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



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<i>Keywords:</i> Bio-ethanol Isobutene Precursors Bifunctional catalyst Cascade reaction	The effects of zinc precursors on the performance of bifunctinal $Zn_1Zr_{10}O_x$ 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 in- corporation 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 bioethanol 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-SiO₂ 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

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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; CO₂-TPD, temperature-programmed desorption with CO₂; NH₃-TPD, temperature-programmed desorption with NH₃; H₂-TPR, H₂ 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

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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-SiO₂ 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/ SiO₂ (the molar ratio of MgO:SiO₂ 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 acidto-base sites to enhance the reactivity, and the formation of interfacial Si-O-Mg linkage in relation to the strong interaction between SiO₂ 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_vO_z binary metal oxide via a threestep 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 Zn₂Zr₈O_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 CO₂-TPD, NH₃-TPD, H₂-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 ZnCl₂) 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 N₂ 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_a 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 $400-4000 \text{ cm}^{-1}$ (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-Ka 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 BaSO₄ as a background, in air at room temperature. Ammonia temperature-programmed desorption (NH₃-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.

sites of the catalysts. In the characterization, about 50 mg of a sample was loaded into a U-type quartz tube reactor and ramped from room temperature to 500 °C with a heating rate of 10 °C /min under flowing helium of 50 ml min⁻¹. Next, the catalyst was maintained at 500 °C for 30 min, then cooled to 50 °C until it was stabilized. After that, NH₃ adsorption were conducted under 5% NH₃/He (50 ml min⁻¹) at 50 °C for 1.0 h, and sample heated from 50 to 600 °C at a heating rate of 10 °C min⁻¹. The variation of the ammonia gas uptake was monitored by a thermal conductivity detector (TCD). The peak area in the TPD profiles quantified the molar NH₃ uptake per gram of catalyst and calibrated with Ag₂O standard. The basic properties of the catalysis were determined by temperature-programmed desorption with CO₂ (CO₂-TPD) as probing molecule. The methods of CO₂-TPD and H₂ temperature programmed reduction (H₂-TPR) were similar to NH₃-TPD. CO₂ adsorption was conducted under 5% CO2/He at 50 °C for 1 h. H2-TPR was employed to analyze the reduction behavior of the samples. The samples were preheated at 500 °C (ramping rate 10 °C min⁻¹) for 30 min under flowing Ar (40 mL min⁻¹), then cooled to 50 °C. After that, H2-TPR experiment was started from 50 to 800 °C with heating rate of 10 °C min⁻¹ under continuous flow of 40 ml min⁻¹10% H₂/Ar.

2.3. Catalytic activity measurements

The ETIB experiments were evaluated in a fixed bed continuous downstream flow reactor containing a tubular quartz reactor (i.d. 5.0 mm). Typically, the experiments were performed at 400–550 °C and atmospheric pressure. Prior to reaction, 200 mg pelletized catalyst sample (size range: 40–60 mesh) was pretreated in N₂ (40 ml/min) at 450 °C for 0.5 h. The flow rate of N₂ was regulated by mass flow controllers. Liquid mixture of ethanol/H₂O (steam/carbon ratio = 1, 2.5, and 5) was injected into a gasification chamber (200 °C) with a liquid pump and then thoroughly mixed with flowing carrier gas of N₂. After that, the reactants were fed to the reactor and ETIB was performed under the conditions of T = 400 °C, 425 °C, 450 °C and so on, P = 1 atm and WHSV = 0.381 g_{ethanol} g_{cat}⁻¹ h⁻¹ otherwise it was specified additionally. Full product was analyzed by the online Shimadzu 2014 Gas Chromatography (GC) with three analyzing channels. The ethanol conversion and product selectivity were defined as follows:

$$Conversion = \frac{(Ethanol_{in} - Ethanol_{out})}{Ethanol_{in}} \times 100\%$$
(1)

$$Selectivity = \frac{(Carbon \text{ in given product})}{(Carbon \text{ in all products})} \times 100\%$$
(2)

$$Yield = Conversion \times Selectivity \times 100\%$$
(3)

It should be noted that therefore all results reported in this work are almost equivalent to those reported by Wang et al. [28].

