Bioethanol conversion into 1,3-Butadiene on single site TaSiBEA and MTaSiBEA (M=Ag, Cu, Zn) zeolite catalysts

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Abstract:

Tantalum-silica based zeolites with isolated framework mononuclear Ta(V) (TaSiBEA) are highly selective catalysts for ethanol/acetaldehyde conversion into 1,3-butadiene. The doping of TaSiBEA with Ag, Cu and Zn changes its catalytic properties in ethanol and ethanol-water mixtures conversion into 1,3-butadiene as a result of modification of redox and acid-base properties. Such modification allows accelerating ethanol dehydrogenation to acetaldehyde and subsequent steps of the ethanol-to-butadiene process. Ethanol conversion and butadiene selectivity over the catalysts increase in the order: TaSiBEA < ZnTaSiBEA < AgTaSiBEA < CuTaSiBEA.

Keywords: BEA zeolite, Ethanol conversion, 1,3-Butadiene.

1. Introduction

Bioethanol is a promising renewable source for the production of motor fuels and valuable chemical products. One such product is 1,3-butadiene (BD), which is commonly used in the manufacture of polymer materials. The synthesis of BD from ethanol (EtOH) has recently been shown to be competitive in price to the production of BD from petrochemical stocks in light of recent environmental legislation, especially in the case of development of highly productive and selective catalysts of the process. BD can be produced in two ways: one-step process – conversion of EtOH over one catalyst in a reactor, and two-step process – conversion of a mixture of EtOH and acetaldehyde (AA), which is produced over a catalyst in the first reactor and then converted to BD over another catalyst in the second reactor.

2. Experimental

Preparation details of the MTaSiBEA catalysts (where M = Ag, Cu, Zn), investigation by XRD, DR UV-vis, XPS, TEM and FTIR (adsorption of pyridine, 2,6-di-tert-butylpyridine, pyrrole and $CDCl_3$), and description of catalytic tests are presented in the papers.[1, 2]

3. Results and discussion

The two-step postsynthesis preparation method has allowed obtaining Ta(V)-single site BEA zeolite, as evidenced by XRD, DR UV-vis, XPS, TEM and FTIR. The results of DR UV-vis, XPS and TEM show the presence of highly dispersed Ag, Cu and Zn species (framework mononuclear and extra-framework oxidized clusters) in the zeolites. The results of FTIR investigation of MTaSiBEA samples with pyridine, 2,6-di-tert-butylpyridine, pyrrole and deuterated chloroform demonstrate these zeolites as well as TaSiBEA possess weak Brønsted acidic, Lewis acidic and basic sites, formed by incorporation of Ta, Ag, Cu and Zn into the BEA zeolite framework.

The main products of ethanol and EtOH/AA mixture conversion over TaSiBEA and MTaSiBEA are BD, AA, ethylene and diethyl ether (DEE). The formation of propylene, ethylene, ethyl acetate and other products are also observed (Table).

We showed that using of dealuminated BEA zeolite matrix (SiBEA with Si/Al ratio of 1300) has allowed preparing single site Ta-containing zeolite catalysts by the two-step postsynthesis method with high (80–90 %) selectivity in the production of BD from EtOH/AA mixture. EtOH conversion over TaSiBEA does not exceed 13.3 %, and BD selectivity – 16.4 %.[1] Deficiency of active sites of EtOH dehydrogenation to AA is the cause of observed low selectivity of BD formation in one-step process over TaSiBEA catalyst (12–29%). So, doping of tantalum-silicate zeolite with Ag, Cu and Zn strongly affects its catalytic properties and entails substantial increase in EtOH conversion and selectivity to BD.[2]

The role of Ag, Cu and Zn consists in modifying of redox and acid-base properties of the TaSiBEA zeolite and allowing proceeding easier EtOH dehydrogenation to AA and subsequent steps of the EtOH-to-BD process. Significant amount of unreacted AA over AgTaSiBEA 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. The significant amount of ethylene and DEE observed in the reaction products (total selectivity of 30 %) over ZnTaSiBEA may be caused by higher number of Brønsted and Lewis acidic sites, accelerating side reaction of EtOH dehydration. The highest values of EtOH conversion (87.9 %) and BD selectivity (72.6 %) are observed over CuTaSiBEA, because the optimal ratio of acid-base and dehydrogenation sites is achieved.

Table 1. Catalytic performance of SiBEA zeolite catalysts (EtOH, WHSV=0.5 h^{-1}, T=598 K).

Catalysts	Conversion (%)	Product selectivity (C mol%)					BD yield (C mol%)
		BD	AA	ethylene	crotonaldehyde	others	
1%TaSiBEA*	31	87	-	9	1	3	27
3%TaSiBEA*	39	85	-	10	1	4	33
1%Ag1%TaSiBEA	83	63	24	8	1	4	52
1%Cu1%TaSiBEA	88	73	15	3	1	8	64
1%Zn1%TaSiBEA	52	43	23	17	13	4	22

*The conversion of EtOH/AA mixture (EtOH/AA=2.7, WHSV=0.8 h^{-1}, T=598 K)

4. Conclusions

Thus, the use of the dealuminated BEA zeolite as a silicate matrix allows forming active sites of the catalyst of the EtOH-to-BD process using the minimum amount of the active component, which is especially important in the case of expensive tantalum. The role of dopants consists in modifying of redox and acid-base properties of the TaSiBEA zeolite and allowing proceeding easier EtOH dehydrogenation to AA and subsequent steps of the EtOH-to-BD process.

References

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