. Thus, the observed difference in the activity of $Ta_{1.0}$BEA and $Ta_{3.0}$SiBEA may be caused by the fact that the number of sterically accessible active sites capable of promoting target process in $Ta_{3.0}$SiBEA is greater than that present in $Ta_{1.0}$SiBEA due to a larger content of tantalum.

Conclusions

TaSiBEA zeolite can be used as efficient catalyst for the conversion of ethanol and acetaldehyde mixture into 1,3-butadiene.

The two-step postsynthesis method of Ta incorporation into vacant T-atom sites of BEA zeolite has allowed preparing highly selective (80–90 % at total conversion of 45–30 %) tantalum-silicate catalysts for the conversion of ethanol and acetaldehyde mixture into 1,3-butadiene.

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Table 1. Catalytic performance of TaSiBEA catalysts in EtOH/AA mixture conversion[a]

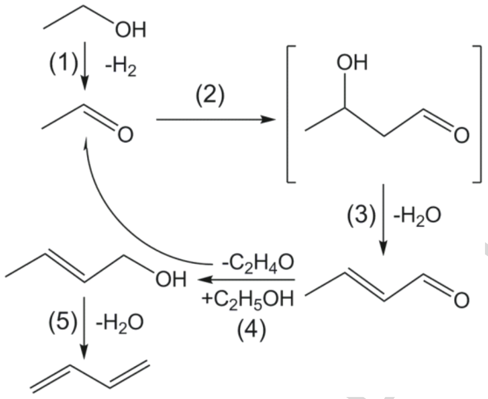
EtOH/AA ratio	Temp. (K)	Total conver. (%)	Selectivity (C mol%)					BD yield (C mol%)
			BD	ethylene	diethyl ether	croton aldehyde	others	
Ta$_{1.0}$SiBEA								
3.2	598	39.2	86.4	7.4	3.4	0.1	2.7	33.9
	623	45.3	78.4	14.4	4.0	0	3.2	35.5
2.7	598	31.2	86.9	9.2	0.6	0.9	2.4	27.1
	623	43.0	79.6	15.0	1.4	0.5	3.5	34.2
2.2	598	26.2	87.3	0.1	0.1	10.2	2.3	22.9
	623	34.9	88.6	0.5	0.1	6.1	4.7	30.9
Ta$_{3.0}$SiBEA								
3.2	598	43.7	80.9	12.1	3.9	0	3.1	35.4
	623	58.9	73.1	20.6	2.8	0	3.5	43.1
2.7	598	39.1	84.6	9.7	1.8	0.6	3.3	33.1
	623	55.2	76.2	17.8	1.8	0.3	3.9	42.1
2.2	598	30.7	90.3	0.3	0.1	4.7	4.6	27.7
	623	42.9	87.5	4.0	0.1	3.5	4.9	37.5

[a] time-on-stream=4 h.

Table 2. Catalytic performance of TaSiBEA catalysts in EtOH conversion[a]

Temp. (K)	Total conver. (%)	Selectivity (C mol%)					BD yield (C mol%)
		BD	AA	ethylene	diethyl ether	others	
				$Ta_{1.0}SiBEA$			
598	13.3	16.4	33.0	28.3	20.8	1.5	2.2
623	31.1	28.9	21.1	33.2	15.3	1.5	9.0
				$Ta_{3.0}SiBEA$			
598	25.6	12.3	23.7	48.6	14.6	0.8	3.1
623	49.1	16.2	17.7	52.5	12.9	0.7	7.9

[a] time-on-stream=4 h.



Scheme 1. Overall scheme of EtOH conversion to BD.

Figure captions

Figure 1. FTIR spectra of adsorbed pyridine over TaSiBEA catalysts after desorption at different temperatures.

Figure 2. FTIR spectra of adsorbed pyrrole over $Ta_{1.0}SiBEA$ catalyst after desorption at 338 K.

Figure 3. FTIR spectra of adsorbed $CDCl_3$ over $Ta_{1.0}SiBEA$ at different temperatures.

