In situ DRIFTS for the mechanistic study of 1,4-butanediol dehydration over *m*-ZrO_2 catalyst

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Abstract: *In situ* DRIFTS (Diffuse Reflectance Infrared Fourier Transform Spectroscopy) technology was employed to study the adsorption and reaction behavior of 1, 4-butanediol (BDO) on *m*-ZrO_2 at different temperatures for the first time. The study shows that the main intermediate active species were monodentate and bidentate butoxides at low temperature, while were monodentate butoxides over *m*-ZrO_2 at high temperature. The conversion of BDO into 3-buten-1-ol involves two consecutive steps, which correspond to BDO conversion into aldehyde species and subsequently to 3-buten-1-ol. The mechanism of BDO dehydration over *m*-ZrO_2 was proposed based on experiment results.

Keywords: 1,4-Butanediol Dehydration, *m*-ZrO_2, *in situ* DRIFTS.

1. Introduction

3-Buten-1-ol (BTO) is a valuable unsaturated alcohol, which is widely used as pharmaceutical intermediate, especially in the synthesis of heterocyclic drugs, antiviral and antitumor agents.[1] The method of BDO dehydration offers mild reaction conditions, good economic benefits and a continuous process compared to other routes. However, mechanism of BDO dehydration is still unclear. DRIFTS is an *in situ* technology which track and characterize reaction adsorption site on the catalyst to get some valuable surface reaction information.[2] In this paper, *in situ* DRIFTS study was first employed to study the adsorption and reaction behavior of BDO over *m*-ZrO_2 at different temperatures. The mechanism of BDO dehydration over *m*-ZrO_2 was proposed according to experiment results.

2. Experimental

The *m*-ZrO_2 was prepared via hydrothermal method. In a typical process, urea (> 99.0%, Sinopharm Chemical Reagent) and zirconium oxynitrate (> 99.5%, Macklin Biochemical) were dissolved in deionized water. The concentration of Zr^{4+} and urea were 0.4 M and 4M, respectively. 60 mL zirconium oxynitrate and urea solution was transferred into a 100 mL Teflon-lined autoclave. Hydrothermal treatment was carried out at 200℃for 6 h. The resulting precipitate was recovered by centrifugation, washed with deionized water and dried at 110 ℃ overnight. The powder was calcined in air at 500 ℃ for 4 h with a heating rate of 1 ℃/min.

In situ DRIFTS of *m*-ZrO_2 was performed on a Nicolet iS50 spectrometer (Thermo Scientific) equipped with a DiffusIR Reflectance Accessory (Pike Technology), which consists of a heat chamber, DRIFT cell with ZnSe window and a MCT-A detector. All spectra were collected in Kubelka-Munk units and were averaged over 32 scans at 4 cm^{-1} resolution. In a typical process, the powder sample was placed in an *in situ* DRIFTS cell which was heated to 450 ℃ in Ar flow (30 mL/min) and held at this temperature for 60 min before the temperature was lowered to desired temperature (100, 200, 300, 400 ℃). After stabilization of the spectrum, the background was collected. The BDO molecule was introduced by flowing 30 mL/min Ar through a room-temperature saturator, and the spectra began to be recorded every 30 seconds, simultaneously.

3. Results and discussion

Figure 1 shows the DRIFT spectra of *m*-ZrO_2 under BDO flow at the temperature ranging from 100 to 400 ℃. The negative bands at 3750, 3734 and 3675 cm^{-1} were assigned to the terminal hydroxyls, bridged $Zr_2(OH)$ groups in defective and regular positions, respectively.[3] The band at *ca.* 3710 cm^{-1} was assigned to the adsorbed alcoholic-hydroxyl of BDO molecules. Therefore, we could deduce that the surface hydroxyl groups were substituted by adsorbed BDO molecules when BDO was introduced to the sample cell. The weak bands at 3029 and 3006 cm^{-1} were assigned to the ν_sC-H and ν_{as}C-H of R=CH_2, which could indicate the production of 3-buten-1-ol. The bands at 2964-2860 cm^{-1} were assigned to the stretching vibration of α-

CH_2 and β-CH_2 of surface species, respectively. The weak bands at 2740 and 2704 cm^{-1} were ascribed to the to the C–H stretching vibration of a reactive intermediate containing an aldehyde species of $\text{H-C}\underset{\cdots}{-}\text{O}$. The band at 1292 cm^{-1} was ascribed to bending vibration of CH_2, which decreased as temperature rising. The possible reason was due to the C-H cleavage of β-H of adsorbed butoxides. The bands at 1150 and 1073 cm^{-1} were assigned to monodentate and bidentate butoxides, respectively. However, bidentate butoxides decreased as temperature rising, which indicated that the intermediate active species were monodentate and bidentate butoxides at low temperature, while were monodentate butoxides over *m*-ZrO_2 at high temperature.

