Conversion of Ethanol to 1,3-Butadiene over Na doped $\text{Zn}_x\text{Zr}_y\text{O}_z$ 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 $\text{Zn}_1\text{Zr}_{10}\text{O}_x$ -1st gen. 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.

Keywords: ethanol; 1,3-butadiene; zinc oxide; zirconia; mixed oxide; Na doped

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 attentions [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 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 form 1,3-butadiene through crotyl alcohol [13, 22, 24]. Bhattacharyya et al., using an alumina zinc oxide catalyst to investigate various 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 $\text{Zn}_x\text{Zr}_y\text{O}_z$ 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 C_4s produced were reported as 1,3-butadiene. This observation indicates that a balance of acidic and basic sites are present on the $\text{Zn}_x\text{Zr}_y\text{O}_z$ which, upon further optimization of reaction conditions such as temperature, could be used for the 1,3-butadiene formation. Here, a $\text{Zn}_x\text{Zr}_y\text{O}_z$ 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 and incipient wetness impregnation methods. 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 (NaNO_3 , Sigma Aldrich, $\geq 99.999\%$) as a precursor. These catalysts are denoted as $\text{Zn}_x\text{Zr}_y\text{O}_z$ -1st gen., where x:y:z represent the molar ratio of each component.

For the incipient wetness impregnation method, $\text{Zr}(\text{OH})_4$ (MELCat. XZO631, > 97%) was used as the support, and a given amount of $\text{Zn}(\text{NO}_3)_2/\text{H}_2\text{O}$ solution (same Zn precursor as 1st gen. method) was added. The mixture was calcined at 400 °C (3 °C/min) for 2 hr and 550 °C (5 °C/min) for 3 hr after drying at room temperature overnight. The concentration of the $\text{Zn}(\text{NO}_3)_2/\text{H}_2\text{O}$ solution was used to control the Zn/Zr ratio of the denoted $\text{Zn}_x\text{Zr}_y\text{O}_z$ -2nd gen. catalysts. For the Cu doped MgO-SiO_2 catalysts, synthesis procedures can be found in [19]. However, for the SiO_2 source, silica gel was used (Sigma Aldrich, high purity, Davisil Grade 635).

2.2 Characterization

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 hr under vacuum. The Brunauer-Emmett-Teller (BET) method was used to calculate surface areas.

X-Ray Diffraction (XRD)

X-ray diffraction patterns were obtained using a Rigaku Miniflex II X-ray diffractometer with a copper anode ($K_{\alpha 1} = 0.154$ nm). Operating conditions were 2.04 °/min, 0.05 ° sampling width, 30 kV, and 15 mA.

NH_3 temperature programmed desorption (NH_3 -TPD)

NH_3 -TPD experiments were conducted in an AutoChem II 2920 chemisorption analyzer equipped with mass spectrometer (ThermoStarsTM GSD 320). After pretreatment at 500 °C for 1 hr and baseline stabilization at 50 °C, 10 vol% ammonia balanced by He was flowed at 30 mL/min for 30 min.

Physisorbed NH_3 was purged for 2 hr 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 ($(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$). A known amount of $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ 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 NH_3 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.

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 hr 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 ramped at 10 °C/min to given temperatures and ramped down to 50 °C for spectra collection.

2.3 Activity testing

The reactions of ethanol to 1,3-butadiene over $\text{Zn}_x\text{Zr}_y\text{O}_z$ mixed oxide catalysts were conducted in a fixed-bed stainless steel reactor (6 mm inner diameter). The desired amount of $\text{Zn}_x\text{Zr}_y\text{O}_z$ catalyst was loaded into the reactor, packed with quartz wool (supplied by Grace Davison Discovery Sciences, AT4033) and SiC to minimize heat transfer effects. A K-type thermocouple was placed at the center of the catalyst bed to monitor reaction temperature. Before the reaction, catalysts were pre-treated at the reaction temperature under a flow of N_2 (50 STP mL min⁻¹) for 0.5 hr. A pure ethanol feed was introduced to the evaporator at 160 °C via a Cole-Parmer single syringe infusion pump and flowing nitrogen gas carried the feed into the reactor. The ethanol and nitrogen flow rates were varied to achieve different residence times