Figure 4. Total conversion (TC) of EtOH/AA mixture (or EtOH), BD selectivity and yield over TaSiBEA catalysts at different EtOH/AA ratios in the feed mixtures at 598 K and 623 K (time-on-stream=4 h).

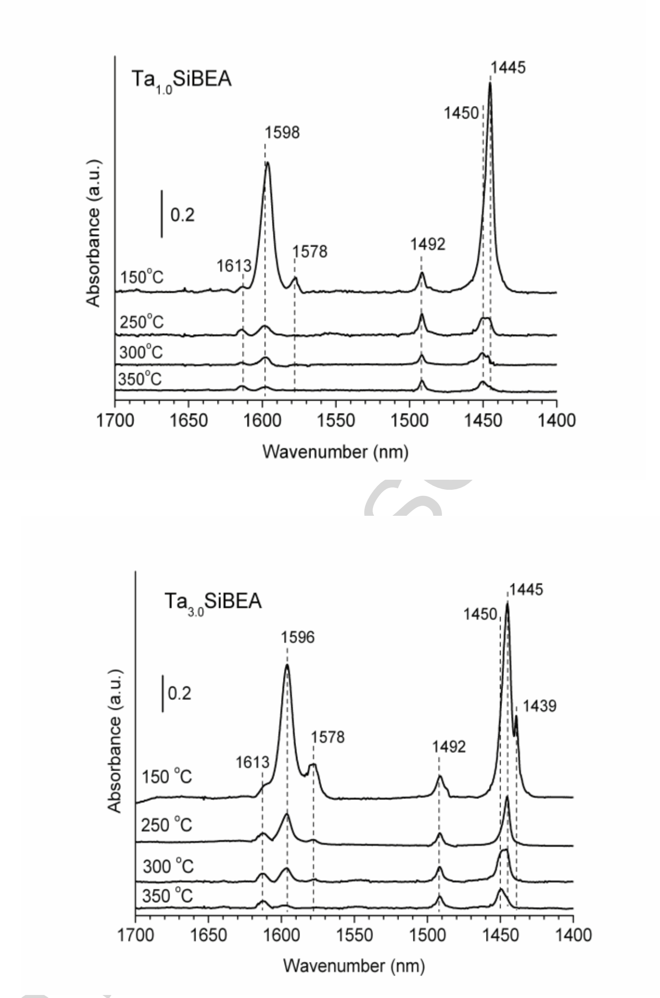

Ta$_{1.0}$SiBEA
Absorbance (a.u.)
0.2
1445
1450
1598
1578
1613
1492
150°C
250°C
300°C
350°C
1700 1650 1600 1550 1500 1450 1400
Wavenumber (nm)
Ta$_{3.0}$SiBEA
Absorbance (a.u.)
0.2
1445
1450
1439
1596
1578
1613
1492
150 °C
250 °C
300 °C
350 °C
1700 1650 1600 1550 1500 1450 1400
Wavenumber (nm)

Fig. 1.