3. Results and discussions

3.1. Catalyst characterization

3.1.1. Surface area/Pore size

Nitrogen sorption-desorption isotherms and the pore size distributions of the as-prepared $Zn_1Zr_{10}O_x$ binary oxide catalysts are illustrated in Fig. 1 (A) and (B), respectively. Zn-Ac, Zn-N, and Zn-Cl samples display the typical type IV isotherm with H3 hysteresis loops in the relative pressure (P/P₀) range from 0.6 to 1.0 [34]. Those types of hysteresis loops are associated with capillary condensation in mesopores signifying the preservation of the mesoporous structure. BET surface areas derived from analysis of the isotherms result to be 90.0, 36.3 and 63.7 m²/g for Zn-N, Zn-Ac, and Zn-Cl samples, respectively. As can also be seen in Table 1, BET surface areas of binary oxide catalysts are closely dependent on the nature of the zinc precursors and anion size. Fig. 1 (B) also shows the effect of different zinc precursors on the average pore sizes of samples. The corresponding pore size distribution curves showed a relatively narrow pore diameter range centered at about 4 nm. The above results indicate that mesoporosity is more likely due to interparticle porosity.

3.1.2. Crystallinity

The crystal structures of the samples are shown in Fig. 2. All catalysts present the typical XRD patterns, especially for the catalyst Zn-Cl that is visibly observed between monoclinic (PDF#65-1024) and tetragonal (PDF#50-1089) phase from ZrO₂. For the Zn-Ac and Zn-N catalysts, tetragonal (PDF#50-1089) phase are both detected; and moreover, the Zn-Ac and Zn-N catalysts contained a small fraction of monoclinic (PDF#65-1022) phase, which is in good agreement with the results of Raman characterizations (Fig. S1). ZnO diffraction signals cannot be detected in all catalyst samples, suggesting a high ZnO dispersion and the formation of particles smaller than the detection limit (1–2 nm) in the XRD technique [35,36].

Not only does the difference of precursors alter crystalline phases and crystallite size, but also affect crystallinity, that, for example, in the case of the Zn-N sample, results to be lower crystallinity than Zn-Ac catalyst (see Fig. 2). Based on the XRD results, it can be understood that, depending on different precursors, a different degree of aggregation or growth of ZrO_2 crystallite and the different crystalline phases are obtainable. These observations are consistent with previous works [37].

3.1.3. Surface group

FTIR measurements are used to identify the presence of functional groups on the surface of synthesized samples. The peak observed near 3430 cm⁻¹ is attributed to the stretching vibration of hydrogen bonded hydroxyl groups due to physically adsorbed H₂O [38], and the band located at 1627 cm⁻¹ is assigned to the bending vibration of coordinated water molecules in Fig. 3 [39]. The band around 1383 cm⁻¹ is ascribed to the absorption of non-bridging OH groups [40]. However, Zn-Cl showed the absence of OH groups at 1383 cm⁻¹. Usually, the bands at 499 and 741 cm⁻¹ are assigned to the Zr-O peaks due to ZrO₂. monoclinic structure [41]. In Zn-Cl, the peaks around 577 cm^{-1} can be assigned to the Zr-O modes in tetragonal ZrO2. In Zn-Ac and Zn-N, however, no bands were found over monoclinic ZrO2 at 499 and 741 cm⁻¹ and tetragonal ZrO₂ at 577 cm⁻¹. Characteristic peaks in the ZrO_2 crystal did not appear in Zn-Ac and Zn-N between 800– 400 cm⁻¹ probably because they have much smaller crystallite size that is beyond the scope of FTIR detection or limited monoclinic ZrO₂. It is clear that the crystalline phase of the product ZrO₂ can be controlled by the selection of a suitable precursor. Interestingly, the results of crystal phase analysis obtained using X-ray powder diffraction show much lower crystallinity of monoclinic ZrO2 than tetragonal ZrO2 in Zn-Cl, but, characteristic peaks intensity of monoclinic ZrO_2 at 499 and 741 cm⁻¹ is much stronger than that of tetragonal ZrO_2 near 577 cm⁻¹, which indicated the monoclinic ZrO₂ is much more FTIR active so that FTIR spectroscopy can be useful for measuring the small fraction of the monoclinic phase in tetragonal/monoclinic ZrO₂.

