Applied Catalysis A, General 558 (2018) 150–160

Contents lists available at ScienceDirect

Applied Catalysis A, General

journal homepage: www.elsevier.com/locate/apcata

Influence of different precursors on isobutene production from bio-ethanol over bifunctional $Zn_1Zr_{10}O_x$ catalysts

Biao Zhao[a], Yong Men[a,*], Anni Zhang[b], Jinguo Wang[a], Rong He[a], Wei An[a], Shenxiao Li[a]

[a] *College of Chemistry and Chemical Engineering, Shanghai University of Engineering Science, Shanghai, 201620, PR China*
[b] *School of Science, Beijing Jiaotong University, Beijing, 100044, PR China*

ARTICLE INFO

Keywords:
Bio-ethanol
Isobutene
Precursors
Bifunctional catalyst
Cascade reaction

ABSTRACT

The effects of zinc precursors on the performance of bifunctional $Zn_1Zr_{10}O_x$ catalysts were investigated for direct conversion of bio-ethanol into isobutene (ETIB). The catalyst derived from zinc acetate precursor exhibited full ethanol conversion and 50% isobutene yield at a WHSV of 0.38 $g_{ethanol}\,g_{cat}^{-1}\,h^{-1}$ at 450 °C. Characterization results based on XRD, FT-IR, UV–vis, Raman, BET, CO_2-TPD, NH_3-TPD, H_2-TPR, and XPS revealed that $Zn_1Zr_{10}O_x$ catalyst prepared by zinc acetate precursor with large anion size possessed the highest zinc dispersion and the strong ZnO-ZrO_2 interaction, and presented the highest ethanol reaction rate and isobutene yield under kinetic control regime. The beneficial effect of larger anion size was rationalized by the shielding effect in the incorporation model dominated by the size of capping anion in zinc precursors. Further durability test showed that the catalyst exhibited slow deactivation against coking formation while isobutene yield was maintained above 45% for 18 h.

1. Introduction

Over the last few decades, the increasing depletion of fossil feedstock has led to a large amount of the research works to seek alternative and sustainable biomass-based resources for valuable fuels and chemical production [1]. As an important building block for the chemical industry, isobutene is mainly used in the polymer industry for the production of a variety of products including butyl rubber as tires [2], ethyltert-butyl ether (ETBE) as a gasoline additive [3], tri-isobutenes as an additive for jet fuel [4], and isooctane as an additive to increase the octane number of gasoline [5]. Since the early seventies of last century, the dominant technology for producing isobutene is the steam cracking of naphtha, where isobutene is obtained as a co-product [6–8]. It is noteworthy, however, that the recent shift toward the use of shale gas for ethylene production has triggered significant research interests to produce C4 light olefins via a bio-based route [9]. Due to the increasing use of bio-ethanol as a bio-fuel in the last decade [10], the production of bio-ethanol via the fermentation of sugars and starch is growing to the industrial scale for fuel use [11–13]. So, there is a growing incentive for sakes of both sustainable development and economic need to explore efficient catalytic systems for the conversion of ETIB.

Direct conversion of bio-ethanol into C4 light olefins is quite complex due to the nature of cascade reaction. Direct conversion of bio-ethanol into C4 light olefins (i.e., butadiene (BD), isobutene, 1-butene and 2-butene) has been studied over a variety of catalysts mainly including (mixed) metal oxides and zeolites [3,14–19]. Particularly, direct conversion of ethanol to butadiene developed by Lebedev over various bifunctional catalysts was industrially-proven catalytic process from the 1920s to the early 1960s. Despite the controversy with respect to the detailed mechanism of the multi-step reaction of ethanol to BD, primary reaction steps for the conversion of ethanol to BD may include: (i) ethanol dehydrogenation to acetaldehyde; (ii) aldol condensation of two acetaldehydes to form acetaldol; (iii) Meerwein-Ponndorf-Verley (MPV) type reduction between ethanol and crotonaldehyde to form acetaldehyde and crotyl alcohol; and (iv) the final dehydration of crotyl alcohol to BD [16,17,19]. Among all the catalysts that were suggested to catalyze this process, MgO-SiO_2 samples have been shown to be very effective catalysts for this reaction. To further improve the performance of the cascade reaction catalysts, attempts have recently been made to pursue an adequate acid/basic balance, which is probably determined by several factors, namely the preparation method, thermal treatment, the nature of the precursors and type of heteroatom dopants. For

