



# The effect of Brønsted acidity of $\text{WO}_3/\text{ZrO}_2$ catalysts in dehydration reactions of C3 and C4 alcohols

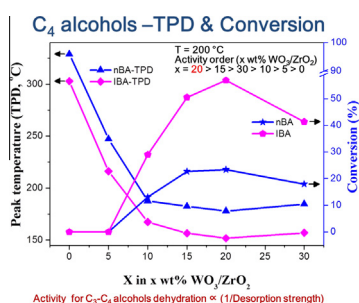
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## HIGHLIGHTS

- Brønsted acidity can be controlled by introduction of  $\text{WO}_3$  content.
- Brønsted acidity was well correlated with the TPD results for C3 and C4 alcohols.
- Brønsted acidity critically influences for conversion of C3 and C4 alcohols in dehydration.
- In IPA dehydration, propene selectivity correlates with increasing Brønsted acidity.
- In IBA and nBA dehydration, Brønsted acidity did not affect initial selectivity to *cis*-2-butene.

## GRAPHICAL ABSTRACT



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## ABSTRACT

$\text{WO}_3/\text{ZrO}_2$  catalysts were synthesized by an excess solution impregnation method, and its applications for the dehydration of *iso*-propanol (IPA) and *n*-butanol (nBA) and *iso*-butanol (IBA) as C3–C4 alcohols were investigated. The catalytic activity was maximized at 20 wt%  $\text{WO}_3$  content in the range of 0–30 wt%  $\text{WO}_3/\text{ZrO}_2$  catalysts. In IPA dehydration, conversion and selectivity to propene were well correlated with Brønsted acidity. In the dehydration of nBA and IBA, conversion was also influenced by Brønsted acidity. However, product selectivity to *iso*-butene, 1-butene, *cis*-2-butene (*c*-butene), and *trans*-2-butene (*t*-butene) was not affected by Brønsted acidity. Below 85% conversion in IBA dehydration, the ratio of *cis/trans* isomer in 2-butenes was almost constant. However, above this range of conversion the catalytic isomerization of *iso*-butene to *t*-butene is accompanied with slight deactivation of catalysts with time on stream. In the nBA dehydration the catalytic isomerization of *t*-butene to 1-butene changes the *cis/trans* ratio in the formation of 2-butenes resulting that below unity in initial period, and gradually increased as the reaction proceeds.

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## 1. Introduction

The alcohol conversion reaction is considered as a model reaction for determining the surface characteristics of solid heterogeneous catalysts [1]. For the *iso*-propanol (IPA) conversion reaction, three different reaction routes can be expressed from par-

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allel reaction pathways [1]. Dehydration, which produces propene, characterizes the acid, or acid–base, properties of catalysts. Acetone is produced by dehydrogenation, which comes from basic properties in the catalysts. Diisopropyl ether (DIPE) is produced by intermolecular dehydration between two IPA molecules. The alcohol conversion reactions of the C4 alcohols, *iso*-butanol (IBA) and *n*-butanol (nBA), are more complex than that of IPA. This is because 2-butene isomers (*cis/trans*) can be produced by catalytic isomerization due to carbocation rearrangement [2–4]. According

to catalytic functions, initial *cis/trans* ratios could be varied [5], giving <1 for metallic,  $\approx 1$  for acidic, and >1 for basic catalysts. Therefore, relative ratios of *cis*-2-butene (*c*-butene) and *trans*-2-butene (*t*-butene) are an important factor in the C4 alcohol dehydration reaction for determining the catalytic function.

Furthermore, alcohol dehydration reactions have been attracting great attention for the production of useful intermediates, such as propene and 1-butene, from renewable resources as bio-alcohols [6–8]. Therefore, propylene and 1-butene products could be obtained by dehydration of bio-alcohols from environmental friendly route compared to the current industrial steam cracking process.