The UV–vis diffuse reflectance spectra of $Zn_1Zr_{10}O_x$ samples with different zinc precursors are shown in Fig. 4 as a function of the wavelength. The absorbance is probably determined by several factors, namely oxygen deficiency, size and structure of nanoparticles, band gap, impurity centers, metal coordination, the geometry and surface roughness [42]. Notably, all the samples show a broad absorption band in the UV range of 250–380 nm, which is mainly associated with oxygen-related defects, such as single charged F centres (F⁺ centres) and 2p orbital of O^{2−} ions [43,44]. The absorption strength followed the order of Zn–Ac > Zn–N > Zn–Cl, which can be well correlated with the anion size of zinc precursors. The lower absorption between 250–380 nm indicated a lower concentration of oxygen-related defects formed on catalyst surface. The Zn-Ac and Zn-N related the corresponding absorption edges locate at around 380 nm, whereas Zn-Cl



Fig. 1. N₂ adsorption-desorption isotherms (A) and the pore-size distribution (B) of catalysts Zn₁Zr₁₀O_x catalysts from different precursors.

hardly exhibits absorption edge due to the low dispersion of ZnO components from the composites, which leads to the decrease in oxygen-related defects [45]. Intense absorption below 400 nm is known as a strong absorption of ZnO and absorption bands are observed in the range of 200–250 nm, which corresponds to the light absorption from the ZrO₂ components [43,46].

3.1.4. Surface composition

The catalysts surface composition and oxidation state were investigated by XPS. All the XPS spectra were referenced to the C1s at binding energy (BE) of 284.8 eV. In Fig. 5A, it can be noticed that these samples exhibit Zn 2p3/2 and Zn 2p1/2 doublet at the BE of 1021.9 eV and 1045.0 eV, respectively, and characteristic Zn²⁺ 2p final state, suggesting the predominant presence of Zn^{2+} on catalyst surface. And as shown in Fig. 5 B, the main Zr 3d spectrum component at BE of 181.5 eV and 183.8 eV were assigned to Zr^{4+} ion in ZrO_2 . It is worthwhile to mention that the peak positions of Zn 2d shift remarkably to the higher binding energy with increasing of the anion size of zinc precursor, indicating the strong interaction between ZnO and ZrO₂ (Table 2). The similar trend was observed in the Zr 3d spectra. The energy shift trends of Zn and Zr might be caused by substitution of Zn²⁺ into the ZrO₂ lattice [47]. Similar results have been observed in earlier articles [48]. The XPS intensity ratio of Zn 2p/Zr 3d values for various $Zn_1Zr_{10}O_x$ catalysts are summarized in Table 2. As the loading of the zinc oxide remained identical in the final catalysts, the ratio of Zn 2p/Zr 3d from different $Zn_1Zr_{10}O_x$ catalysts may reflect the zinc dispersion on zirconia support. It is found that the intensity of Zn 2p/Zr 3d peaks decreases with the sequence of Zn-Ac > Zn-N > Zn-Cl. In



Fig. 2. XRD patterns of $Zn_1Zr_{10}O_x$ catalysts with different precursors.

combination with the H₂-TPR and UV–vis results, it can be concluded that Zn-Ac possesses the highest dispersity of bivalent zinc species among these three samples. Fig. 5 C displays the O_{1s} XPS spectra of all the samples and the peaks centered at 529.6 and 531.3 eV were assigned to the oxygen in the ZrO₂ lattice (O_L) and the surface-chemisorbed oxygen species (O_C, i.e., O²⁻, O⁻, OH⁻), respectively [49]. Obviously, the ratio of O_C/O_L gradually increased with the increase in anion size of the zinc precursors, which is in good agreement with the results of UV–vis, as shown in Fig. 4.

Table	1
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Physical and	chemical	parameters o	of Zn ₁ Zr ₁	οO _v c	atalvsts

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Catalysts	S _{BET} (m ² /g)	V _p (cm ³ /g)	D _p (nm)	$V_p(cm^3/g)$ $D_p(nm)$ Crystallite size(nm) ^a	Crystallite size(nm) ^a	Number of acid and basic (cm^3/m^2)		Number of acid and basic (cm ³ /m ²)		T_B/T_A	$\Delta T(^{\circ}C)^{d}$
					Total acid ^b (T _A)	Total base ^{c} (T _B)					
Zn-Ac	36.3	0.14	11.0	13.6	0.13	0.13	1.04	99.4			
Zn-N	90.0	0.19	7.1	11.2	0.14	0.11	0.78	129.5			
Zn-Cl	63.7	0.17	8.4	16.1	0.18	0.05	0.27	189.5			

^a ZrO₂ crystallite sizes are calculated by Scherrer equation using the XRD peak at $2\theta \approx 30.4^{\circ}$.

