



Research Paper

Improving 1,3-butadiene yield by Cs promotion in ethanol conversion

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ARTICLE INFO

Keywords:

Bio-butadiene
Supported catalysts
Cs-promotion
Aldol condensation
Acid-base balance

ABSTRACT

Gas phase conversion of ethanol into butadiene was studied over silica-supported ZnO, ZrO₂ and ZnO-ZrO₂ catalysts in a fixed-bed reactor. Surface active sites were characterised using a variety of techniques including temperature-programmed desorption (TPD) of NH₃ and CO₂ as well as Fourier transform infrared (FTIR) spectroscopy of adsorbed pyridine. An increased concentration of acid and base sites was found in the following order: ZnO < ZrO₂ < ZnO-ZrO₂. In addition, new acid and base sites were generated when alkaline metal promoters were introduced. Typical reaction products for all catalysts include acetaldehyde, butadiene, ethylene, propylene, butenes, diethyl ether and C₄ oxygenates. Compared to single oxide supported catalysts, a remarkable acid-base synergetic effect was observed on the binary oxides supported catalysts with or without alkali metal modification. The improved catalytic activity and selectivity can be attributed to the right balance between acid and base sites, minimising dehydration to ethylene while promoting dehydrogenation to acetaldehyde. Furthermore, the existence of acid-base pairs with the appropriate configuration and strength promotes the aldol condensation and Meerwein-Ponndorf-Verley (MPV) reduction efficiently.

1. Introduction

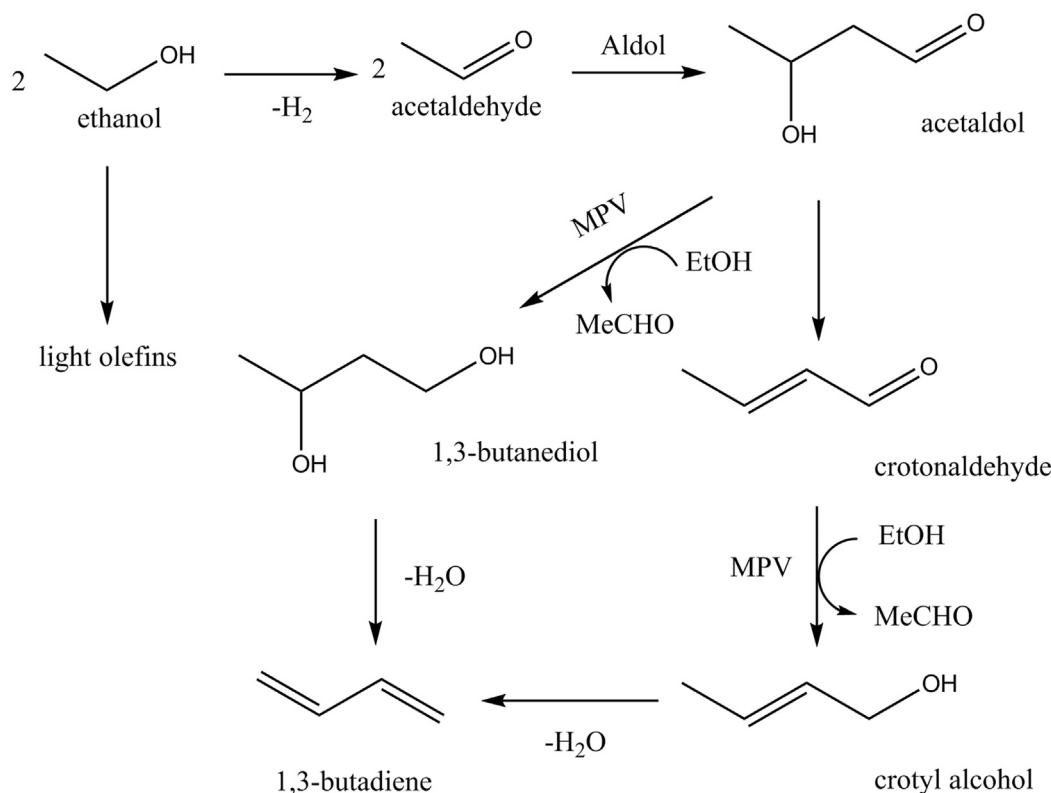
Due to growing concerns on depletion of petroleum resources and climate change resulting from the consumption of petrochemicals and fuels, the last few decades have witnessed a renewed interest in converting biomass-derived feedstocks into value-added chemicals [1]. Currently bio-ethanol is being produced in abundant quantities through biomass fermentation and its increased availability opens up new opportunities for the synthesis of renewable bulk chemicals [2,3]. Therefore, it is highly attractive to develop heterogeneous catalytic systems to efficiently convert ethanol to 1,3-butadiene (BDE), one of the most important chemical intermediates in the production of various polymers (e.g. styrene-butadiene rubber, car tyres and plastics) [3,4]. Currently BDE is obtained as a by-product of naphtha steam cracking to produce olefins, where an expensive separation by extractive distillation is required [5]. Although the current low oil price strongly benefit this route for BDE production, the trend of shifting to lighter feedstocks such as shale gas will significantly decrease the BDE yield, thus making on-purpose BDE even more attractive and necessary.