and ethanol partial pressures. The products, kept at temperatures greater than 150 °C to prevent condensation of certain products, were analyzed by a Shimadzu GC-2014. This online GC was equipped with an auto-sampling valve, an HP-Plot Q column, a flame ionization detector (FID), and a thermal conductivity detector (TCD). It was capable of detecting short-chain alkanes (up to C₄s), and small oxygenates such as acetone, acetaldehyde, and acetic acid. A cold trap, kept at 6 °C, collected heavier hydrocarbons.

The carbon balance for the experiments in this study were usually ~80% and was calculated based on the moles of carbon fed in the reactor in the ethanol feed and the moles of carbon-containing products analyzed by the online GC. Coke accounts for 3-4% of the spent catalyst's weight. Compounds with higher carbon chains that are not identified by GC likely account for the remaining unaccounted carbon. These compounds are likely from self- and cross-aldol condensation of intermediates like acetaldehyde and crotonaldehyde. Indeed, hexatrienes form after dehydration of the resulting aldehydes [30]. C₆ oxygenates were also observed in other works and proposed to be from further reaction of C₄ intermediates (e.g. crotonaldehyde) and side products (e.g. 1-butanol, butanal) [31, 32].

In the proposed reaction pathway, ethanol undergoes dehydrogenation to acetaldehyde (Eq. 1). Acetaldehyde undergoes aldol addition to form acetaldol (Eq. 2), followed by acetaldol dehydration to form crotonaldehyde (Eq. 3). The crotonaldehyde is then reduced by ethanol to form crotyl alcohol via the Meerwein-Ponndorf-Verley (MPV) process (Eq. 4), during which ethanol itself is converted into acetaldehyde. Finally, crotyl alcohol dehydrates to form 1,3-butadiene (Eq. 5) [15].

Below are the definitions used for selectivity, yield, and conversion.

$$\text{Ethanol conversion (\%)} = (\text{Carbon}_{\text{in}} - \text{Carbon}_{\text{out}} / \text{Carbon}_{\text{in}}) \times 100$$

$$\text{Product selectivity (\%)} = (\text{Carbon}_{\text{in particular product}} / \text{Carbon}_{\text{in all products}}) \times 100$$

$$\text{1,3-butadiene yield (\%)} = (\text{Ethanol conversion} \times \text{1,3-butadiene selectivity}) / 100$$

3. Results and discussion

3.1 Catalyst characterization

Fig. 1. XRD diffraction patterns of catalysts with varying Zn/Zr ratios. ($\text{Zn}_1\text{Zr}_2\text{O}_2$ -1st gen. – black, $\text{Zn}_1\text{Zr}_{10}\text{O}_2$ -1st gen. – grey, $\text{Zn}_1\text{Zr}_{30}\text{O}_2$ -1st gen. – light grey. Conditions: 2.04°/min, 0.05° sampling width, 30 kV, 15 mA).

BET surface areas measured by nitrogen sorption for $\text{Zn}_1\text{Zr}_2\text{O}_2$ -1st gen., $\text{Zn}_1\text{Zr}_{10}\text{O}_2$ -1st gen., and $\text{Zn}_1\text{Zr}_{30}\text{O}_2$ -1st gen. are 103.02 m²/g, 119.47 mg²/g, and 135.08 m²/g, respectively. This agrees well with previous results [27]. XRD patterns of the catalysts with varying Zn/Zr ratios (Fig. 1) showed only diffraction peaks that are characteristic of tetragonal ZrO_2 diffraction peaks (JCPDS PDF Card 042-1164) (Fig. 2). No ZnO diffraction was detected, suggesting the highly dispersed nature of ZnO.

Fig. 2. The distribution of surface acidity identified by NH₃-TPD A) and IR-Py spectra B) of the Zn_xZr_yO_z-1st gen. catalysts with different Zn/Zr ratio. (Conditions: Pretreatment: 450°C for 30 min, Spectra taken after desorption at 250°C for 30 min, spectra taken at 50°C).