^b Number of acid site is quantified by NH₃-TPD.

^c The number of the basic sites is quantified by CO₂-TPD.

 d ΔT means the temperature difference between the reduction peak of zinc and the reduction peak of zirconium.



Fig. 3. FT-IR spectra of various $Zn_1Zr_{10}O_x$ samples with different precursors.



Fig. 4. Diffuse-reflectance UV–vis spectra of the as-prepared $\mathrm{Zn_1Zr_{10}O_x}$ samples.

3.1.5. Basicity/Acidity

In general, the acid–base chemistry of the oxides are affected by the addition of dopants such as transition metals and metal oxides that alter adsorbate-binding strength and generating coordination unsaturated oxygen vacancies/metal cations [31,50]. Besides, crystallinity, crystallite size, concentration of heteroatom dopants, and so on can modulate the acid–base properties of metal oxides [50–52]. At the same time, the results of phase analysis obtained using X-ray powder diffraction identified difference of crystallite size and crystallinity and the change of crystalline phases due to different precursors. As such, different zinc precursors on the $Zn_1Zr_{10}O_x$ catalysts can change the acid–base chemistry of the oxides surface. Similar results have been observed in the previous reports [53].

In order to shed lights on the role of both basic and acidic sites involved in isobutene synthesis reaction, CO_2 -TPD and NH_3 -TPD measurements were carried out to determine the distribution of surface acidity and basicity and the number of acidic and basic sites of the various investigated catalysts. The desorption profiles were shown in Fig. 6 and quantitative data was summarized in Table 1. In Fig. 6A, two broad desorption peaks of NH_3 were resolved near 107 °C and 259 °C for all catalysts, which were attributed to NH_3 chemisorbed on weak and medium acidic sites, respectively. However, the strong acid sites have not been observed, which might be passivated by zinc oxide due to the



Fig. 5. X-ray photoelectron spectra of $Zn_1Zr_{10}O_x$ showing the characteristic peaks of A) Zn, B) Zr, and C) O.

strong interaction of zinc and zirconium oxide [33]. The remarkably enhanced acidic sites were found over Zn-Cl, which might be due to residual chloride affecting significantly on acid-base properties of the composite catalysts as evidenced by the residual chloride on the Zn–Cl detected by XPS in our and also Touroude's study [54]. In conclusion, there were mainly two NH₃ desorption peaks for $Zn_1Zr_{10}O_x$ catalysts, which indicated that two types of adsorption sites with different acidity coexisted on the surface of the solid samples.

Table 2 Summary of XPS results for $Zn_1Zr_{10}O_x$ catalysts.

Catalysts	Zn/Zr	Zn/Zr/O ratio	Positions(eV)		
			Zn 2p _{3/2}	Zr 3d _{5/2}	OL
Zn-Ac Zn-N Zn-Cl	0.30 0.25 0.19	1/3.3/8.9 1/4.0/10.4 1/5.2/13.0	1022.0 1021.6 1021.5	181.9 181.7 181.5	529.6 529.5 529.5

The strength and the amount of surface basic sites on mesoporous $Zn_1Zr_{10}O_x$ nano-oxides also have been studied by CO_2 -TPD, showing that the basicity was greatly affected by the different precursors. All the results were summarized in Table 1. As shown in Fig. 6B, three different basic sites coexisted on the surface of Zn₁Zr₁₀O_x catalysts, which were attributed to the special structure of the samples. The total number of basic sites from different samples followed the order of Zn - Ac >Zn - N > Zn - Cl, which is consistent with the anion size in the zinc precursors. Thus, a broad weak basic sites attributed to CO₂ desorption peak existed at around 103 °C on all catalysts. Desorption peaks of CO2 centered are shown on all samples in 415 °C, representing strong basic sites. The strong basic sites might be generated by the incorporation of Zn^{2+} in the t-ZrO₂ and m-ZrO₂ lattice, and such active sites were firmly anchored to the vacant site on the substrate. This type of basic sites was highly resistant to structural collapse, which led to the $Zn_1Zr_{10}O_y$ catalysts with extraordinary activity and durability (see Fig. 13).