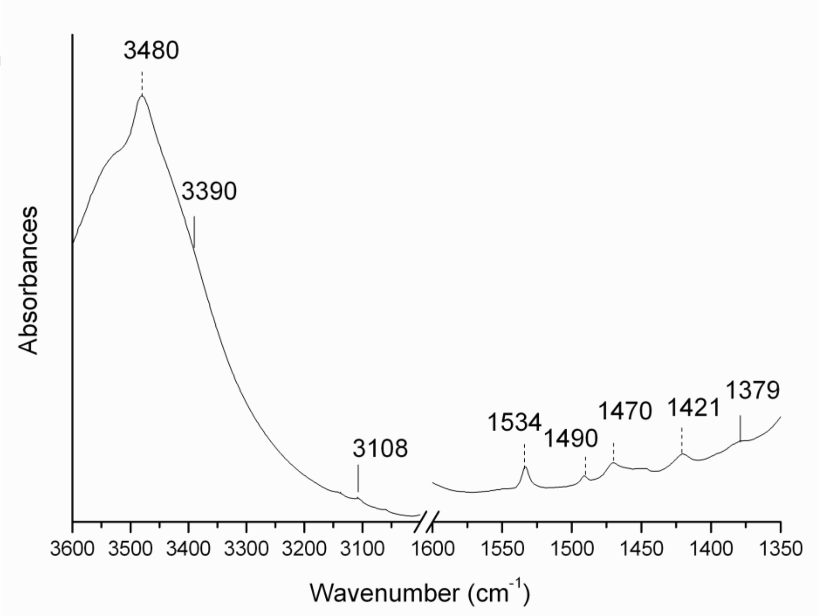
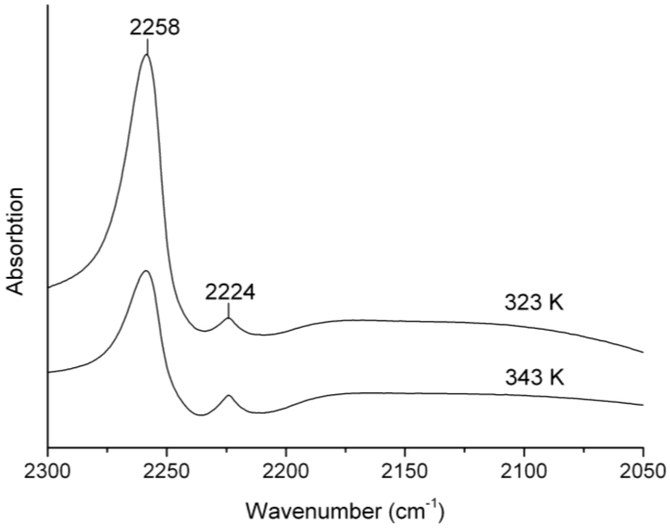

Absorbances
3480
3390
3108
1534
1490
1470
1421
1379
3600 3500 3400 3300 3200 3100 1600 1550 1500 1450 1400 1350
Wavenumber (cm^{-1})

Fig. 2


2258
2224
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343 K
Absorbtion
2300
2250
2200
2150
2100
2050
Wavenumber (cm^{-1})