---

Abbreviations: BET, Brunauer-Emmett-Teller; BJH, Barrett-Joyner-Halenda; S_{BET}, surface areas; V_P, pore volume; D_P, pore diameter; XRD, X-ray diffraction; FT-IR, Fourier transform infrared; Raman, Raman spectroscopy; CO_2-TPD, temperature-programmed desorption with CO_2; NH_3-TPD, temperature-programmed desorption with NH_3; H_2-TPR, H_2 temperature programmed reduction; XPS, X-ray photoelectron spectroscopy; BE, binding energy; TCD, thermal conductivity detector; GC, gas chromatography; ETIB, bio-ethanol to isobutene; ETBE, ethyltert-butyl ether

[*] Corresponding author.
E-mail address: men@sues.edu.cn (Y. Men).

https://doi.org/10.1016/j.apcata.2018.04.003
Received 11 December 2017; Received in revised form 21 March 2018; Accepted 4 April 2018

example, Niiyama et al. argued that it is important to control the acidity and basicity of the catalyst in BD formation from ethanol [20]. Weckhuysen et al. showed that the equimolar MgO-SiO_2 catalysts prepared by wet-kneading was the best performing catalysts due to the appropriate balance among a small amount of strong basic sites, an intermediate amount of acidic sites and weak basic ones [21]. Sels et al. reported an optimal content of 0.66 MgO to achieve 55% BD selectivity with complete ethanol conversion [22]. Our group reported that MgO/SiO_2 (the molar ratio of MgO:SiO_2 was 65:35) using wet-kneading method highly active and selective in terms of ethanol conversion and BD yield, and the preparation methods and catalyst compositions were found to influence significantly on the BD selectivity [19]. The crucial factor to butadiene formation required a subtle optimum ratio of acid-to-base sites to enhance the reactivity, and the formation of interfacial Si—O—Mg linkage in relation to the strong interaction between SiO_2 and MgO was considered to be critical for high performance catalysts.

Most research to date, not surprisingly, is focusing on the selective production of BD from bio-ethanol, whereas there are only few reports on the direct conversion of ETIB. Hutchings et al. reported conversion of acetone to isobutene over ß-zeolite with high selectivity, but the catalyst was deactivated easily due to the coke deposition [23]. Tago et al. found that simultaneous ion exchange of Na, K, Rb and Cs alkali metal ions with BEA zeolites resulted in an active catalyst, giving a high yield (55%) of acetone conversion to isobutene [24]. Iwamoto et al. found formation of isobutene from ethanol on Ni-M41 [25]. Later on, Iwamoto et al. also reported appreciable amounts of isobutene formed over modified In_2O_3 oxide in ethanol to propylene reactions [26,27]. In their case, the effective elimination the strong acidic sites and inhibition the formation of aromatics and coke by the ion exchange were in fact considered to be of the prime importance for its good catalytic activity. By adjusting the acid-base balance, it has been proved to be feasible to produce isobutene from ethanol over bifunctional catalysts. Recently, Wang and co-workers reported for the first time that $Zn_xZr_yO_z$ mixed oxide catalyst with balanced acid-base sites was very active for the direct conversion of ETIB [28,29]. They found that zirconium oxide converted ethanol mostly to ethylene, and zinc oxide converted the ethanol mostly to acetone. When forming $Zn_xZr_yO_z$ mixed oxide, zirconia's strong Lewis acidic sites were selectively passivated and Bronsted acidic sites were also weakened, while basicity was simultaneously introduced. The reaction mechanism was hypothesized to occur through the dehydrogenation of ethanol to acetaldehyde for the first step, followed by condensation and decomposition of acetaldehyde to acetone and then, acetone undergoes self-condensation through an aldol pathway to mesityl oxide or mesityl oxide like surface species as the presumed intermediate [12,23,30], which eventually undergoes a C—C bond cleavage step producing isobutene (Scheme 1). Very recently, Román-Leshkov et al. reported the synthesis of isobutene from bio-derived acetic acid over a $Zn_xZ_yO_z$ binary metal oxide via a three-step cascade reactions involving condensation and decomposition, aldol-condensation and C—C hydrolytic bond cleavage reactions, with the highest yield of 50% isobutene on the optimal $Zn_2Zr_8O_z$ catalyst [31]. Our recent experimental and theoretical studies highlighted the key role of $Cr^{\delta+}$ in promoting ethanol-to-acetaldehyde dehydrogenation and therefore the production of isobutene thanks to redox capability of $Cr^{\delta+}$. For the synergistic effect to work, it requires the structure of a composite that provides highly dispersed Cr and Zn species, and a proper surface acid/base balance and favourable redox properties on the surface of $Cr_xZn_yZr_zO_n$ composite catalysts [32].