3.1.6. Reducibility

The reducibility and interaction between Zn^{2+} and support Zr^{4+} of the catalysts synthesized by incipient wetness impregnation method are studied by H₂-TPR. As shown in Fig. 7, all catalysts exhibit two H₂ consumption peaks. The H₂ consumption shoulder peak around 432 °C can be attributed to the reduction of Zn^{2+} ions incorporated into octahedral vacancies, surface vacant sites on the exposed plane of ZrO_2 [32,55]. The second one exhibited a rather broad TPR peak with a shoulder in the temperature range 423–573 °C, corresponding to hydrogen consumption from the ZrO₂ surface [32,56]. The position of T_{max1} remains almost unchanged, while T_{max2} is slightly shifted to lower temperatures with increasing anion size of zinc precursors. It is important to note that the temperature difference between these two reduction peaks decreased with the increasing anion size of zinc precursors, which indicates that the strong interaction between Zn and Zr



Fig. 7. H2-TPR profile for various catalysts including Zn-Ac, Zn-N and Zn-Cl.

is responsible for the shift of the reduction of ZrO_2 to a lower temperature. In other words, the addition of different Zn precursors brings about different contact and interaction over ZrO_2 surface, and modifies the redox performance on the catalyst surface. Obviously, the catalyst prepared from largest zinc precursor is most redox active due to the strongest interaction among these three composite catalysts.

3.2. Catalytic performances

The effect of the zinc precursors on the catalytic behavior of the $Zn_1Zr_{10}O_X$ oxides catalysts were tested for ETIB reaction at 450 °C and S/C ratio of 2.5, and the results measured at steady state of reaction were shown in Fig. 8. A complete ethanol conversion was achieved under the reaction conditions employed over the three catalysts. By contrary, the differences between three catalysts are evident in terms of product selectivity. The similar products obtained under the conditions used in this experiment were methane (i.e. crack of acetone and target isobutene), acetaldehyde (formed by dehydrogenation of the raw material ethanol), acetone (condensation and decomposition pathway of the primary products acetaldehyde), carbon dioxide (by-product of prepared acetone and isobutene), isobutene (the desired product) ethylene (dehydration of ethanol) and C3 light olefins. In the case of the



Fig. 6. NH_3 -TPD (A) and CO_2 -TPD (B) profile for various $Zn_1Zr_{10}O_x$ catalysts with different precursors.



Fig. 8. The product distribution at 450 °C on $Zn_1Zr_{10}O_X$ oxides catalysts with different precursors. Reaction condition: $m_{cat} = 200 \text{ mg}$, S/C = 2.5, WHSV = 0.381 $g_{ethanol} g_{cat}^{-1}h^{-1}$, $x_{ethanol} = 1.51 \text{ mol } \%$, P = 1 atm.

samples studied in this work, little ethylene and propylene were detected. Consequently, the reaction proceeded almost entirely along the route of dehydrogenation of ethanol. It is obvious that the yield of desired isobutene follows the order of Zn-Ac \cong Zn-N > Zn-Cl. Under the condition of incomplete ethanol conversion, Zn-Ac catalyst presents the highest isobutene yield at a high space velocity of 3.43 g_{ethanol} g_{cat}⁻¹ h⁻¹ (Fig. S2). In association with the result of N₂ adsorption, the Zn-Ac with smallest specific surface area exhibited much higher catalytic activity than Zn-Cl and the very close reactivity to Zn-N (Fig. 8), suggesting that the catalytic activity couldn't be simply correlated with the surface area of the catalysts, but rather appeared to be determined by their intrinsic catalytic properties.

Three $Zn_1Zr_{10}O_X$ catalysts showed different selectivity towards the target product at 450 °C. Catalyst Zn-Ac and Zn-N exhibited a high selectivity of 50% during the reaction. This high selectivity can be ascribed to several effects: (i) balanced acid-base ratio and the number of acid and base sites of the $Zn_1Zr_{10}O_x$ oxides catalysts surface, (ii) higher zinc dispersion on ZrO_2 support, (iii) strong metal oxide-support interaction. In the case of Zn-Cl catalyst, the isobutene and methane selectivity was obviously much lower than the Zn-Ac and Zn-N catalysts at the same reaction condition. Meanwhile, significant level of acetone is formed, indicating acetone could not be effectively converted over the Zn-Cl catalyst. Due to the nature of ETIB cascade reaction, acetone may be formed as an intermediate in the conversion of ethanol to isobutene. The variations of isobutene, acetone and methane in the products are attributed to their distinct chemical nature of catalyst surface.

