

Impact of temperature ramping rate during calcination on characteristics of nano-ZrO₂ and its catalytic activity for isosynthesis

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Abstract

This paper studied the effect of temperature ramping rate during calcination on characteristics of nanoscale zirconia and its catalytic performance for isosynthesis. The physical properties, i.e. BET surface area, cumulative pore volume, cumulative pore diameter and the phase composition in zirconia, acid-base properties and surface properties such as Zr³⁺ quantity, were characterized. Increase in the temperature ramping rate of calcination resulted in a higher composition of the tetragonal phase, but it showed insignificant influence on the other physical properties. Considering the catalytic activity, the acid sites did not affect the activity, but the basic sites depended on the fraction of the tetragonal phase in zirconia which was related to the selectivity to isobutene. The intensity of Zr³⁺ on the surface varied with the change in the heating rate of calcination. Both the tetragonal phase composition in zirconia and the quantity of Zr³⁺ were the key factors affecting the selectivity to isobutene in hydrocarbons. Moreover, the maximum value of the product selectivity to isobutene on the ZrO₂ (5.0) catalyst was attained at the highest concentration of Zr³⁺. © 2007 Elsevier B.V. All rights reserved.

Keywords: Isosynthesis; Tetragonal phase; ZrO₂; Zr³⁺; Isobutene

1. Introduction

At present, the octane enhancer demand is continuously increasing with the increased fuel consumption. Isobutene is an important raw material for the production of important octane enhancers such as methyl *tert*-butyl ether (MTBE) and ethyl *tert*-butyl ether (ETBE). Typically, isobutene is extracted from the C₄ stream in petroleum refining process; however, the supply of isobutene from the petroleum products is possibly inadequate in the near future. It is expected that an alternative source for the production of isobutene needs to be explored. It is evident that one of the promising sources for isobutene synthesis can be provided by syngas derived from a renewable resource such as biomass. This route is attractive due to the following reasons

(i) the chosen resource of isobutene production is renewable, then being more green than the conventional petroleum sources, which are about to face shortage in the near future, (ii) carbon dioxide, a by-product of fermentation process, is substantially consumed to produce syngas, thus reducing the CO₂ emission to the atmosphere and (iii) the ratio of carbon monoxide to hydrogen of 1:1 for the syngas from fermentation of biomass is suitable for the reaction of isobutene synthesis.

As is well known, isosynthesis is the catalytic reaction that converts syngas to branched chain hydrocarbons, especially isobutane and isobutene. The early work [1] showed that suitable catalysts for the isosynthesis reaction are hardly reducible oxides such as zirconia rather than other reduced transition metals. It has been reported that zirconia is the most selective catalyst for isosynthesis [2–6]. The effect of characteristics of catalysts on their catalytic performance was investigated by some researchers. For instance, the characteristic and catalytic performance of the nanoscale zirconias prepared by various methods

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such as the precipitation method, the supercritical fluid drying method and the freeze-drying method for isosynthesis were studied by Su et al. [4]. They found that the different preparation methods affected catalytic performance, and better product selectivity of isobutene resulted from higher ratios of base to acid sites on the catalyst surface. As reported by Maruya et al. [6], the crystal phases such as monoclinic phase in zirconia influenced catalytic performance. Moreover, the acidity and basicity could play an important role on the catalytic performance because of bifunctionality of zirconia [4,7–9]. In addition, effects of these factors such as crystallite size, the phase composition and acid-base sites of zirconia on catalytic performance were also studied in our previous paper [10]. However, the studies of surface properties of catalysts such as acid-base sites related with the crystal phase of zirconia and the quantity of Zr^{3+} on the surface were not investigated. From the study of Zr^{3+} [11], it was found that Zr^{3+} ion was related to the selectivity to isobutene in the reaction on zirconia.

In this work, the effect of temperature ramping rate during calcination on characteristics and catalytic performance for isosynthesis of zirconia catalysts was investigated. The synthesized nanoscale zirconia catalysts were prepared using the precipitation method. Various physical characteristics of zirconia catalysts such as the phase composition in zirconia, acid-base properties and surface properties including quantity of Zr^{3+} on the catalyst surface were determined. The obtained information was useful for describing the change in catalytic performance of the synthesized catalysts.

