



Short communication

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



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ARTICLE INFO

Article history:

Received 13 August 2015

Received in revised form 19 January 2016

Accepted 22 January 2016

Available online 23 January 2016

Keywords:

Tantalum

BEA

Ethanol

1,3-Butadiene

Catalysis

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.

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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–Al₂O₃, (ZnO, CuO)/MgO–SiO₂, etc.) [4–11], and in two-step process, using Ta₂O₅–silica [12–14] as well as ZrO₂–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–SiO₂ 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 SiO₂ 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.

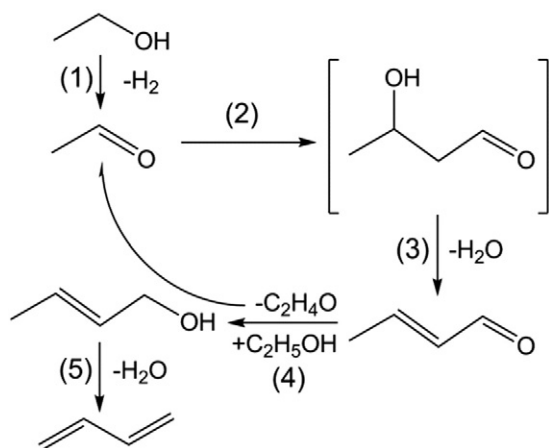
In this paper we report the remarkable selectivity achieved in production of BD from EtOH and AA over TaSiBEA zeolite catalysts with isolated mononuclear Ta(V). To the best of our knowledge, this is the first time that such catalytic properties of Ta-zeolite catalysts in this process have been reported.

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 (CDCl₃) followed by infrared spectroscopy. Catalytic activity tests were carried out in a fixed-bed flow reactor. EtOH or EtOH/AA mixtures with the

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Scheme 1. Overall scheme of EtOH conversion to BD.

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 $\text{Ta}_{1.0}\text{SiBEA}$ and $\text{Ta}_{3.0}\text{SiBEA}$ 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 $\text{Ta}_{3.0}\text{SiBEA}$ is higher than that for $\text{Ta}_{1.0}\text{SiBEA}$. 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. The 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 $\text{Ta}_{1.0}\text{SiBEA}$ 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 $\text{Ta}_{1.0}\text{SiBEA}$ 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.

3.2. 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 $\text{Ta}_{1.0}\text{SiBEA}$ and $\text{Ta}_{3.0}\text{SiBEA}$ 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 possess 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

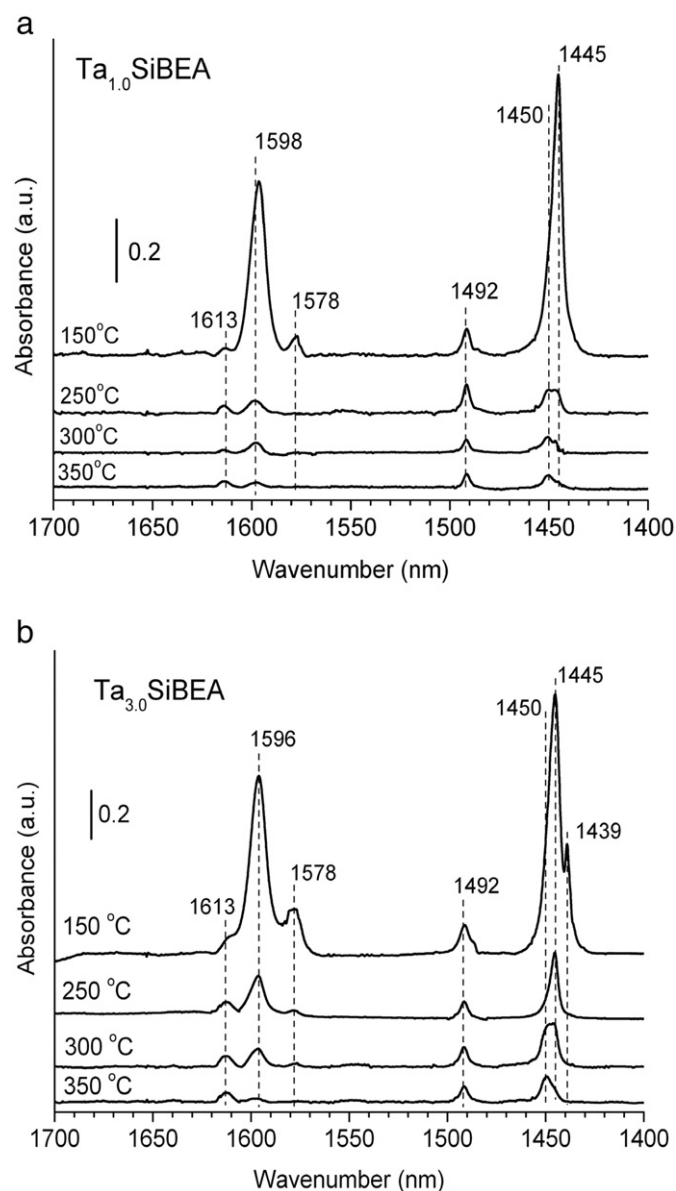


Fig. 1. FTIR spectra of adsorbed pyridine over TaSiBEA catalysts after desorption at different temperatures.

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