NH₃-TPD was used to further identify acidic sites of the Zn_xZr_yO_z-1st gen. catalysts (Fig. 2). From Fig. 2A, the total surface acid sites first increased and then decreased as Zn/Zr ratio increased from 1/30 to 1/2. The highest surface acid site concentration was reached at Zn/Zr of 1/10. Regarding the distribution of acidity, when Zn/Zr ratio increased from 1/30 to 1/10, strong and weak acid sites on Zn_xZr_yO_z-1st gen. decreased. Interestingly, medium acid sites increased significantly, contributing to the increase of total acid sites. Further increasing Zn/Zr ratio reduced acid sites of all strengths, but the reduction of medium ones was more dramatic. IR-Py was also used to compare the change of the type of acidity. Peaks, characteristic of both Brønsted acid sites (1545 cm⁻¹) and Lewis acid sites (1450, 1608 cm⁻¹), were observed on Zn₁Zr₃₀O₂-1st gen. When Zn/Zr ratio increased from 1/30 to 1/10, the surface Brønsted acid sites decreased slightly, but the Lewis acid sites changed to a greater extent. This can be evidenced by the shift of the peak from 1446 to 1452 cm⁻¹. Upon further increase of Zn/Zr ratio to 1/2, only slight changes for Lewis acid sites but noticeable reduction of Brønsted acid site was observed. Combined with the NH₃-TPD results, it was clear that as Zn/Zr increases, ZnO first covered mainly the strong Lewis and possibly strong Brønsted acid sites on ZrO₂ (O-Zr⁺-O) and then passivated medium Brønsted acid sites. The improved medium and weak acid sites on Zn₁Zr₁₀O₂-1st gen. also suggested that the addition of a

suitable amount of ZnO facilitated the formation of new Lewis acid sites with medium strength possibly via facile creation of oxygen vacancy on the $\text{Zn}_x\text{Zr}_y\text{O}_z$ -1st gen. mixed oxides.

Fig. 3. The distribution of surface acidity identified by NH₃-TPD A) and IR-Py spectra B) of the $\text{Zn}_1\text{Zr}_{10}\text{O}_z$ -1st gen. catalysts with different Na loadings. (Conditions: Pretreatment: 450°C for 30 min, Spectra taken after desorption at 250°C for 30 min, spectra taken at 50°C).

As a strong base, like other alkali metals, Na has been widely used to titrate surface acidic sites. Na has also been reported to add additional basic sites to catalytic surfaces [33-35]. It was hypothesized that Na doping on these $\text{Zn}_x\text{Zr}_y\text{O}_z$ -1st gen. catalysts would reduce the number of acidic sites that catalyzed the undesired ethanol dehydration to ethylene. Herein, we doped the best performing catalyst – $\text{Zn}_1\text{Zr}_{10}\text{O}_z$ -1st gen. – with Na (2000 ppm and 3000 ppm loading) to further suppress unwanted acid sites that catalyzed ethylene formation. NH₃-TPD revealed that as Na loading increased, the total number of acid sites decreased. Furthermore, the distribution of acidity changed significantly. The strength of acid sites shifted from strong and medium, to medium and weak. As shown in Figure 3A, when Na was 2000 ppm, all of the strong acidic sites were blocked as indicated by the increase in the medium sites. Further increasing Na to 3000 ppm significantly reduced the number of medium acid sites and increased the number of weak ones. IR-Py results revealed that, upon addition of 500 ppm Na, the intensity of peaks representing both Brønsted and Lewis acid sites decreased. Further adding Na only slightly reduced both Brønsted and Lewis acid sites. Even with 2000 ppm Na, both types of acidities could be differentiated.

The results of NH_3 -TPD and IR-Py suggested that Na doped both the strong Brønsted and Lewis acid sites.

