Short communication

Highly selective catalytic conversion of ethanol to propylene over yttrium-modified zirconia catalyst

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ABSTRACT

The yttrium-modified zirconia catalysts were prepared by co-precipitation method. N_2 adsorption/desorption method, temperature programmed desorption and X-ray diffraction were used to characterize the Y/ZrO_2 catalyst. All the catalysts were tested in the conversion of ethanol to propylene. The propylene yields showed a volcano-shaped dependence on the Y amount. The maximum yield of propylene reached 44.0%. The results implied that Y/ZrO_2 catalyst with tetragonal structure or bigger specific BET surface area showed better performance. Reaction pathways were suggested to be ethanol to ethylene on the acidic sites, and ethanol → acetaldehyde → acetone → propylene on the basic sites.

1. Introduction

The chemical industry is mainly based on light olefins such as ethylene and propylene [1]. In the recent years, the demand of propylene was constantly increasing due to the growing need of its derivatives. Traditional process for the production of propylene unable to meet the market needs. Much attention has been focused on renewable energy. The reaction of ethanol to propylene (ETP) has attracted more attention since the bioethanol got rapid developed [2]. However, only a few researches reported the conversion of ethanol to propylene over modified ZSM-5 and other zeolite catalysts [3–15]. Based on the literature, the selectivity of propylene of ETP over zeolite catalysts is 20–30%, which is still not sufficient to satisfy economic feasibility. Also the stability of catalyst has not satisfied the need.

Recently, various metal oxides have been examined for the conversion of ethanol [16–18], CeO_2 doped with yttrium showed the most stable activity for the conversion of ethanol, the yields of propylene and ethylene were 25% and 50% respectively. Zirconia is an acid-base oxide which has several advantages, such as an improved catalytic stability and a lower deactivation rate. Among the metal oxides with acid/base or redox sites, zirconia is the most widely used due to its unique features. Metal doped zirconia catalysts were also widely used in many kinds of chemical reactions. However the ETP reaction has not been studied over Y/ZrO_2 catalyst. In this work, we investigated the conversion of ethanol to propylene over Y/ZrO_2 catalyst. Recently, we synthesized ZrO_2 catalyst with different amount of Y-doped by co-precipitation method. The N_2 adsorption/desorption method (BET), X-ray diffraction (XRD), Temperature programmed desorption of ammonia (NH_3-TPD) and temperature programmed desorption of carbon dioxide (CO_2-TPD) were used to characterize the Y/ZrO_2 catalyst. Their physical and chemical properties were characterized. The ethanol to propylene reaction was carried out over these synthesized Y/ZrO_2 catalysts to discuss the effect of amount of Y-doped on the catalytic performance. Results show that the Y/ZrO_2 is very effective for the highly selective conversion of ethanol to propylene. The maximum yield of propylene on Y/ZrO_2 reached 44.0%.

2. Experimental

2.1. Preparation of the Y/ZrO_2 catalysts

Y/ZrO_2 catalyst samples were prepared by co-precipitation from the corresponding chemicals: $ZrO(NO_3)_2 \cdot 2H_2O$ and $Y(NO_3)_3 \cdot 6H_2O$ at a nominal composition. The $ZrO(NO_3)_2 \cdot 2H_2O$:$Y(NO_3)_3 \cdot 6H_2O$ molar ratios were 100:0, 99:1, 97:3, 96:4, and 95:5 named as ZrO_2, $Y(1)/ZrO_2$, $Y(3)/ZrO_2$, $Y(4)/ZrO_2$, and $Y(5)/ZrO_2$, respectively. Zirconium and yttrium precursors were dissolved in the 500 mL deionized water. The precipitant $NH_3 \cdot H_2O$ were added into the solvent with stirring at 293 K for 30 min to reach a pH value of 9.0. Thereafter, the solution was kept at

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Table 1
Characteristics of the synthesized Y/ZrO_2 catalysts.

Sample	$Y(NO_3)_3 \cdot 6H_2O$ %	BET surface area $(m^2 \cdot g^{-1})$	Pore volume $(cm^3 \cdot g^{-1})$	Pore size (Å)
ZrO_2	0	54.1	0.129	72.1
$Y(1)/ZrO_2$	1	59.7	0.145	72.2
$Y(3)/ZrO_2$	3	79.8	0.145	51.8
$Y(4)/ZrO_2$	4	75.6	0.121	45.0
$Y(5)/ZrO_2$	5	85.9	0.125	40.2

Zirconium precursor: $ZrO(NO_3)_2 \cdot 2H_2O$. Precipitant: $NH_3 \cdot H_2O$.

293 K for 24 h. After crystallization, the Y/ZrO_2 samples were centrifuged, washed thoroughly with deionized water for 3 times, dried at 383 K for 16 h. After that, the catalysts were calcined in air at 823 K for 4 h with a heating rate of 4.5 K/min.

2.2. Characterization of the Y/ZrO_2 catalysts

Surface areas and pore volumes were determined by the N_2 adsorption-desorption method (BET method) at 77 K by using a volumetric unit (Micromeritics ASAP 2020). Prior to the adsorption measurements, each sample was degassed at 623 K for 10 h under reduced pressure. XRD patterns of the Y/ZrO_2 catalysts were measured with a powder X-ray diffractometer (Rigaku, RINT 2000) with Cu Kα monochromatized radiation (λ = 0.154178 nm) at 40 kV and 40 mA. NH_3-TPD and CO_2-TPD were also used (BEL-CAT-32) to investigate the acidic and basic site properties of the catalysts respectively. Each catalyst sample (0.1 g) was placed in a small quartz tube and dried in a He flow (99.99%, 30 mL/min) at 773 K for 1 h. The sample was cooled to 373 K, the adsorption of NH_3/He or CO_2/He (30 mL/min) for 1 h took place at 373 K, and then the catalyst was flushed with He (30 mL/min) at the same temperature for 1 h to remove NH_3 or CO_2 that were physically adsorbed on the sample surface. TPD measurements were carried out (NH_3-TPD from 373 to 873 K and CO_2-TPD from 323 to 873 K) with a heating rate of 10 K/min, with He as the carrier gas. The desorbed NH_3 or CO_2 were quantified with a thermal conductivity detector.

