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Research article

Remarkably enhanced selectivity for conversion of ethanol to propylene over ZrO_2 catalysts

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ABSTRACT

In this work, various bi-functional ZrO_2 catalysts were synthesized by precipitation method with different zirconium precursor and precipitant under different calcination temperature. N_2 adsorption-desorption method (BET), temperature programmed desorption (TPD) and X-ray diffraction (XRD) were used to characterize the ZrO_2 catalyst. Conversions of ethanol to propylene were studied on these various ZrO_2 catalysts. Results showed that the excellent catalytic performance of ethanol to propylene was obtained over ZrO_2 catalyst. The highest propylene yield was 40.2%, which is obtained on ZrO_2 synthesized by the precipitation of $ZrO(NO_3)_2\cdot 2H_2O$ and $NH_3\cdot H_2O$ and then calcined at 823 K. The effects of reaction contact time on the conversion of ethanol to propylene were also investigated over ZrO_2 catalysts. Based on the results, the reaction pathways were suggested to be ethanol → ethylene, and ethanol → acetaldehyde → acetone → propylene.

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1. Introduction

Propylene is one of the basic chemical feedstocks for the synthesis of polypropylene, acrylonitrile, propene oxide and many other highly valuable chemicals [1]. It is mainly produced as co-product in the steam thermal cracking of the naphtha and in the fluid catalytic cracking. In recent years, the production of propylene was in short supply, because of the increasing demand for its derivatives. Due to the limited reserve of petroleum and the immaturity of other non-petrochemical routes, it is necessary to explore a new route for the production of propylene [2,3].

The reaction of ethanol to propylene (ETP) has attracted more attention since the bioethanol got much developed. Bioethanol can be produced in larger scale by fermentation of lignocellulosic biomass. According to the Renewable Fuels Association (RFA) reports, the benefits associated with using ethanol–from reducing petroleum imports to decreasing greenhouse gas emissions–are well known [4]. However, ETP process has not been fully investigated and has not yet been used in industrial application. Only a few researches reported the conversion of ethanol to propylene over ZSM-5 catalysts [5–18]. A recent review by Liu et al. summarizes the performed report on the bioethanol to propylene over catalytic materials, such as zeolites and transition metals. HZSM-5 zeolite is the best catalyst and support known for bioethanol dehydration reaction so far [19]. The yield of propylene is about 20–32%, which is still not sufficient to satisfy economic feasibility, and this selectivity decreased with time-on-stream.

Various metal oxides have been examined for the conversion of ethanol [20–22], 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%. The propylene yield of Sc/ln_2O_3 was higher, but the activity of this catalyst gradually decreased with duration at 30 vol% of ethanol. Among the metal oxides with acid/base or redox sites, zirconia is the most widely used due to its unique features. With the change of temperature, the crystalline phases changed. Catalysis by zirconia, previously uncharted, has become a popular field recently. Zirconia and supported zirconia catalysts have many applications in chemical synthesis [23–25]. To the best of our knowledge, only a few researches reported the ZrO_2 as catalyst in the reaction of ethanol to ethylene. The previous studies showed that WO_3/ZrO_2 and WO_3/TiO_2 are excellent catalysts for ethanol dehydration [19]. Acid sites are widely recognized to lead to dehydration of ethanol, giving ethylene, while basic sites lead to dehydrogenation to yield acetaldehyde, and then to yield propylene. Thus, different products can be produced by ethanol conversion over acid-base bifunctional metal oxides. However, there is a lack of fundamental understanding about ETP reaction over ZrO_2 catalyst.

In this study, we synthesized ZrO_2 catalyst with different zirconium precursors and precipitants. The N_2 adsorption-desorption method (BET), X-ray diffraction (XRD), temperature programmed desorption (NH_3-TPD and CO_2-TPD) were used to characterize the ZrO_2 catalyst. The ethanol conversion reaction was systematically investigated using these catalysts according to the synthesis, post-treatment process, and reaction conditions. The results show that ZrO_2 catalyst showed better

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Table 1
Characteristics of the synthesized zirconium dioxide catalysts.