ZrO<sub>2</sub> is well known material which has both acidic and basic properties with thermal stability [9]. Due to its surface properties, ZrO<sub>2</sub> has been applied to the isomerization of olefins, esterification of alcohols, CO oxidation, nitrous oxide decomposition, epoxides, and the dehydration of alcohols [10,11]. However, the reactivity of ZrO<sub>2</sub> in alcohol dehydration reactions is very low as it contains only Lewis acid sites. Macht et al. [12] reported that the dehydration of alcohols more effectively proceeds on Brønsted acid sites than Lewis acid sites and Brønsted acid functionality could be introduced by using materials such as sulfate (SO<sub>4</sub><sup>2-</sup>) and tungsten oxide (WO<sub>3</sub>) to improve the catalytic performance in alcohol dehydration reactions. Although sulfated zirconia shows excellent catalytic activities in isomerization and alkylation [13], it is thermally unstable due to partial loss of sulfate during thermal treatment leading to deactivation [14,15]. On the other hand, ZrO<sub>2</sub>-supported WO<sub>3</sub> catalyst could be a promising candidate for the improvement of catalytic performance as a strong solid acid catalyst [16,17].

In this study, ZrO<sub>2</sub>-supported WO<sub>3</sub> catalysts were synthesized with various WO<sub>3</sub> content (0–30 wt%). Brønsted acidity could be controlled by the amount of introduced WO<sub>3</sub>. Thus, we focused on the correlation between Brønsted acidity and catalytic activity in the dehydration reactions of IPA, IBA, and nBA as C3 and C4 alcohols at different temperatures: namely 150 and 170 °C for IPA, 200 and 250 °C for IBA, and 250 °C for nBA.

## 2. Experimental

### 2.1. Catalyst preparation

#### 2.1.1. Preparation of ZrO<sub>2</sub> support

Zirconium hydroxide was prepared by a precipitation method using an aqueous solution of ZrOCl<sub>2</sub>·8H<sub>2</sub>O (Samchun, 98%), and NH<sub>4</sub>OH (SK Chemical, 28 wt%) as a precipitant. ZrOCl<sub>2</sub>·8H<sub>2</sub>O (0.5 M) was dissolved in deionized (DI) water and then NH<sub>4</sub>OH was added dropwise to solution until pH = 9.5. This solution was then vigorously stirred at 100 °C for 24 h. The solid precipitant was filtered and completely washed chloride ions with DI water. The obtained zirconium hydroxide was dried in the oven at 100 °C for 24 h, and crystalline tetragonal ZrO<sub>2</sub> was formed by calcination at 600 °C for 4 h under flowing air.

#### 2.1.2. Preparation of WO<sub>3</sub>/ZrO<sub>2</sub> catalysts

WO<sub>3</sub>/ZrO<sub>2</sub> catalysts were prepared by an impregnation of H<sub>2</sub>WO<sub>3</sub> (Kanto Chemical, 95%) on ZrO<sub>2</sub> support in excess solution. First, a predetermined amount of H<sub>2</sub>WO<sub>3</sub> (5, 10, 15, 20 and 30 wt% of WO<sub>3</sub>) and (COOH)<sub>2</sub>·2H<sub>2</sub>O (Duksan chemical, 99.5%) with a molar ratio of (COOH)<sub>2</sub>·2H<sub>2</sub>O:H<sub>2</sub>WO<sub>3</sub> fixed at 10, were dissolved in DI water. ZrO<sub>2</sub> support (3 g) was added into this tungstic acid–oxalic acid complex at 70 °C with vigorous stirring for 3 h. The WO<sub>3</sub>/ZrO<sub>2</sub> particles were obtained after evaporation of excess solvent in a rotary evaporator at 70 °C. The particles recovered were dried at 100 °C for 24 h, and finally calcined at 550 °C for 2 h under flowing