2.3. Catalytic apparatus and ethanol transformation reaction

Ethanol (99.5%, Wako) was used without further purification. All the synthesized Y/ZrO_2 samples were powdered, pressed, crushed, and sieved with a 14–22 mesh. The ethanol transformation reaction was carried out at 1.11 MPa using a continuous-flow fixed-bed quartz tubular reactor described in our previous paper [13]. Prior to each reaction, the catalyst (0.72 g) was pretreated in a flow of N_2 (flow rate:
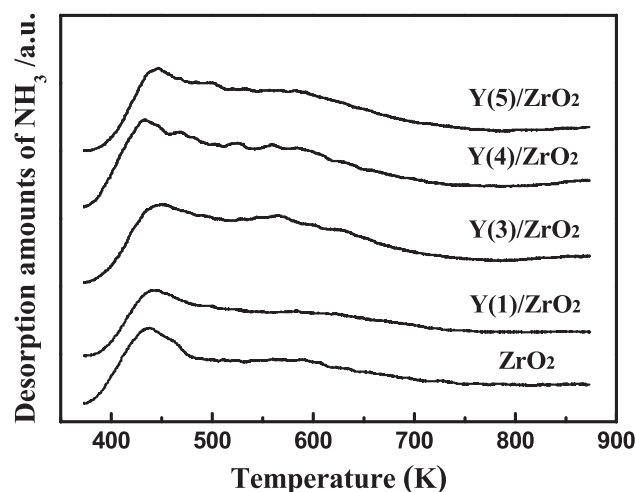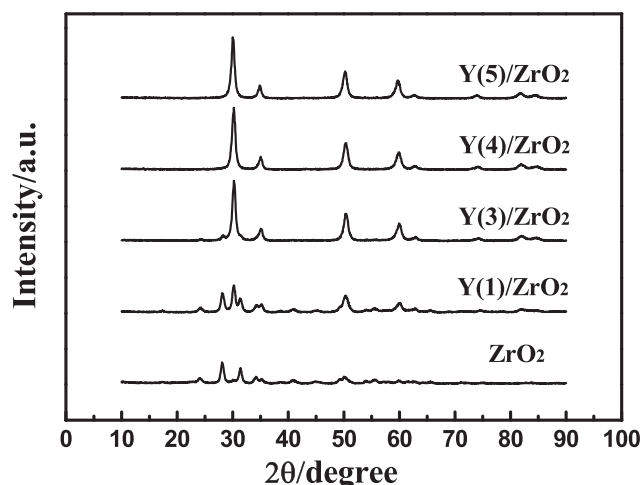

Fig. 2. NH_3-TPD profiles of the series of synthesized Y/ZrO_2 catalysts.

100 mL/min) at 873 K for 1 h. Reaction temperature (723 K) was monitored by a thermocouple in the catalyst bed. Reactants (ethanol:H_2O:N_2 = 1:1:1) were fed into the reactor by means of a micro pump and were vaporized before entering the reactor. The contact time W/F is 0.045 g/mL·min^{-1} (The contact time is defined as W/F, where W denotes the catalyst weight (g) and F denotes the total flow rate (mL/min)). The products of the ethanol transformation were analyzed using on-line gas chromatography (hydrogen-flame ionization detector with RT-alumina PLOT (Restek, USA) for C_1–C_4 hydrocarbon, and thermal conductive detector with Shincarbon ST (Shinwa Chem. Ind. Ltd., Japan) for N_2 and H_2).

3. Results and discussion

3.1. Characterization of catalysts

In this work, we synthesized Y/ZrO_2 catalyst by co-precipitation method. All the synthesized catalyst samples were firstly characterized by nitrogen adsorption/desorption method (BET). Table 1 summarized nitrogen adsorption/desorption (BET) results for these ZrO_2 catalysts. As listed in Table 1, it can be noted that the introduction of Y caused a clear increase in the BET surface area, which is attributed to the large specific surface area of yttrium oxide. In contrast, the pore size decreased with increasing Y doping. The textural properties such as

Fig. 1. XRD patterns of the series of synthesized Y/ZrO_2 catalysts.
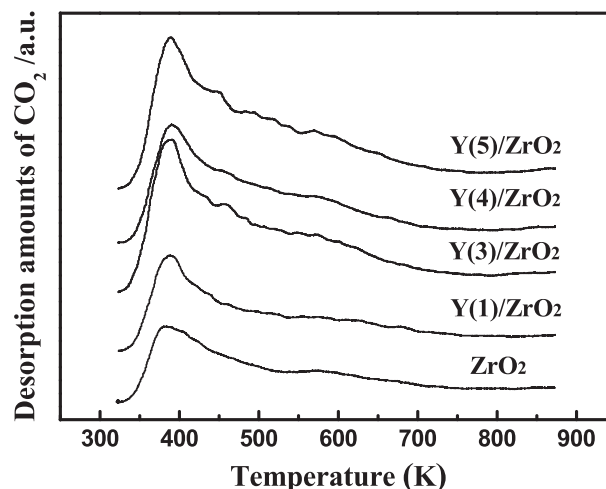
Fig. 3. CO_2-TPD profiles of the series of synthesized Y/ZrO_2 catalysts.