



Conversion of ethanol to 1,3-butadiene over Na doped $Zn_xZr_yO_z$ mixed metal oxides



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ABSTRACT

Despite numerous studies on different oxide catalysts for the ethanol to 1,3-butadiene reaction, few have identified active sites (i.e., type of acidity) correlated to the catalytic performances. In this work, the type of acidity needed for ethanol to 1,3-butadiene conversion has been studied over Zn/Zr mixed oxide catalysts. Specifically, synthesis method, Zn/Zr ratio, and Na doping have been used to control the surface acid–base properties, as confirmed by characterizations such as NH_3 -TPD and IR-Py techniques. The 2000 ppm Na doped $Zn_{1.5}Zr_{1.5}O_{2.5}-H$ with balanced base and weak Brønsted acid sites was found to give not only high selectivity to 1,3-butadiene (47%) at near complete ethanol conversion (97%), but also exhibited a much higher 1,3-butadiene productivity than other mixed oxides studied.

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1. Introduction

As countries expand and societies become more dependent on technological advances, energy demands will continue to rise and place even more stress on limited fossil fuel resources. Biomass is well established as a viable, renewable and sustainable alternative to the current, non-renewable use of crude oil reserves [1,2]. Because of this, bio-ethanol production is already in place and is currently used as blends in transportation liquid fuels [3]. Given by the recent innovation and thus increased availability of bio-ethanol [4], further upgrading bio-ethanol to value added chemicals/commodities has attracted increasing attention [5–7].

1,3-Butadiene is a widely used chemical in the rubber and chemicals industries. It serves as a precursor to synthetic materials (rubber and nylon), various polymers such as acrylonitrile-butadiene-styrene (ABS) resins, and block copolymers such as styrene-butadiene latex, nitrile rubber, and adiponitrile (ADN) [8,9]. It is predominantly produced as a by-product of naphtha steam cracking during ethylene production from crude oil.

According to Chemical Marketing Associates, Inc. in 2005, the 1,3-butadiene global demand was 9 million metric tons [10]. In 2010, it rose to 10.5 million and in the next five years, the global demand is projected to increase at a rate of ~3% per year [9].

Since the early 1900s, ethanol to 1,3-butadiene conversion has been reported in one- and two-step processes over various mixed metal oxides. Metal oxides with both acidic and basic properties are efficient for converting ethanol to 1,3-butadiene [7,11–23]. Lebedev was the first to report butadiene production from ethanol in a one-step process around 1910. Yields as high as 70% were claimed even though the exact nature of the catalyst was not disclosed [13]. Ostromislensky reported a two-step process in which ethanol is first oxidized to acetaldehyde, and acetaldehyde is then converted into 1,3-butadiene over a tantalum oxide-silica gel catalyst. Zirconia was later reported as a successful replacement for tantalum oxide [7].

To better understand the reaction mechanism, Quattlebaum studied co-feeding ethanol with possible reaction intermediates. It was found that a mixture of crotonaldehyde and ethanol gave better butadiene selectivity than co-feeding ethanol and acetaldehyde, suggesting that crotonaldehyde is a key intermediate [22]. Toussaint et al. also proposed the currently accepted reaction pathway in which ethanol dehydrogenates to acetaldehyde, followed by aldol condensation of acetaldehyde to form crotonaldehyde, which undergoes subsequent hydrogenation and dehydration to 1,3-butadiene through crotyl alcohol [13,22,24]. Bhattacharyya et al., using an alumina zinc oxide catalyst to investigate various

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possible pathways by co-feeding intermediates with ethanol, concluded that crotonaldehyde reduction with ethanol is more likely than that with hydrogen in a Meerwein-Ponndorf-Verley (MPV) reaction [12].

Work on such catalysts continued throughout the 1980s due to a reduced cost of ethanol resulting from a raw sugar abundance. Much research has been focused on the silica-magnesia catalyst system. Kityama et al., Kvisle et al., and Makshina et al. all focused on catalytic systems with magnesium oxide and silica. It is known that magnesium oxide provides basic sites for dehydrogenation and silica provides acidic sites for dehydration. Kvisle et al. suggested that adding oxygen or acetaldehyde to the feed could increase butadiene yield [18]. They concluded that the rate determining step occurs before hydrogen transfer due to the accumulation of C₂-entities and not C₄-oxygenated species in TPD results. Kityama et al. also attributed results to acidic and basic properties of their nickel magnesium silicate catalyst rather than surface area [17]. Makshina et al. in 2012 found that the balance between acidic and basic components of the catalyst as well as its redox properties of additional promoters affect butadiene yield. Their best catalysts were composed of Mg-Si materials with either a silver or copper promoter. These promoters are believed to contribute to acetaldehyde production by increasing ethanol dehydrogenation activity [19,25].

Jones et al. in 2011 was the only to report ethanol to butadiene conversion over a catalyst with the Zn/Zr combination. They impregnated these transition metals onto a silica support and found the highest butadiene selectivity to be 67.4% with 44.6% ethanol conversion [15]. Tsuchida et al. also reported minor 1,3-butadiene production from ethanol over hydroxyapatite and correlated ethylene, 1-butanol, and 1,3-butadiene selectivities with acid and base properties [26].

