On the deactivation mechanism of zeolite catalyst in ethanol to butadiene conversion

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ABSTRACT

Despite of extensive attention on the ethanol to butadiene (ETB) conversion, the catalyst deactivation during ETB conversion is rarely investigated and poorly understood. Here, the mechanism of the catalyst deactivation during the ETB conversion over Zn-Y/Beta was investigated through several complementary approaches, including XPS, TGA, GC–MS, in situ DRIFTS, UV–vis and ^{13}C CP MAS NMR spectroscopy. Acetaldehyde was observed to be the first reactive intermediate formed in the ETB conversion, which was rapidly involved in a subsequent aldol condensation with the simultaneous production of acetone. Due to a self- and cross-condensation of acetaldehyde and acetone, long chain unsaturated aldehydes/ketones were formed and further converted to 2,4-dimethyl benzaldehyde via a cyclization reaction, which could gradually cover the active sites and led to catalyst deactivation. Fortunately, the deactivating species could be removed from catalyst surface via simple calcination and the complete regeneration of Zn-Y/Beta could be realized.

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1. Introduction

Growing concerns regarding environment deterioration and the gradual depletion of fossil resources become a key driving force for the sustainable production of important chemicals [1]. Bioethanol obtained from the fermentation of sugars and starch is regarded as a most attractive renewable material to produce basic chemicals like acetaldehyde, acetic acid, isobutene, and butadiene [2–4]. In particular, the conversion of ethanol to butadiene (ETB) is becoming an attractive route since butadiene is an important monomer for the production of polymers and polymer intermediates [1]. The bioethanol-based route to butadiene possesses an apparent advantage over the traditional naphtha-based one according to the techno-economic analysis, life-cycle assessment, and green chemistry principles [5].

Recently, extensive attention has been focused on the ETB conversion. The reaction mechanism and network of the ETB conversion

have been extensively investigated [6–11], and several key reaction steps are now generally accepted, including (i) the dehydrogenation of ethanol to acetaldehyde, (ii) the aldol condensation of acetaldehyde to acetaldol, (iii) the dehydration of acetaldol to crotonaldehyde, (iv) the Meerwein-Ponndorf-Verley reduction of crotonaldehyde to crotonyl alcohol, and (v) the dehydration of crotonyl alcohol to butadiene [3,12]. On the other hand, a variety of catalysts have been explored to achieve high butadiene yield and productivity in ETB conversion. In the most cases, mixed metal oxides are studied as candidating catalysts, such as doped magnesia-silica catalysts prepared via different procedures [4,13–28]. Moreover, with addition of metal or metal oxides to Lewis acidic catalysts, e.g. zeolite Zr-Beta or ZrO_2/SiO_2, the two-step ETB catalysts could be transferred into one-step ETB catalysts, and the butadiene yields could be significantly promoted [9,29–37]. Our recent work indicates that Zn–Y/Beta zeolite containing dehydrogenation, condensation and Lewis acid sites exhibits a remarkable ETB activity, and a state-of-the-art butadiene productivity of 2.33 $g_{Butadiene}/g_{Cat}/h$ with butadiene selectivity of 63% could be obtained by well balancing the different types of active sites [12,38]. Despite of the significant achievements made so far, the catalyst stability remains a key problem for the long-running of the ETB conversion and the reasons for

catalyst deactivation are not understood yet. An improved knowledge on the detailed deactivation mechanism of an ETB catalyst is essential for its industrial application [1], and, therefore, the main goal of the present work.

In this work, Zn- and Y-modified zeolite Beta was utilized as a model catalyst for investigating the deactivation mechanism during the ETB conversion. The catalytic performance of the zeolite Zn-Y/Beta in the ETB conversion for a time-on-stream of up to 70 h was evaluated on a fixed-bed reactor. The intermediary products formed during the initial stages of the ETB conversion were monitored by on-line MS, while the reactive intermediates formed during the whole process of the ETB conversion were investigated by *in situ* DRIFTS and UV–vis spectroscopy. Moreover, the physicochemical properties of the catalysts before and after ETB conversion were analyzed by XRD, nitrogen physisorption, and XPS. The organic deposits occluded in the zeolite catalyst as a result of the ETB conversion were determined by TGA, GC–MS, and ^{13}C CP MAS NMR spectroscopy. According to the catalytic performance of the Zn-Y/Beta zeolite and the spectroscopic results, the deactivation behaviors of this catalyst were disclosed, and the deactivation mechanism was discussed in detail. The methodology employed here can be extended to the other cascade heterogeneous catalytic reactions.

2. Experimental section

2.1. Catalyst preparation

The Zn-Y/Beta zeolite was prepared via a two-step metallation procedure [38]. First, the dealuminated zeolite Si-Beta was obtained by treating the commercial H-Beta zeolite (n_{Si}/n_{Al} = 13.5, Sinopec Co.) in 13 mol/L nitric acid aqueous solution. Afterwards, zinc and yttrium were introduced to Si-Beta by mixing Si-Beta with desired amounts of zinc and yttrium nitrates, followed by calcination in flowing air at 823 K for 6 h. The final product 5% Zn-5%Y/Beta (5% refers to the weight loading), hereinafter abbreviated as Zn-Y/Beta, was directly utilized as a solid catalyst in the ETB conversion.