Fig. 9 shows the Arrhenius plots for ETIB on the different $Zn_1Zr_{10}O_x$ catalysts. As the surface area may be one of the most important factors in influencing the catalytic activities, the impact of surface area was ruled out through calculating the isobutene production rate on the normalized unit surface area under kinetically controlled regime. The catalytic activities increased in the sequence of Zn-Ac > Zn-N > Zn-Cl. The apparent activation energy of Zn-Ac was 151.3 kJ/mol, which was smaller than those of the others. Based on the above analysis, the difference in ETIB reactivity should be related to the different chemical natures on the catalysts surface such as acidic and basic properties, zinc dispersion and metal oxide-support interaction.

The effect of reaction temperature on ETIB reactivity is investigated over Zn-Ac composite catalyst. As illustrated from Fig. 10 that a full ethanol conversion is achieved in the whole temperature range, while the product distributions are found to be strongly dependent on the



Fig. 9. Arrhenius plots of isobutene production rate over the three samples.

reaction temperature. With increasing temperature from 400 °C to 450 °C at a given weight hourly space velocity and a ethanol molar fraction (1.51 vol.%), a decrease in acetone selectivity coincides with an increase in isobutene and CH₄ selectivity, and meanwhile selectivity to CO2 and C3H6 also increase slightly, demonstrating that higher temperature facilitates acetone conversion towards the desired isobutene product. However, in addition to an increased production of isobutene, it is apparent that increasing temperature also favors acetone decomposition, which results in increasing CH₄ formation. The catalyst of Zn-Ac is most selective at 450 °C. While the temperature further increases from 450 °C to 550 °C, acetone almost disappears. However, selectivity to isobutene appears to decline dramatically with rising temperature. Methane and ethylene formation becomes more pronounced in the elevated temperatures [57-59]. Reaction temperature of 450 °C was optimized to maximize isobutene yield while minimizing undesired side reactions.

Feed composition is important in affecting the product selectivity of ethanol-related chemistry. Murthy et al. studied the generation of acetone from ethanol employing Fe_2O_3 -Mn, Fe_2O_3 -CaO and Fe_2O_3 -ZnO in the presence of water [60]. They proposed that ethanol is firstly dehydrogenated to acetaldehyde and then, transformed into acetaldol



Fig. 10. Effect of reaction temperature on the product distribution. Zn-Ac: $m_{cat} = 200 \text{ mg}$, WHSV = 0.381 $g_{ethanol} g_{cat}^{-1} h^{-1}$, $x_{ethanol} = 1.51 \text{ mol }$ %, S/C = 2.5, P = 1 atm.



Fig. 11. Effect of steam to carbon ratio. Zn-Ac: $m_{cat} = 200 \text{ mg}$, $T = 450 \,^{\circ}\text{C}$, WHSV = 0.381 $g_{ethanol} g_{cat}^{-1} h^{-1}$; $x_{ethanol} = 1.51 \text{ mol}$ %, P = 1 atm.

via the aldol condensation. Hutchings et al. studied that Zeolite ß demonstrates markedly enhanced selectivity to isobutene and selectivity over 80% can be achieved for conversions up to 65% when water was present as a co-reactant [23]. As can be seen from the above, the water was very important in the reaction of ETIB. Therefore, the effect of varying S/C ratio on ethanol conversion and products selectivities for ETIB over Zn-Ac catalyst was investigated by varying the steam content of the reaction feed while maintaining a constant ethanol partial pressure of 1.51 vol% at a reaction temperature of 450 °C. As shown in Fig. 11, the increase in S/C ratio from 1 to 2.5 promotes isobutene yield significantly over Zn-Ac. With a further increase in S/C ratio up to 5, the selectivity to isobutene dropped from 50% to 41% accompanied with the increasing selectivities to CO₂ and acetone. It is clear that water has been deeply involved in the cascade ETIB reaction by suppressing the dehydration of ethanol, and in turn promoting the ethanol dehydrogenation to acetaldehyde, follow-up condensation pathway toward acetone and eventual formation of isobutene. [33,61]. Apart from this, water could also enhance the stability of ethoxide surface

species formed during the dissociation process of ethanol [62].