Sample No.	Zirconium Precursor	Precipitant	BET surface area ($m^2\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)	Pore size (Å)
1	$ZrOCl_2 \cdot 8H_2O$	Ethylenediamine	54.2	0.141	80.4
2	$ZrO(NO_3)_2 \cdot 2H_2O$	Ethylenediamine	55.5	0.126	69.0
3	$ZrOCl_2 \cdot 8H_2O$	$NH_3 \cdot H_2O$	56.2	0.196	110.6
4	$ZrO(NO_3)_2 \cdot 2H_2O$	$NH_3 \cdot H_2O$	54.1	0.129	72.1
5	$ZrOCl_2 \cdot 8H_2O$	NaOH	53.5	0.152	78.6
6	$ZrO(NO_3)_2 \cdot 2H_2O$	NaOH	55.9	0.133	67.9

performance for propylene production than that on zeolite and other metal oxide catalysts. The physical and chemical properties of the ZrO_2, the crystalline phase of the ZrO_2 and operating conditions affect the catalytic performance for the conversion of ethanol to propylene.

2. Experimental

2.1. Preparation of the ZrO_2 catalysts

Zirconium dioxide catalyst samples were prepared by precipitation method from the corresponding chemicals: $ZrO(NO_3)_2 \cdot 2H_2O$ or $ZrOCl_2 \cdot 8H_2O$ at a nominal composition. Zirconium precursors were dissolved in the 500 mL deionized water. The precipitant ($NH_3 \cdot H_2O$, ethylenediamine, and NaOH aqueous solvent) 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 293 K for 24 h. After crystallization, the zirconium dioxide samples were centrifugated, washed thoroughly with deionized water for 3 times, dried at 383 K for 16 h. After that, the catalysts were calcined in air at a nominal temperature (823, 873, 923, and 973 K, respectively) for 4 h with a heating rate of 4.5 K/min. Other ZrO_2 catalysts were prepared through direct calcination method from the corresponding chemical: $ZrO(NO_3)_2 \cdot 2H_2O$. $ZrO(NO_3)_2 \cdot 2H_2O$ were calcined in air at a nominal temperature (823, 873, 923, and 973 K, respectively) for 4 h with a heating rate of 4.5 K/min.

2.2. Characterization of the 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, the samples were degassed at 623 K for 10 h under reduced pressure. XRD patterns of the ZrO_2 catalysts were measured with a powder X-ray diffractometer (Rigaku, RINT 2000) with Cu Kα monochromatized radiation ($\lambda = 0.154178$ nm) at 40 kV and 40 mA. Temperature programmed desorption of ammonia (NH_3-TPD) and carbon dioxide (CO_2-TPD) were also used (BEL-CAT-32) to investigate the acidic and basic properties of the catalysts. Each catalyst sample (0.1 g) was placed

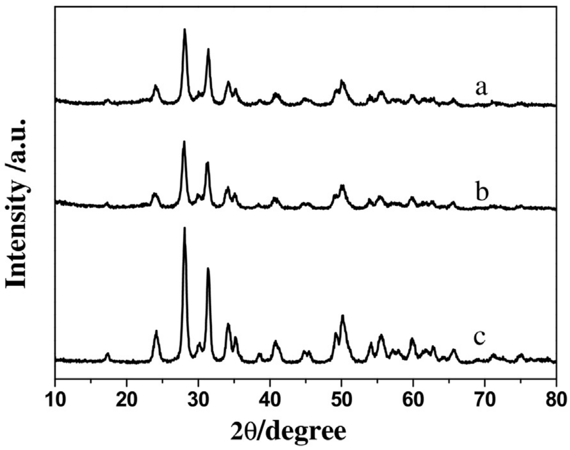

Fig. 1. XRD patterns of ZrO_2 catalysts synthesized with $ZrO(NO_3)_2 \cdot 2H_2O$ and different precipitant: (a) $NH_3 \cdot H_2O$; (b) ethylenediamine; (c) NaOH. Calcination temperature: 823 K.