In 2011, Sun et al. reported a Zn_xZr_yO_z catalyst with balanced acid-base pairs, on which up to 83% isobutene theoretical yield was achieved from bio-ethanol [27]. Liu et al. optimized reaction and catalyst synthesis parameters for the same catalyst system, achieving up to 79% isobutene theoretical yield from bio-ethanol using the same catalyst under industrially relevant reaction conditions. They identified weak Brønsted sites as the active site for acetone to isobutene conversion [28]. Interestingly, under reaction conditions at relatively low temperature (i.e., 400 °C) and with a feed with an ethanol molar fraction of 3.6% and steam to carbon ratio of 5, 78% of the C₄s produced were reported as 1,3-butadiene. This observation indicates that a balance of acidic and basic sites are present on Zn_xZr_yO_z which, upon further optimization of reaction conditions such as temperature, could be used for the 1,3-butadiene formation. Here, a Zn_xZr_yO_z catalyst was studied and compared with other promising catalysts reported in the literature.

2. Experimental details

2.1. Catalyst preparation

Two methods were used to prepare the catalysts with controlled acidity, namely the hard template (-H) and incipient wetness impregnation methods (-I). The details for the hard template method can be found elsewhere [27–29]. Briefly, calculated amounts of zinc nitrate hexahydrate (Sigma-Aldrich, reagent grade, 98%) and zirconium (IV) oxynitrate hydrate (Sigma-Aldrich, 99%) precursors were dissolved into water by using ultrasonic bath. Before impregnation, BP2000 (carbon black pearl 2000, Cabot Corp.) was dried at least overnight at 180 °C. The resulting mixture was dried overnight at room temperature and then at 80 °C for 4 h before calcination. The calcination program consisted of 400 °C for 4 h (3 °C/min) and then 550 °C for 20 h (3 °C/min) in air. Resulting white powders were either used as support for further Na doping or

directly pressed and sieved to appropriate mesh for activity testing (60–100 mesh). For Na doping, incipient wetness impregnation was employed using sodium nitrate (NaNO₃, Sigma Aldrich, ≥99.999%) as a precursor. These catalysts are denoted as Zn_xZr_yO_z-H, where x:y:z represent the molar ratio of each component.

For the incipient wetness impregnation method, Zr(OH)₄ (MEL-Cat. XZO631, >97%) was used as the support, and a given amount of Zn(NO₃)₂/H₂O solution (same Zn precursor as hard template method) was added. The mixture was calcined at 400 °C (3 °C/min) for 2 hr and 550 °C (5 °C/min) for 3 h after drying at room temperature overnight. The concentration of the Zn(NO₃)₂/H₂O solution was used to control the Zn/Zr ratio of the denoted Zn_xZr_yO_z-I catalysts. For the Cu doped MgO-SiO₂ catalysts, synthesis procedures can be found in [19]. However, for the SiO₂ source, silica gel was used (Sigma Aldrich, high purity, Davisil Grade 635).

2.2. Characterization

2.2.1. Nitrogen sorption

Nitrogen adsorption-desorption isotherms were obtained at –196 °C with a Micromeritics TriStar 2 3020 physisorption analyzer. Samples were pretreated at 300 °C for 1 h under vacuum. The Brunauer-Emmett-Teller (BET) method was used to calculate surface areas.

2.2.2. X-ray diffraction (XRD)

X-ray diffraction patterns were obtained using a Rigaku Mini-flex II X-ray diffractometer with a copper anode (K_{α1} = 0.154 nm). Operating conditions were 2.04°/min, 0.05° sampling width, 30 kV, and 15 mA.

2.2.3. NH₃ temperature programmed desorption (NH₃-TPD)

NH₃-TPD experiments were conducted in an AutoChem II 2920 chemisorption analyzer equipped with mass spectrometer (ThermoStars™ GSD 320). After pretreatment at 500 °C for 1 h and baseline stabilization at 50 °C, 10 vol% ammonia balanced by He was flowed at 30 mL/min for 30 min. Physisorbed NH₃ was purged for 2 h under a He flow of 50 mL/min. TPD was done under a He flow of 50 mL/min using a ramp rate of 10 °C/min to 650 °C. The mass spectrometer was calibrated using the thermo decomposition of ammonium oxalate monohydrate ((NH₄)₂C₂O₄·H₂O). A known amount of (NH₄)₂C₂O₄·H₂O was loaded into the sample tube, plots of m/z ion current from the mass spectrometer (normalized by PKR) vs. time were generated and integrated, and integration areas were correlated with amount of generated species to form calibration curves.

In order to quantify the weak, medium, and strong acidic sites, peaks (intensity vs. time) were deconvolved using asymmetric peaks, integrated, and peak areas were correlated with the mass of NH₃ adsorbed. Three peaks were identified and labeled as the following categories: weak, medium, and strong sites. In the cases where two peaks were identified, they were labeled as weak and medium.

2.2.4. Infrared analysis of adsorbed pyridine (IR-Py)

A Bruker Tensor 27 FTIR spectrometer was used to collect IR-Py spectra. About 20 mg of the catalyst sample was pretreated at 500 °C for 1 h in an *in situ* cell. After being cooled down to 50 °C under 50 STP mL min⁻¹ He, a background spectra was recorded. Pyridine adsorption took place at 50 °C through a bubbler for 5–10 min while He flowed at 10 STP mL min⁻¹. A pyridine purge took place at 50 °C under a He flow of 50 STP mL min⁻¹ for 30 min. Spectra were taken during adsorption to ensure pyridine saturation. Spectra were recorded at 50 °C after 30 min of He purging to remove physisorbed pyridine. The sample's temperature was

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