2. Experimental

2.1. Catalyst preparation

The nanoscale zirconia (ZrO_2) was prepared by the precipitation method. It was carried out by slowly adding a solution of zirconium salt precursors such as zirconyl nitrate [$ZrO(NO_3)_2$] (0.15 M) into a well-stirred precipitating solution of ammonium hydroxide (NH_4OH) (2.5 wt%) at room temperature. The pH of the solution was carefully controlled at 10. The resulting precipitate was removed, and then washed with deionized water. The obtained sample was then dried overnight at $110^\circ C$ and calcined at $450^\circ C$ for 3 h at various temperature ramping rates such as 1.0, 2.5, 5.0, 7.5 and $10.0^\circ C/min$. Zirconia catalysts prepared by using these temperature ramping rates were denoted as ZrO_2 (1.0), ZrO_2 (2.5), ZrO_2 (5.0), ZrO_2 (7.5) and ZrO_2 (10.0), respectively.

2.2. Catalyst characterization

2.2.1. N_2 physisorption

Measurements of BET surface area, cumulative pore volume and average pore diameter were performed by the N_2 physisorption using a Micromeritics ASAP 2020 surface area and porosity analyzer.

2.2.2. X-ray diffraction (XRD)

The XRD spectra of catalysts were measured by a SIEMENS D5000 X-ray diffractometer using $Cu K\alpha$ radiation with a nickel

filter over the 2θ ranging from 20° to 80° . The crystal sizes of the prepared catalysts were obtained by XRD line broadening using Scherrer's equation. The characteristic peaks at $2\theta = 28.2^\circ$ and 31.5° for $(-1\ 1\ 1)$ and $(1\ 1\ 1)$ reflexes, respectively, were assigned to the monoclinic phase in ZrO_2 . The characteristic peak at $2\theta = 30.2^\circ$ for the $(1\ 1\ 1)$ reflex in the XRD patterns represented the tetragonal phase in ZrO_2 .

The percents of tetragonal and monoclinic phases in ZrO_2 were calculated by a comparison of the areas for the characteristic peaks of the monoclinic phase and the tetragonal phase. The percent of each phase was determined by means of the Gaussian areas $h \times w$, where h and w are the height and half-height width of the corresponding XRD characteristic peak as follows [4]:

$$\begin{aligned} & \% \text{ monoclinic phase} \\ & = \frac{\sum(h \times w) \text{ monoclinic phase}}{\sum(h \times w) \text{ monoclinic and tetragonal phase}} \end{aligned}$$

$$\begin{aligned} & \% \text{ tetragonal phase} \\ & = \frac{\sum(h \times w) \text{ tetragonal phase}}{\sum(h \times w) \text{ monoclinic and tetragonal phase}} \end{aligned}$$

2.2.3. Transmission electron microscopy (TEM)

Catalyst crystallite size and the diffraction pattern were obtained using a JEOL JEM-2010 transmission electron microscope operated at 200 kV with an optical point to point resolution of 0.23 nm at National Metal and Materials Technology Center (MTEC). The sample was dispersed in ethanol prior to the TEM measurement.

2.2.4. Temperature-programmed desorption (TPD)

Temperature-programmed desorption of ammonia and carbon dioxide (NH_3 - and CO_2 -TPD) was used to determine the acid-base properties of catalysts. TPD experiments were carried out using a flow apparatus. The catalyst sample (0.1 g) was treated at its calcination temperature ($450^\circ C$) in a helium flow for 1 h and then saturated with a 15% NH_3/He mixture or a pure CO_2 flow after cooling to $100^\circ C$. After purging with the helium at $100^\circ C$ for 1 h to remove weakly physisorbed NH_3 or CO_2 , the sample was heated to $450^\circ C$ at a rate of $20^\circ C/min$ in a helium flow ($50\text{ cm}^3/min$). The amount of acid-base sites on the catalyst surface was calculated from the desorption amount of NH_3 and CO_2 , respectively. It was determined by measuring the areas of the desorption profiles obtained from a Micromeritics ChemiSorb 2750 pulse chemisorption system analyzer. For the broad desorption peak, it was separated into many sub-peaks by using the Fityk program for peak fitting. All areas of sub-peaks were summed to calculate the total amount of acid and base sites.

2.2.5. Electron spin resonance spectroscopy (ESR)

Electron spin configuration was detected by using electron spin resonance spectroscopy (ESR) (JEOL model JES-RE2X) at the Scientific and Technological Research Equipment Center (STREC), Chulalongkorn University. The sample was degassed before measurement at room temperature.

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