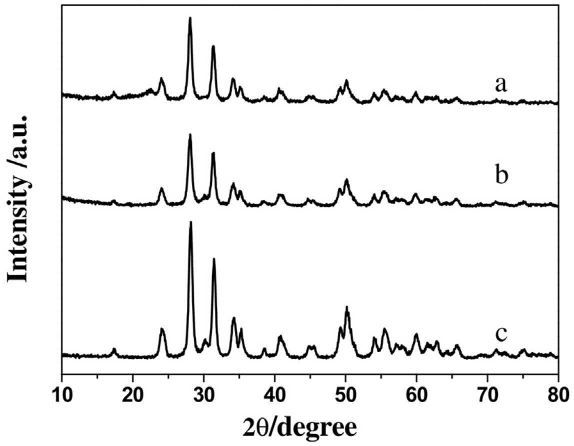

Fig. 2. XRD patterns of ZrO_2 catalysts synthesized with $ZrOCl_2 \cdot 8H_2O$ and different precipitant: (a) $NH_3 \cdot H_2O$; (b) ethylenediamine; (c) NaOH. Calcination temperature: 823 K.

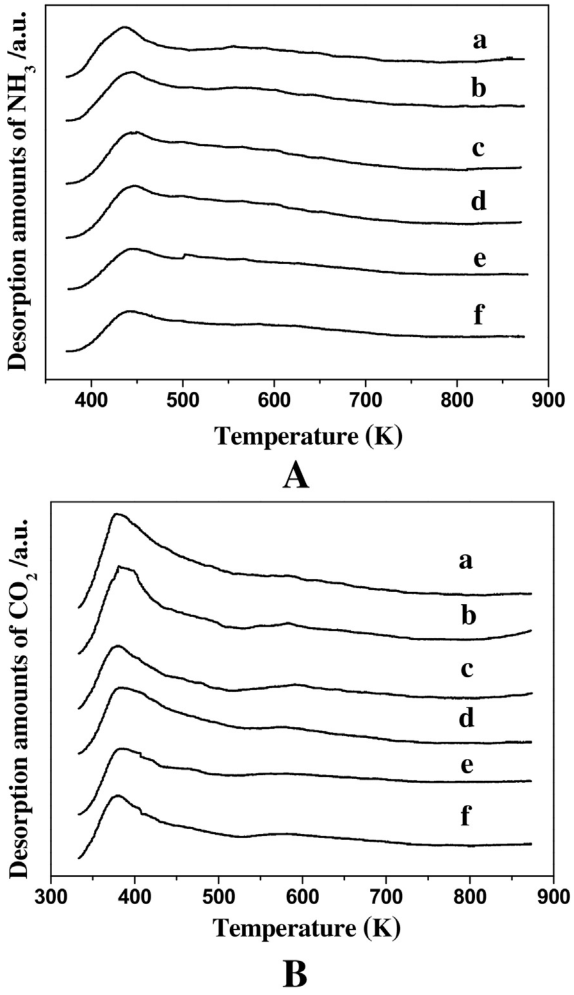

Fig. 3. TPD profiles of the series synthesized ZrO_2 catalysts (A) NH_3-TPD and (B) CO_2-TPD synthesized by (a) $ZrO(NO_3)_2 \cdot 2H_2O + NH_3 \cdot H_2O$; (b) $ZrOCl_2 \cdot 8H_2O + NH_3 \cdot H_2O$; (c) $ZrO(NO_3)_2 \cdot 2H_2O$ + ethylenediamine; (d) $ZrOCl_2 \cdot 8H_2O$ + ethylenediamine; (e) $ZrO(NO_3)_2 \cdot 2H_2O$ + NaOH; (f) $ZrOCl_2 \cdot 8H_2O$ + NaOH.

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