3.2 Activity testing

3.2.1 Effect of Zn/Zr ratio

Fig. 4. Effect of Zn/Zr ratio on 1,3-butadiene selectivity over $\text{Zn}_x\text{Zr}_y\text{O}_2$ -1st gen. (Conditions: 100 mg catalyst, $P_{\text{EtOH}} = 2.5\%$ 100% EtOH, W/F 0.23 s.g./mL, WHSV = 0.789 g EtOH/g cat hr⁻¹, T = 350°C. Note: W/F = Weight of catalyst/flow of reactant ratio. Other minor products from intermediates' side reactions included methane and carbon dioxide, propene, isobutene, acetic acid, and acetone, diethyl ether, and 1-butanol. Selectivity to all minor products were < 10%).

Because Zn and Zr both have different acidic and basic properties [27], varying the Zn/Zr ratio was hypothesized to have an effect on the delicate acid-base balance and in turn, be used to determine the optimal ratio for 1,3-butadiene yield. As the Zn/Zr ratio increased for $\text{Zn}_x\text{Zr}_y\text{O}_2$ -1st gen. catalysts, dehydration activity (i.e., ethylene selectivity) decreased and dehydrogenation activity (i.e., acetaldehyde and its secondary products like 1,3-butadiene) increased monotonically. The decreasing dehydration activity matched well with the decreased strong acid sites when Zn/Zr ratio increased from 1/30 to 1/10. This was evidenced by the aforementioned NH_3 -TPD and IR-Py results. Interestingly, as Zn/Zr increased from 1/10 to 1/2, dehydration activity further decreased while Lewis acid sites barely changed. Instead, medium Brønsted acid sites reduced significantly, suggesting that ethanol dehydration activity is higher on Brønsted acid sites than on Lewis acid sites. While the decreased Brønsted acid sites mitigated the ethanol dehydration side reaction, the secondary acetaldehyde to butadiene reaction became less

favorable, evidenced by the decreased yield to 1,3-butadiene and increased acetaldehyde. It suggested that Brønsted acid sites could be beneficial to the acetaldehyde to butadiene reaction.

To further confirm this hypothesis, we designed $\text{Zn}_x\text{Zr}_y\text{O}_z$ -2nd gen. catalysts with no surface Brønsted acidity, confirmed by IR-Py (Fig. S1A). Activity data showed that ethylene selectivity on $\text{Zn}_x\text{Zr}_y\text{O}_z$ -2nd gen. catalysts is ~21%, which is much lower than that of $\text{Zn}_x\text{Zr}_y\text{O}_z$ -1st gen, indicating the lower dehydration activity of Lewis acidity than Brønsted acidity. More importantly, only minor amounts of butadiene were produced, and instead selectivity to acetaldehyde reaches up to ~50% (Fig. S1B) with appreciable amounts of crotonaldehyde being formed (7%). It further confirmed that that Brønsted acidity indeed played a key role in the further conversion of acetaldehyde to 1,3-butadiene via crotonaldehyde intermediate. This agrees with Ordonsky's work over magnesia and zirconia over silica [36].

In addition, other minor products included acetone, isobutene, 1-butanol, and ethyl acetate. Acetone and isobutene are from the ketonization of acetaldehyde and aldolisation of acetone reaction mechanism in the presence of water formed from ethanol dehydration, which has been addressed in our previous work [27]. Ethyl acetate is formed from the reaction between ethanol and acetic acid formed during the ketonization of acetaldehyde reaction [30].

It should be mentioned that, despite the varied Zn/Zr ratio, ethylene selectivity (>25% for $\text{Zn}_1\text{Zr}_2\text{O}_z$ -1st gen.) was still much higher than that of the ethanol-to-isobutene (ETIB) reaction (e.g, <10% vs 50% on $\text{Zn}_1\text{Zr}_{10}\text{O}_z$ -1st gen.). In the ETIB case, an ethanol aqueous solution (H_2O molar ratio/ethanol = 10) was used as feedstock while pure anhydrous ethanol is used in this reaction. The low ethylene selectivity was due to the weakened surface acidity by H_2O [5].

3.2.2 Effect of Na Doping

Fig. 5. Effect of Na doping on 1,3-butadiene selectivity over $\text{Zn}_1\text{Zr}_{10}\text{O}_z$ -1st gen.. (Conditions: $P_{\text{EtOH}} = 2.5\%$ 100% EtOH, W/F 0.23 s.g./mL, WHSV = 0.789 g EtOH/g cat hr^{-1} , $T = 350^\circ\text{C}$).