Therefore, the mechanism of BDO dehydration over *m*-ZrO_2 was proposed based on the aforementioned results as shown in Figure 2. The surface hydroxyl of *m*-ZrO_2 was substituted by adsorbed BDO molecules after the BDO molecules were introduced into the cell. Adsorbed BDO molecules were transformed to an intermediate of mono- and bi-dentate butoxides. The β-H of butoxides were adsorbed and dissociated to form carbanion by C-H cleavage. The carbanion can be transformed to $\text{H-C}\underset{\cdots}{-}\text{O}$ species and then the hydroxyl was dissociated to form 3-buten-1-ol.

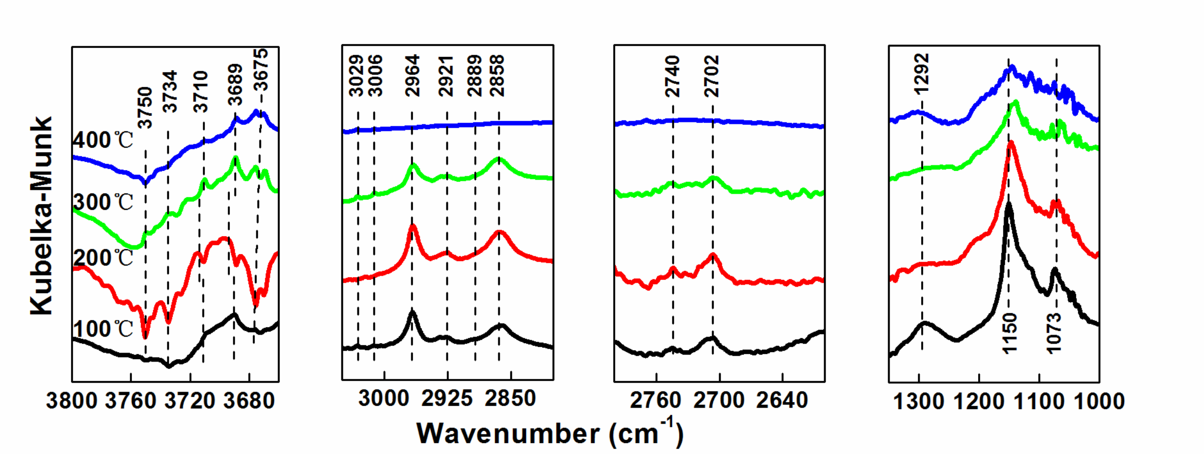

Figure 1. DRIFTS of BDO adsorbed on *m*-ZrO_2 at 100, 200, 300, 400 ℃.

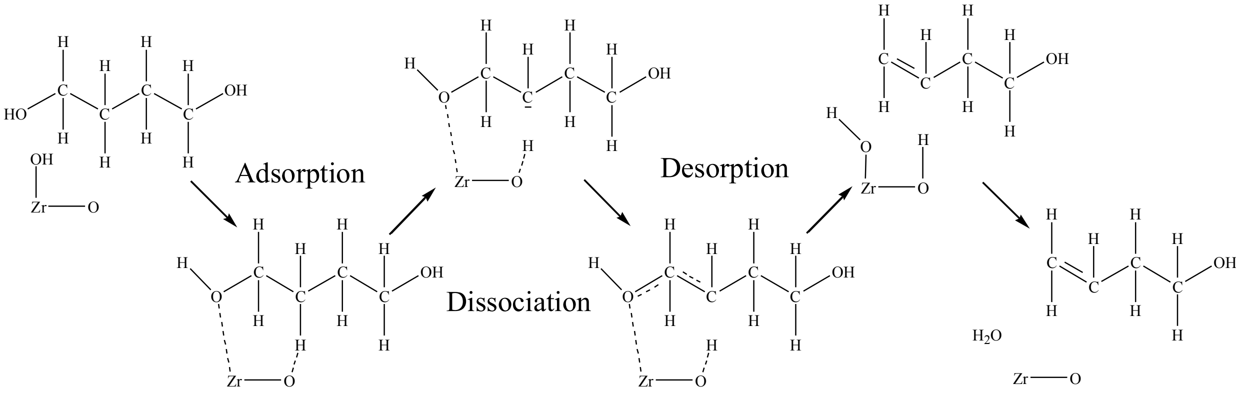

Figure 2. Possible reaction mechanism of BDO dehydration to 3-buten-1-ol

4. Conclusions

In order to verify the reaction mechanism, the BDO adsorption on the surface of *m*-ZrO_2 was investigated via *in situ* DRIFTS for the first time. According to the results, BDO adsorbed on *m*-ZrO_2 to form mono- and bi- dentate butoxide species, and only monodentate butoxide exists at high temperature. The conversion of BDO into 3-buten-1-ol involves two consecutive steps, which correspond to BDO conversion into aldehyde species and subsequently to 3-buten-1-ol. The mechanism of BDO dehydration over *m*-ZrO_2 was also proposed.

References

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