In this work, a series of binary catalysts ($Zn_1Zr_{10}O_x$) were prepared by impregnating $Zn(NO_3)_2$, $Zn(Ac)_2$, and $ZnCl_2$ precursors over $Zr(OH)_4$. The influence of the different zinc precursors on the activity of bifunctional catalysts ($Zn_1Zr_{10}O_x$) for ETIB was investigated at a temperature range of 400–550 °C and a steam to carbon (S/C) ratio in a range of 1–5. The surface acid/basic property, zinc dispersion and the surface reducibility were characterized using various techniques including CO_2-TPD, NH_3-TPD, H_2-TPR, and XPS. As a result, we were able to gain insight into the principles required for the rational design of a high-performance ETIB catalyst by correlating the acidic–basic property, zinc dispersion, and their catalytic performance. Kinetic study and stability test were also carried out to examine the origin of the activity difference of the $Zn_1Zr_{10}O_x$ catalysts.

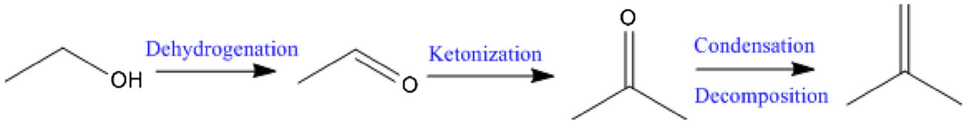
2. Experimental section

2.1. Catalyst preparation

$Zn_1Zr_{10}O_x$ mixed oxides were synthesized using the incipient wetness impregnation method. $Zn(NO_3)_2$, $Zn(Ac)_2$ and $ZnCl_2$ and $Zr(OH)_4$ were purchased from Aladdin Chemistry Co. Ltd. (Shanghai, China) and used as received without further purification. $Zr(OH)_4$ was used as supports and initially dried overnight at 110 °C to remove any excess water on the surface before impregnation. In a typical synthesis, 2.5 ml aqueous solution of Zn-salts (0.00152 mol of Zn-salts, $Zn(NO_3)_2$, $Zn(Ac)_2$ and $ZnCl_2$) were added on 0.0152 mol of $Zr(OH)_4$ to achieve wet impregnation, respectively. After impregnation, the catalysts were dried overnight at room temperature followed by 4 h at 105 °C. The catalysts were further heated to 400 °C (3 °C /min) and held for 2 h followed by a 5 °C /min ramp to the final calcinations temperature (i.e., 550 °C) and held for 3 h [33]. The catalysts synthesized by zinc acetate, zinc nitrate, and zinc chloride are labeled as Zn–Ac, Zn–N, and Zn–Cl, respectively.

2.2. Catalyst characterizations

At 77K N_2 adsorption-desorption isotherms were determined by applying the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) models to the desorption branches after a pre-treatment at 120 °C for 6 h in He flow, with a Micromeritics ASAP 2460, where the specific surface areas (S_{BET}), pore volume (V_P) and pore diameter (D_P) were calculated. The crystallites phases were detected through X-ray diffraction (XRD) technique (BRUKER D2 PHASER) using a Cu K_α radiation ($\lambda = 1.54056$ Å) generated at 30 kV and 10 mA, and recorded at 2θ values in the range of 5–80° with a scanning rate of 4.0° min^{-1}. Fourier transform infrared spectroscopy (FT-IR) was recorded using a Nicolet 380 spectrometer (USA) infrared spectrometer with KBr pellets at room temperature. A certain amount of samples were mixed with dried KBr and pulverized in a mortar. The mixture was then pressed into a pellet, which was quickly transferred to in the IR cell to record the IR spectrum in the range of 400–4000 cm^{-1} (A spectrum of the empty infrared cell was used as the instrument background). The Raman spectra were obtained using a Renishaw Raman InVia Microscope (Spectra-Physics model 163), operated at the argon ion laser with a wavelength of 532 nm. X-ray photoelectron spectra (XPS) of the catalysts were obtained with a VG Microtech Multilab ESCA 3000 spectrometer using a non-monochromatized Mg-Kα X-ray source. The UV–Vis absorbance spectra were performed in the range 200–450 nm wavelength range with UV-2450 spectrophotometer (Shimadzu, Japan) using $BaSO_4$ as a background, in air at room temperature. Ammonia temperature-programmed desorption (NH_3-TPD), using Micromeritics Autochem II 2920, was used to investigate the properties of the acidic



Scheme 1. Commonly proposed mechanism for the conversion of ethanol into isobutene.