



Isosynthesis via CO hydrogenation over $\text{SO}_4\text{-ZrO}_2$ catalysts

Watcharapong Khaodee^a, Nicha Tangchupong^a, Bunjerd Jongsomjit^a, Navadol Laosiripojana^b, Piyasan Praserttham^a, Suttichai Assabumrungrat^{a,*}

^a Center of Excellence in Catalysis and Catalytic Reaction Engineering, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand

^b The Joint Graduate School of Energy and Environment, King Mongkut's University of Technology Thonburi, Bangkok 10140, Thailand

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ABSTRACT

Catalytic performances of sulfated zirconia catalysts with various contents of sulfur (from 0.1 to 0.75%) on isosynthesis were studied. It was firstly found that undoped-zirconia synthesized from zirconyl nitrate provided higher activity towards isosynthesis reaction ($106 \mu\text{mol kg-cat}^{-1} \text{s}^{-1}$) compared to that synthesized from zirconyl chloride ($84.9 \mu\text{mol kg-cat}^{-1} \text{s}^{-1}$). Nevertheless, the selectivity of isobutene in hydrocarbons was relatively lower. It was then observed that the catalytic reactivity and selectivity significantly improved by sulfur loading. The most suitable sulfur loading content seems to be at 0.1%, which gave the highest reaction rate and selectivity of isobutene. By applying several characterization techniques, i.e. BET, XRD, NH_3 - and CO_2 -TPD and SEM, it was revealed that the high reaction rate and selectivity towards isosynthesis reaction of sulfated zirconia catalysts are related to the acid–base properties, Zr^{3+} quantity and phase composition.

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1. Introduction

Isobutene is an important feedstock for the production of oxygenated compounds. Currently, it is mainly produced from the extraction of petroleum feedstock. However, as the petroleum supply is becoming limited due to the progressive increase of fuel consumption, alternative route for isobutene production is of interest. Isosynthesis is a reaction that catalytically converts synthesis gas predominantly to branched chain hydrocarbons, especially isobutane and isobutene. Among various catalysts studied, zirconia and ceria have been reported as selective catalysts for isosynthesis in many studies [1–7]. It was further demonstrated that cerium coprecipitated with zirconia, as called ceria–zirconia, can improve the catalytic activity [8]. A number of research efforts have focused on determining the relation between catalyst characteristics and their catalytic performance. As reported by Postula et al. [8], zirconias prepared by precipitation method and hydrothermal method were tested over isosynthesis reaction. The precipitated ones showed higher activity, whereas the hydrothermal ones offered greater selectivity of isobutene in C_4 hydrocarbons with corresponding to the high basicity on surface of zirconia. Su et al. [3] investigated the catalytic performance towards isosynthesis of various nanoscale zirconias synthesized by several techniques, such

as precipitation method, supercritical fluid drying method and freeze-drying method. They concluded that better formation of isobutene is resulted from higher ratios of base to acid sites on catalyst surface. The results were in good agreement with those reported by Feng et al. [9], even they synthesized zirconia by different techniques (i.e. calcination of zirconyl salt and modified sol–gel method). The effect of the crystal phase such as monoclinic phase in zirconia on the catalytic performance was also investigated by Maruya et al. [5]. Due to the bifunctionality of zirconia, the acid–base properties could play an important role on the catalytic performance [3,10–13]. Several researches have proposed that catalytic activity is dependent on acid sites, while base sites or ratio of base sites to acid sites affect the selectivity of isobutene. Nevertheless, Lu et al. [14] revealed differently that the catalytic activity is dependent on strong basic site.

In our previous works, micron- and nanoscale zirconia and ceria were tested for the isosynthesis [15,16]. We reported that not only the acid–base properties, but the crystallite size and crystal phase also essentially influence the catalytic performance. At the same crystallite size, ceria shows higher activity than zirconia [15]. The effect of temperature ramping rate during calcination on characteristics of nanoscale zirconia and its catalytic performance for isosynthesis was investigated [16]. It was found that both tetragonal phase in zirconia and intensity of Zr^{3+} influence the selectivity to isobutene. In addition, the isosynthesis over $\text{ZrO}_2\text{-CeO}_2$ mixed oxide catalysts synthesized by coprecipitation and physical mixing methods with various contents of CeO_2 was also

* Corresponding author. Tel.: +66 2 218 6868; fax: +66 2 218 6877.

E-mail address: Suttichai.A@chula.ac.th (S. Assabumrungrat).

studied [17]. We reported that catalysts prepared by physical mixing method offer higher catalytic activity than those prepared by coprecipitation method. In addition, the change in the selectivity of isobutene in hydrocarbons of the catalysts was well-correlated with the change in intensity of Zr^{3+} .