It is obvious that appropriate proportion of ethanol and water (i.e. S/C = 2.5 in the current case) is essential to get good isobutene selectivity, whereas either too much or too little water undoubtedly favors undesired side reactions related to the competitively adsorption of ethanol and water on the active sites [28].

Nakajima et al. found that ZnO-CaO catalyst is the best for the conversion of ethanol to acetone in the presence of water vapor, and suggested that acetone is a key intermediate in ETIB reaction [63]. Similar conclusion has also been drawn by Wang's group [28]. In addition, the isobutene yield below theoretical value is mainly caused by the decomposition of ethanol and acetone.

The effect of space velocity on the ETIB reactivity was examined over Zn-Ac catalyst. As presented in Fig. 12, isobutene was detected as main product at the low WHSV of ethanol (i.e. $0.38 \text{ g}_{\text{ethanol}} \text{ g}_{\text{cat}}^{-1} \text{ h}^{-1}$). Upon increasing space velocities, isobutene selectivity went up through a maximum, and then started to decrease. Meanwhile, upon increasing WHSV of ethanol, acetone selectivity increased with a decrease in CO₂



Fig. 12. Effect of space velocity on the product distribution at 450 °C over Zn-Ac catalysts. Reaction condition: $m_{cat} = 200 \text{ mg}$, S/C = 2.5, $x_{ethanol} = 1.51 \text{ mol }$ %, P = 1 atm.

and CH₄ selectivity. At the highest WHSV, trace amounts of acetaldehyde and a small amount of acetone were detected, strongly suggesting that acetaldehyde and acetone are two key intermediates in the cascade transformation of ethanol to isobutene. In our previous work, we have found that co-feeding acetaldehyde and water vapour produced acetone and carbon dioxide. According to Takezawa et al. [64] and Bowker and co-workers [65,66], the reaction mechanism for the formation of acetaldehyde and acetone from ethanol was hypothesized to occur through the dehydrogenation of ethanol to acetaldehyde for the first step followed by condensation and decomposition of acetaldehyde to acetone the following mechanism. Our results agreed with the reaction pathway proposed previously [67–70], in which ethanol was first dehydrogenated to acetaldehyde, and in turn converted into acetone. Here, 0.38 g_{ethanol} g_{cat}⁻¹ h⁻¹ was identified as the optimal space velocity for the ETIB reaction over Zn-Ac composite catalyst.

The stability test of the Zn-Ac composite catalyst was performed at reaction temperature = 450 °C and S/C = 2.5 with time-on-stream of 18 h. As shown in Fig. 13, a slow deactivation was noticed after 4 h commencement of ETIB reaction. Isobutene yield can be stabilized above 45% with an increasing acetone selectivity in the course of stability test. Meanwhile, the selectivities to other products remained

constant for 18 h during time-on-stream operation. The colour of the spent catalyst has changed from white to black after being used in the catalytic reaction, indicating that coking was the primary reason that resulted in the catalyst deactivation.

3.3. Key factors to affect the ETIB reactivity

As documented in the literatures, it was generally accepted that balanced acidic/basic sites on the catalyst surface is important to achieve a high yield of isobutene from ethanol. As a measure for the strength and distribution of basicity and acidity, we chose the ratio of the total amounts of basic sites to acidic sites to be correlated with isobutene selectivity about different precursors (Table 1). As depicted in Table 1, isobutene yield rapidly increases with increasing basicity to acidity ratio. By contrast, a high acetone yield is achieved on the catalyst surface with more acidic sites. Obviously, a proper balance of surface acidic and basic sites is essential to obtain higher isobutene selectivity. Different precursors lead to dramatic change in the relative strength and distribution of the acid and base functionalities of all catalysts. Our results also show that the catalyst prepared from zinc acetate possesses more surface basic sites which are more favorable for



Fig. 13. Stability of Zn-Ac catalyst. Reaction condition: $m_{cat} = 200 \text{ mg}$, S/C = 2.5, $x_{ethanol} = 1.51 \text{ mol }\%$, $WHSV = 0.381 \text{ g}_{ethanol} \text{ g}_{cat}^{-1} \text{ h}^{-1}$, $T = 450 \degree \text{C}$, P = 1 atm.

isobutene production from ethanol among the investigated catalysts.