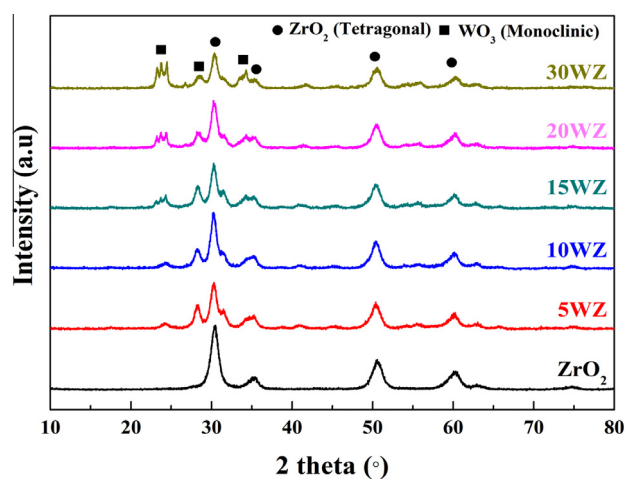


Fig. 1. XRD patterns of WO<sub>3</sub>/ZrO<sub>2</sub> catalysts with different WO<sub>3</sub> content.

Table 1

BET surface area and total pore volume of WO<sub>3</sub>/ZrO<sub>2</sub> catalysts with different WO<sub>3</sub> contents. The catalysts were calcined at 550 °C for 2 h under flowing air.

| Catalyst         | S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> ) | Total pore volume (cm <sup>3</sup> g <sup>-1</sup> ) |
|------------------|--|--|
| ZrO <sub>2</sub> | 89   | 0.347  |
| 5WZ              | 87   | 0.278  |
| 10WZ             | 83   | 0.305  |
| 15WZ             | 81   | 0.260  |
| 20WZ             | 74   | 0.273  |
| 30WZ             | 62   | 0.224  |

air. The resultant WO<sub>3</sub>/ZrO<sub>2</sub> catalysts were named XWZ, in which 'X' refers to the WO<sub>3</sub> content in wt%.

### 2.2. Characterization

To identify the crystalline structure of WO<sub>3</sub>/ZrO<sub>2</sub> catalysts, X-ray diffraction (XRD) measurement was performed on Siemens D5005 using Cu K $\alpha$  radiation. The diffraction intensity was measured in  $2\theta$  range between 10° and 80° with a scan rate 0.4° min<sup>-1</sup>. In order to measure the specific surface area and total pore volume of the catalysts, N<sub>2</sub> sorption analysis (Micromeritics, ASAP2020) was carried out. Prior to measure N<sub>2</sub> adsorption–desorption isotherms, the samples were degassed at 250 °C for 5 h under vacuum. The specific surface area was calculated by Brunauer–Emmett–Teller (BET) method in the range of  $P/P_0 = 0.05–0.2$  and total pore volume was measured at  $P/P_0 = 0.995$ , respectively. The desorption behavior of C3 and C4 alcohols was analyzed by temperature-programmed desorption (TPD). The catalysts (0.1 g) were pretreated at 300 °C for 1 h under flowing Ar. After cooling to room temperature, samples were exposed to certain alcohols flow pressures (4.5 kPa for IPA and 1 kPa for IBA and nBA) with total flow of 30 cm<sup>3</sup> min<sup>-1</sup> for 0.5 h and subsequently purged with Ar flow (30 cm<sup>3</sup> min<sup>-1</sup>) for 0.5 h. The desorbed products were then detected by a quadruple mass spectrometer (QMS, Pfeiffer vacuum D-35614) between room temperature and 600 °C, with a heating rate of 10 °C min<sup>-1</sup>. For pyridine-infrared (IR) spectroscopy (BIO-RAD, FTS-175C), the pelletized sample was heated under flowing He (100 cm<sup>3</sup> min<sup>-1</sup>) to 500 °C at a heating rate 10 °C min<sup>-1</sup> and maintained for 0.5 h. After cooling to 50 °C, the pretreated samples were exposed to pyridine, and outgassed at this temperature for 0.5 h. FT-IR spectra were obtained at room temperature.

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