2.2. Catalyst evaluation

The ETB conversion was performed in a fixed-bed reactor at atmospheric pressure as described in our previous work [12]. In a typical experiment, 0.3 g of the Zn-Y/Beta catalyst (sieve fraction, 0.25–0.5 mm) was placed in a fixed-bed reactor and treated in flowing He (20 mL/min) at 723 K for 1 h. After cooling down to 623 K, ethanol was introduced into the reactor utilizing a Shimadzu LC-2AT Dual Reciprocating Plunger HPLC pump at the rate of 0.5 mL/h. After the ETB reaction, the catalyst was regenerated by calcination in flowing air (20 mL/min) at 823 K for 6 h. The reaction products were analyzed by an on-line gas chromatograph (Shimadzu GC-2010 plus) with a Poraplot Q-HT column (40 m × 0.18 mm × 0.18 μm) and a flame ionization detector (FID).

To get more information about the main reaction products formed during the ETB conversion, the fixed-bed reactor was also connected with a downstream gas sampling mass spectrometer (MS, Pfeiffer Omnistar).

2.3. Characterization of the fresh and spent Zn-Y/Beta catalysts

The X-ray diffraction (XRD) patterns of the fresh and spent catalysts were recorded on a Rigaku SmartLab powder diffractometer using Cu-Kα radiation (λ = 1.5418 Å) with a scanning rate of 5°/min in the range of 2θ = 5–50°.

The surface areas and pore volumes of the fresh and spent catalysts were measured by means of nitrogen sorption on a Quantachrome iQ-MP gas adsorption analyzer at 77 K. Before the nitrogen adsorption, samples were dehydrated at 573 K for 6 h. The total surface area was calculated via the Brunauer-Emmett-Teller (BET) equation while the micropore volume was determined using the t-plot method.

X-ray photoelectron spectra (XPS) of the fresh and spent catalysts were recorded on a Thermo Scientific ESCALAB 250Xi spectrometer using a monochromatic Al-Kα X-ray source (hν = 1486.6 eV) as the excitation source. High-resolution spectra were recorded by using an aperture slot of 300 × 700 μm. The binding energies (±0.1 eV) were determined with respect to the position of the C 1s peak at 284.8 eV.

2.4. In situ DRIFTS and UV–vis studies of the ETB conversion over the Zn-Y/Beta catalyst

The nature of organic intermediates formed during the ETB conversion was *in situ* monitored by DRIFTS, and UV–vis spectroscopy as described in Ref. [39] and [40], respectively. DRIFT spectra were recorded on a Bruker Tensor 27 spectrometer equipped with a liquid N$_2$ cooled high sensitivity MCT detector and an *in situ* reaction chamber. About 20 mg of the catalyst powder was placed in the reaction chamber. Before starting the reaction, the catalysts were activated under flowing He (10 mL/min) at 723 K for 1 h. Subsequently, the temperature was decreased to 623 K for collecting the DRIFT background spectra. Afterwards, the ethanol was injected into the chamber at the constant rate of 0.025 mL/h (WHSV = 1.0 h^{-1}) and the *in situ* DRIFT spectra were recorded with a resolution of 4 cm^{-1} and an accumulation of 128 scans.

UV–vis spectra were recorded via an AvaSpec-2048 Fiber Optic spectrometer using an AvaLight-DH-S deuterium light source by Avantes and a glass fiber reflection probe HPSUV1000A by Oxford Electronics. Before the ETB reaction, the glass fiber reflection probe was placed in the fixed-bed reactor on the top of the catalyst with a gap of ca. 1.0 mm. Reference UV–vis spectra of the catalysts were recorded at reaction temperature prior to starting the ethanol injection. *In situ* UV–vis spectra were recorded in the diffuse reflection mode and over a spectral range of 200–600 nm [40].

2.5. TGA, GC–MS analysis, and ^{13}C CP MAS NMR investigations of organic deposits on spent Zn-Y/Beta catalysts

The amounts of entrapped organic species on the Zn-Y/Beta catalysts after the ETB reaction for different time-on-stream (TOS) were analyzed by TGA using a Setram Setsys 16/18 thermogravimetric analyzer. Typically, 0.1 g of spent catalyst was placed in an Al$_2$O$_3$ crucible and heated at the constant rate of 10 K/min in flowing O$_2$/Ar (20 vol%/80 vol%, 30 mL/min).

The nature of occluded organic compounds in the catalysts after the ETB reaction with different TOS was analyzed by GC–MS and ^{13}C CP MAS NMR spectroscopy. For GC–MS analysis, 0.1 g of the spent catalyst sample was carefully dissolved in 1 M HF solution. This solution was treated with CH$_2$Cl$_2$ to extract the organic compounds and the residual water was removed by the addition of sufficient sodium sulfate solid. Then, 0.2 μL of the organic extract were analyzed by GC–MS (GCMS-QP2010 SE) with a RXI-5MS column (30 m, 0.25 mm i.d., stationary phase thickness 0.25 μm). The following temperature program was employed: Isothermal heating at 313 K for 6 min, heating to 553 K with a rate of 10 K/min, and isothermal heating at 553 K for 10 min.

^{13}C CP MAS NMR measurements were performed on a Bruker Avance III 400WB spectrometer at the resonance frequency of 100.6 MHz, with cross polarization of 4 ms, the repetition time of 4 s, and the sample spinning rate of 8.0 kHz. To avoid contact with