Additionally, Zn₁Zr₁₀O_x samples synthesized based on different zinc precursors have exhibited distinct characteristics in zinc dispersion, strong metal oxides-support interaction, and reducibility of samples. The relationship between these differences in zinc precursors and characteristics could be correlated to both the surface structure of the ZrO₂ support and the properties of zinc precursors, because the synthesis process and zinc loading are kept the same. Chen et al. had thoroughly investigated the interaction between metal oxide and support from various supported metal oxide catalysts in a series of their previous works [71–73]. According to the incorporation model, Zn²⁺ ions could be dispersed by the incorporation of cations into the available surface vacant sites of the ZrO₂ support with the accompanying anion groups positioning on the top of the occupied sites for charge compensating. On the surface of ZrO₂ support, because of the strong affinity of the surface vacancies, the dispersed zinc species preferentially fill the cation vacancies on the surface of the support and aggregated on a twodimensional surface until it reaches a single layer after which then developed into in three dimensions. Based on the characterization results of XPS and cation vacancy density of the ZrO₂ support, Zn₁Zr₁₀O_x catalysts were over monolayer dispersion capacity, which would produce shielding effect to enable the fine distribution of large zinc species over the vacant sites on ZrO₂ surface. Due to the shielding effect of the capping anions, more available surface vacancies would be shielded by larger anions, which led to the higher zinc dispersion.

In this work, the size of anions follows the order chloride < nitrate < acetate. For Zn–Ac, the largest acetate anions lead to the greatest shielding effect, and it would be hardest for Zn^{2+} to incorporate into the available surface vacant sites. As a result, Zn–Ac has the highest zinc dispersion, followed by Zn–N and Zn–Cl. This was in good agreement with XPS, H₂-TPR, and UV–vis. Zn/Zr atomic ratios quantified by XPS can be used in principle, as a measure of the zinc dispersion. The highest zinc dispersion will, in turn, endow Zn–Ac the strongest metal oxide-support interaction, and therefore, the strongest sruface basicity, the greatest H₂ reducibility and most abundant adsorbed surface oxygen species. Consequently, the surface properties of samples may be governed by the choice of zinc precursors, which then dictate the ETIB reactivity.

Using these different precursors using simple incipient wetness impregnation, we are able to prepare a series of catalysts, which differ in their acid-base, reducibility, zinc dispersion, and strong metal oxidessupport interaction. The physical properties, such as specific surface area, the pore volume and the structure themselves are certainly influenced by the different precursors, and keep in the broad range. Aside from this, it is worthy to point out that isobutene yield of Zn-Ac is nearly double than that of Zn-Cl in direct conversion of ETIB, but under the condition with only half of the specific surface area of Zn-Cl. Thus, studying the catalytic behavior of those composite catalysts allows further insights into the principles required for the rational design of ETIB bifunctional catalyst. Anyway, the differences between the catalytic behavior of samples prepared with different Zn precursors are well established from the obtained results.

4. Conclusions

The present work identifies the important role of anion size of the different precursors played in distributing Zn^{2+} on the available surface vacant sites of ZrO_2 . Upon calcinations, $Zn_1Zr_{10}O_x$ samples based on different precursors could present distinct characteristics in acid-base properties, zinc dispersion and strong metal oxide-support interaction. These characteristics demonstrate to have profound impact on the cascade ETIB reaction. The highest steady isobutene yield obtained was ~ 50% at a WHSV of 0.38 g_{ethanol} g_{cat}⁻¹ h⁻¹ (S/C = 2.5, P = 1 atm) at 450 °C over Zn-Ac catalyst. The best-performing catalysts for the production of isobutene by ETIB were those having a subtle balance of surface basicity/acidity, high zinc dispersion, the strongest metal oxide-

support interaction, and enhanced reducibility. The catalysts that did not possess these characteristics undoubtedly resulted in enhanced undesired side reactions. 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. Stability test of Zn-Ac sample showed the slow catalyst deactivation with time-onstream due to coke formation deposited over the catalyst surface.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.apcata.2018.04.003.

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