In order to minimize ethylene selectivity and maximize 1,3-butadiene selectivity, $\text{Zn}_1\text{Zr}_{10}\text{O}_z$ with the best performance for 1,3-butadiene production was used for Na doping to suppress strong acidic sites. Several Na dopant loading levels were screened (500, 1000, 2000, 3000 ppm) on $\text{Zn}_1\text{Zr}_{10}\text{O}_z$ -1st gen. Consistent with NH_3 -TPD results that all the strong acid sites on $\text{Zn}_1\text{Zr}_{10}\text{O}_z$ vanished when $\text{Na} > 500$ ppm, the ethanol dehydration to ethylene dropped by almost 50%, namely from 50 to 25%. Meanwhile, both acetaldehyde and butadiene increased. 2000 ppm Na doping demonstrated the lowest ethylene selectivity (16%) coupled with a 1,3-butadiene selectivity of 41%. Further Na doping (i.e. 3000 ppm loading) neutralized even more medium acid sites, which lowered overall activity, indicating that the delicate balance of acidic sites of various strengths might be needed for optimal performance.

3.2.3 Durability and regeneration of the catalyst

Fig. 6. Effect of deactivation on conversion and main product selectivities. Reaction conditions: 2000 ppm Na doped $\text{Zn}_1\text{Zr}_{10}\text{O}_z$ -1st gen., $P_{\text{EtOH}} = 2.5\%$ 100% EtOH, W/F 0.9 s.g./mL, WHSV = 0.2 g EtOH/g cat hr⁻¹, T = 350°C. Regeneration conditions: T = 450°C, 12 vol% O₂, N₂ balance

Ethanol to 1,3-butadiene has been widely studied over a variety of catalysts. However, the catalyst deactivation and regeneration is rarely reported. Herein, we further studied the catalyst stability and regenerability as shown in Fig. 6. The fresh catalyst showed an initial ethylene selectivity of >25%, and a rapid decrease in ethylene selectivity with time on stream (TOS) was observed. Meanwhile, selectivity to acetaldehyde and 1,3-butadiene increased. After ~2 h of TOS, selectivity to ethylene as well as to acetaldehyde and 1,3-butadiene became stable. The initial rapid decrease of ethylene selectivity indicated the presence of some strong Brønsted acid sites that favor the ethanol dehydration. With TOS, the catalyst lost the strong Brønsted acid sites, which were passivated. This highlights the dehydrogenation pathway to acetaldehyde and 1,3-butadiene. Interestingly, although the selectivity to acetaldehyde and 1,3-butadiene remained constant, the selectivity to 1,3-butadiene decreased slowly with the concurrent increase of acetaldehyde. This suggested that the catalyst lost active sites for acetaldehyde to 1,3-butadiene conversion. In order to understand what caused the deactivation, cyclic stabilities were investigated. A loss of 20% in conversion and 1,3-butadiene selectivity was defined as a cycle. The

length of the first cycle was nearly 60 hours, and the length of the second was 30 hours. It was found that the reactivity could be recovered in 30 minutes at 450 °C in the presence of ~ 12 vol% O₂. This suggested that the deactivation of the catalyst was mainly due to the coking of the active sites for secondary acetaldehyde to 1,3-butadiene reaction. Slow deactivation and repeatable regenerations make this Na doped catalyst a desirable one for 1,3-butadiene production.

3.3 Comparison of 2000 ppm Na doped Zn₁Zr₁₀O₂-1st gen. and Cu doped MgO-SiO₂ catalyst systems for ethanol to 1,3-butadiene conversion

Fig. 7. Catalytic activity comparison of Cu doped MgO-SiO₂ and 2000 ppm Na doped Zn₁Zr₁₀O₂-1st gen. (Conditions: P_{EtOH} = 2.5% 100% EtOH, T = 350°C. For Cu-doped MgO-SiO₂: WHSV = 0.3 g EtOH/(gcat*hr). For 2000 ppm Na doped Zn₁Zr₁₀O₂-1st gen.: WHSV = 6.2 g EtOH*(g_{cat}⁻¹*hr⁻¹)).