Catalytic production of BDE from ethanol can be achieved through either the one-step process developed by Lebedev or a two-step process based on Ostromislensky reaction, both of which have been known since the beginning of the twentieth century. However both processes

were abandoned after the 1960s due to the lack of competitiveness with petrochemical-based routes [6]. An early investigation by Union Carbide revealed that tantalum oxide and zirconium oxide were able to provide a good selectivity toward butadiene during ethanol conversion. Mixed oxide systems, including MgO-SiO₂, ZnO-Al₂O₃, ZrO₂-SiO₂ and Zn_xZr_yO_z are still widely investigated for the Lebedev synthesis [7–13]. Recent progress on catalyst development for converting ethanol to BDE, either in one or two-steps, has been reviewed by Pomalaza et al. [14]. In this review, it was pointed out that the optimum balance between basic, acid and redox sites are crucial for achieving high BDE selectivity using a single catalyst. For MgO-SiO₂ system, the Mg/Si ratio, the synthesis method as well as the effect of dopands were found to be critical parameters affecting BDE production [7]. Both metallic Cu and Ag have been identified as effective dopants, promoting lower temperature dehydrogenation [7,9,10]. In the case of MgO-SiO₂ catalysts, structure-activity relationship studies revealed that not only it is important to fine tune the strength of acid-base sites but also to have a suitable configuration of these sites since the reaction pathway involves a series of sequential steps [11]. In another study, sol-gel synthesised ZrO₂-SiO₂ catalysts showed enhanced performance in ethanol-acetaldehyde reaction given that the addition of ZrO₂ creates new Lewis acid sites, thus promoting the aldol condensation step despite its low dehydrogenation capability [12]. Jones et al. reported a significant

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Scheme 1. Reaction pathway during butadiene formation from ethanol adapted from Jones et al. [15].

selectivity towards BDE (39%) at moderate ethanol conversion (46%) over mesoporous SiO_2 supported ZnO-ZrO_2 catalysts, where the addition of copper can increase the BDE selectivity further to 67% [15,16]. The importance of the synergistic effect between ZnO and ZrO_2 to enhance the aldol condensation rate and to provide additional Lewis acid sites was also reported by Larina et al. [17]. By adjusting surface acid-base properties of $\text{Zn}_x\text{Zr}_y\text{O}_z$ mixed oxide with Na ions, the catalyst deactivation was significantly decreased, while BDE selectivity was improved [13].

Although widely investigated, the reaction mechanism of ethanol to BDE is still a matter of debate. It is generally accepted that the efficient production of BDE requires several critical steps displayed in Scheme 1, adapted from Ref. [15]. The first step is the ethanol dehydrogenation for producing acetaldehyde, followed by the aldol condensation between two acetaldehyde molecules yielding acetaldol which is subsequently dehydrated to crotonaldehyde. Then, the carbonyl group of crotonaldehyde can be reduced to the hydroxyl of ethanol by Meerwein-Ponndorf-Verley (MPV) reduction, and the further dehydration of crotyl alcohol leads to butadiene [18]. Alternatively, MPV reduction may happen between acetaldol and ethanol, thus forming 1,3-butanediol, which can be dehydrated to the target product, BDE. It is important to stress that reaction intermediates such as 1,3-butanediol, crotonaldehyde, and crotyl alcohol, proposed base on literature, were not detected under our reaction conditions. In addition, Scheme 1 also includes a reaction pathway to account for the production of light olefins. Indeed, ethylene is always produced, sometimes in large quantities, via direct or indirect dehydration of ethanol, while C_3 – C_4 olefins are formed in rather small quantities, probably via an acid catalysed mechanism similar to that of Ethanol-to-Olefins (ETO) process.

In this contribution, we report on the influence of alkali metal promoters on the selective ethanol conversion to BDE over SiO_2 supported Zn-Zr catalysts. Special emphasis is placed on the role of acid-base centers on the improvement of the catalytic performance of $\text{ZnO-ZrO}_2/\text{SiO}_2$ catalysts.

2. Experimental

2.1. Catalyst preparation and characterisation

Supported catalysts were prepared by incipient wetness impregnation method with different contents of metal oxides (ZnO : 1 wt%, ZrO_2 : 5 wt%) and 0.5 wt% of alkali-promoters (Li_2O , Na_2O , K_2O , Cs_2O) using commercially available fumed silica, zirconium oxynitrate, zinc nitrate, lithium nitrate, sodium nitrate, potassium nitrate, rubidium chloride and cesium nitrate as precursors. For comparison, catalysts with the same molar loading of alkali-metals were also prepared. Specifically, the molar ratio of Zn/alkali-metal was fixed at 6.9. All catalysts were dried at 110 °C overnight and then calcined at 500 °C for 4 h prior to any measurements. The resulting supported catalysts were named as $x\text{M}_2\text{O-yZnO-zZrO}_2/\text{SiO}_2$ where x, y and z are the loadings of the corresponding oxides and alkali metal promoters (M represents the alkali metals). Powder X-ray diffraction (XRD) patterns of the samples were recorded using a Bruker D8 Advance diffractometer with Ni-filtrated $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) produced by a Cu anode operated at 40 kV and 40 mA. N_2 physisorption was carried out at $-196 \text{ }^\circ\text{C}$ on a Micromeritics ASAP 2020 analyser. The samples were degassed at 200 °C for 24 h prior to adsorption measurements. Temperature-programmed desorption (TPD) of NH_3 was carried out on a Thermo Scientific TPDRO 1100 apparatus equipped with a thermal conductivity detector (TCD). A 100 mg sample was pretreated at 500 °C for 1 h under argon flow before NH_3 adsorption at 150 °C for 1 h. After adsorption, the sample was flushed with Ar for 1 h and then the temperature was increased to 800 °C using a heating rate of 10 °C/min while the desorption of NH_3 was monitored using TCD. The peak area was correlated with the amount of adsorbed NH_3 based on calibration values obtained from the injection of NH_3 pulses. The strength and concentration of base sites were determined by CO_2 -TPD in the same system described above. Using a similar procedure, CO_2 adsorption at 30 °C instead of 150 °C, followed by temperature-programmed desorption. Infrared spectroscopy (FT-IR) of adsorbed pyridine was recorded in a BIO-RAD

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