Fig. 3

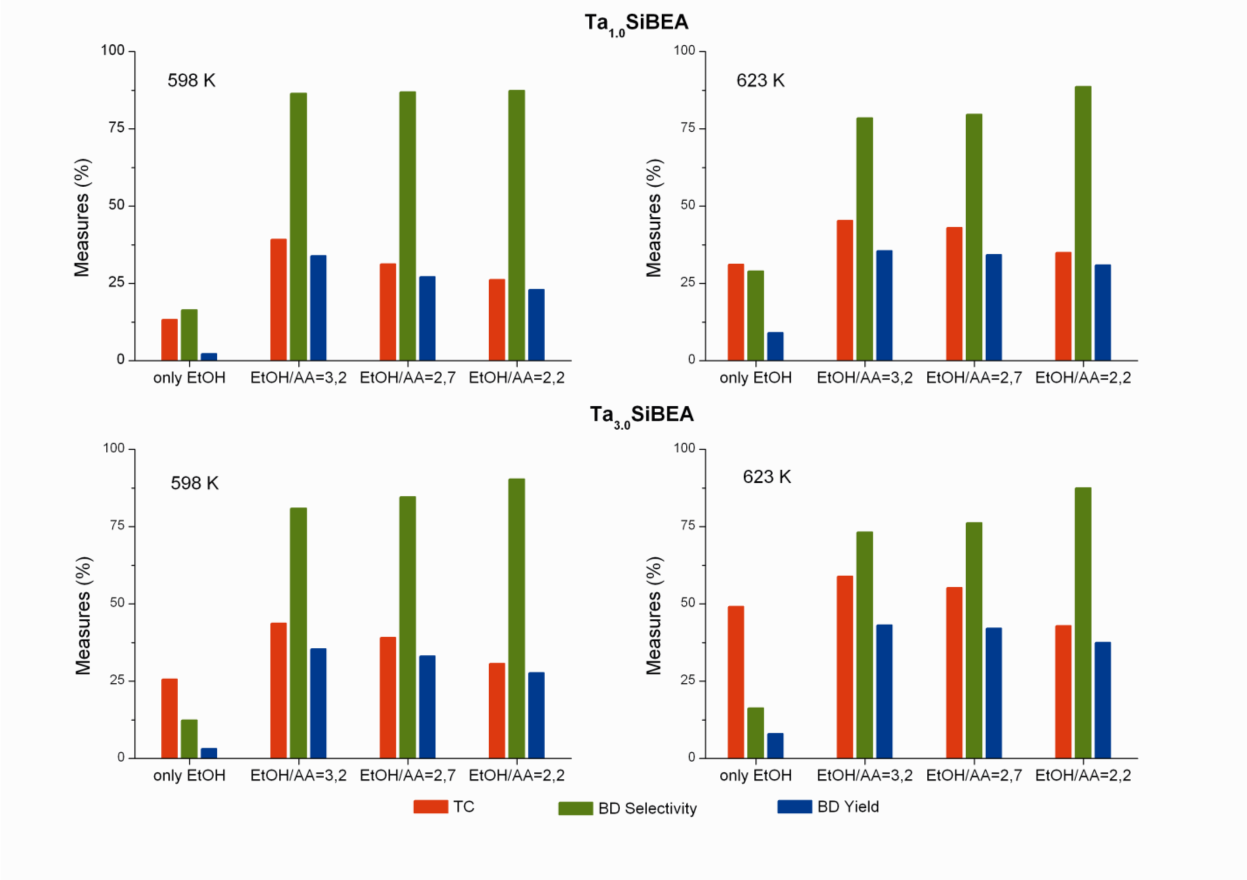
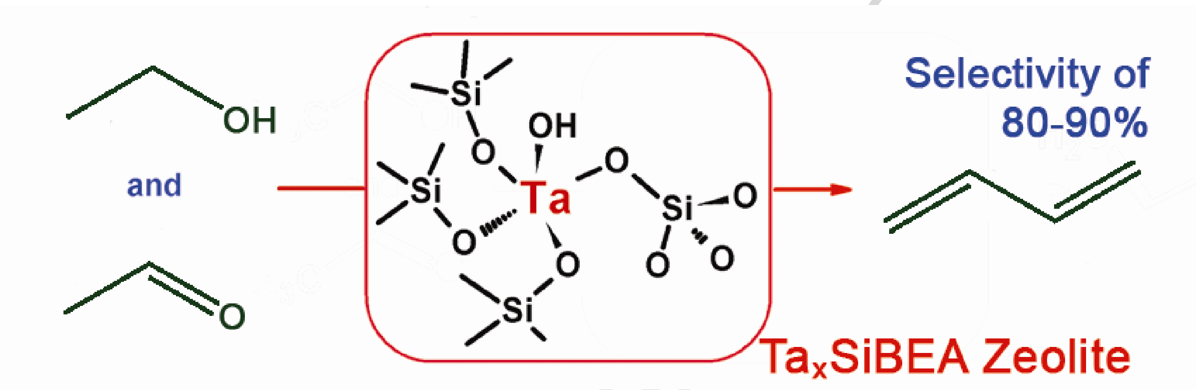

Ta$_{1.0}$SiBEA
598 K
623 K
Ta$_{3.0}$SiBEA
Measures (%)
0
25
50
75
100
only EtOH
EtOH/AA=3,2
EtOH/AA=2,7
EtOH/AA=2,2
TC
BD Selectivity
BD Yield

Fig. 4

Graphical abstract



Highlights

TaSiBEA catalysts were prepared by Ta incorporation into zeolite framework.

Ta-containing zeolites were firstly studied in ethanol/acetaldehyde to 1,3-butadiene conversion.

1,3-butadiene selectivity of 80-90 % with yield of up to 43 % was achieved.