As abovementioned, many studies have been done on the catalytic conversion of ethanol to 1,3-butadiene, especially with the MgO-SiO₂ system. In order to understand how our Zn_xZr_yO_z system compared to a well reported catalyst system, a Cu-doped MgO-SiO₂ catalyst with one of the top selectivities to 1,3-butadiene reported was synthesized with a few precursors from different sources [19]. At ~50% conversion, although the Cu doped MgO-SiO₂'s 1,3-butadiene selectivity is slightly higher than our catalyst (40 % vs. 26 %), there was a marked difference between the overall activities of these two

catalysts. The 2000 ppm Na doped $\text{Zn}_1\text{Zr}_{10}\text{O}_z$ -1st gen. produces 0.49 g C_4H_6 /g catalyst each hour while the Cu doped MgO-SiO_2 gives 0.04 g C_4H_6 /g catalyst each hour.

Catalyst	T_{reaction} (°C)	Conver- sion (%)	WHSV (h ⁻¹)	Selectivity			Productivity [g C_4H_6 /g $\text{cat}^{-1}\text{hr}^{-1}$]	References
				C_2H_4	CH_3CHO	C_4H_6		
2.0Ag/Mg O-SiO ₂	400	50	1.2	2	24	41	0.15	[25]
CuO _x /MgO -SiO ₂	400	86.3	0.73	12		53	0.2	[19]
AgO _x /MgO -SiO ₂	400	91.8	0.73	12		54	0.2	[19]
2000 ppm Na doped $\text{Zn}_1\text{Zr}_{10}\text{O}_z$ - 1 st gen.	350	97	0.2	15.9	11	47	0.06	This work
2000 ppm Na doped $\text{Zn}_1\text{Zr}_{10}\text{O}_z$ - 1 st gen.	350	54.4	6.2	28	37	26	0.49	This work
$\text{Zn}_1\text{Zr}_{10}\text{O}_z$ - 1 st gen.	350	98	0.8	51	11	26	0.06	This work

Table 1. Comparison of 1,3-butadiene productivity for top performing catalysts reported in recent literature.

The 2000 ppm Na doped $\text{Zn}_1\text{Zr}_{10}\text{O}_z$ 1st gen. catalyst was also compared with MgO-SiO_2 based catalysts under each catalyst's best conditions reported in literature, and the experimental results such as conversions, selectivities, and productivities are summarized in Table 1. In terms of catalyst activity, it clear that $\text{Zn}_x\text{Zr}_y\text{O}_z$ -1st gen catalyst out performs other reported catalysts with space-time-yield reaching up to 0.49 g C_4H_6 ·g $\text{cat}^{-1}\text{hr}^{-1}$.

4. Conclusions

A combination of employing Zn/Zr ratio and Na doping was found to be efficient to control the surface basicity and acidity, as confirmed by NH_3 -TPD and IR-Py. While $\text{Zn}_1\text{Zr}_{10}\text{O}_z$ -2nd gen. with only Lewis acid-base pairs produced a wide variety of products, a well-balanced basicity and Brønsted acidity on $\text{Zn}_1\text{Zr}_{10}\text{O}_z$ -1st gen. was found to be efficient to suppress the ethanol dehydration and favor the reaction

pathway to ethanol dehydrogenation and the aldol-condensation pathway toward 1,3-butadiene. 2000 ppm Na doped $\text{Zn}_1\text{Zr}_{10}\text{O}_z\text{-1}^{\text{st}}$ gen. gave among the top selectivities to 1,3-butadiene – 47 mol%. Most importantly, this catalyst exhibits a much higher 1,3-butadiene productivity than other mixed oxides studied. Although the 2000 ppm Na doped $\text{Zn}_1\text{Zr}_{10}\text{O}_z\text{-1}^{\text{st}}$ gen. catalyst suffers deactivation via coking, it can be readily regenerated in air.

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Graphical Abstract

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