Metal oxides, such as ZrO_2 , Al_2O_3 , and TiO_2 , are acid catalysts; their acidity could be enhanced by sulfation. Previously, several sulfated acid catalysts have been tested [18–23]. Among those acid catalysts, sulfated zirconia (SO_4 - ZrO_2 abbreviated as SZ) has been the subject of extensive research work since its ability to catalyze isomerization of linear to branched light hydrocarbons. This catalyst is known as solid super acid and was reported to be active for *n*-butene isomerization even at low temperature, giving relatively high selectivity [23]. This catalyst may be a good choice for isosynthesis and, therefore, in this paper, the catalytic performances of sulfated zirconia on isosynthesis via CO hydrogenation were investigated. The catalysts were prepared by incipient wetness impregnation method using H_2SO_4 as a sulfating species. It is noted that two different zirconia salt precursors were employed for synthesizing zirconia via precipitation method. The catalytic performances of synthesized catalysts with different sulfur contents were then tested. In addition, various physical characteristics of synthesized catalysts, i.e. acid–base properties and surface properties including quantity of Zr^{3+} on the catalyst surface were determined in order to relate these properties with the catalytic performance.

2. Experimental

2.1. Catalyst preparation

2.1.1. Preparation of zirconia

Zirconia (ZrO_2) was synthesized via the precipitation method. A solution of zirconium salt precursors such as zirconyl chloride ($ZrOCl_2$) or zirconyl nitrate [$ZrO(NO_3)_2$] (0.15 M) was slowly dropped into a well-stirred precipitating solution of ammonium hydroxide (NH_4OH) (2.5 wt%) at room temperature. The solution was controlled at pH of 10. The obtained precipitate was removed, and then washed with deionized water until Cl^- was not detected by a silver nitrate ($AgNO_3$) solution. Then, the solid sample was dried overnight at 110 °C and calcined at 450 °C for 3 h with a temperature ramping rate of 5 °C/min.

2.1.2. Preparation of sulfated zirconia

Sulfated zirconia was prepared by the incipient wetness impregnation method. Different amounts of sulfuric acid were doped on zirconia (having sulfur contents of 0.1, 0.25, 0.5 and 0.75%) at room temperature. The obtained sample was then dried overnight at 110 °C and calcined at 450 °C for 3 h with a temperature ramping rate of 5 °C/min.

2.2. Catalyst characterizations

2.2.1. N_2 physisorption

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

2.2.2. X-ray diffraction (XRD)

The X-ray diffraction (XRD) patterns of powder were performed by X-ray diffractometer. The crystallite size was estimated from line broadening according to the Scherrer equation and α - Al_2O_3 was used as a standard. In addition, the characteristic peaks of crystal phase from XRD spectra were used to calculate the fraction of crystal phase in catalyst.

2.2.3. Electron spin resonance spectroscopy (ESR)

Electron spin configuration was detected by using electron spin resonance spectroscopy (ESR) with JEOL model JES-RE2X. The sample was degassed before measurement at room temperature.

2.2.4. Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) was used to determine the catalyst granule morphology. The model is JEOL JSM-5800LV and operated using the back scattering electron (BSE) mode at 20 kV.

2.2.5. Temperature-programmed desorption (TPD)

Temperature-programmed desorption techniques with ammonia and carbon dioxide (NH_3 - and CO_2 -TPD) were 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 °C) in helium flow for 1 h and then saturated with 15% NH_3 /He mixture or pure CO_2 flow after cooling to 100 °C. After purging with helium at 100 °C for 1 h to remove weakly physisorbed NH_3 or CO_2 , the sample was heated to 450 °C at a rate of 20 °C/min in a helium flow of 50 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 by measuring the areas of the desorption profiles under the desorption temperature range of 100–450 °C. For the broad peak of desorption curve, it was deconvoluted to sub-peaks by peak fitting program equipped with the Micromeritics ChemiSorb 2750 pulse chemisorption system analyzer, and then converted to the amount of desorbed NH_3 or CO_2 by calibration curve of each desorbed gas.

2.3. Reaction study

Isosynthesis was carried out at 400 °C and atmospheric pressure in a fixed-bed quartz reactor packed with 2 g of catalyst. The inlet feed was a mixture of $CO/H_2/N_2$ (10/10/5 cm^3 /min). The compositions of carbon monoxide and hydrogen in the feed and product streams were analyzed by a gas chromatography (Shimadzu model 8A (GC-8A)) equipped with thermal conductivity detector (TCD) and molecular sieve column, while carbon dioxide in the product stream was analyzed by the same GC with Poropak-Q column. Hydrocarbons in the product stream were analyzed by a gas chromatography Shimadzu model 14B (GC-14B) equipped with flame ionization detector (FID) with VZ-10 column.

3. Results and discussion

In this work, ZrO_2 and SO_4 - ZrO_2 catalysts were used and tested for the catalytic performance on isosynthesis. The synthesized ZrO_2 obtained from $ZrOCl_2$ and $ZrO(NO_3)_2$ were denoted as ZrO_2 -Cl and ZrO_2 -N, respectively. The SO_4 - ZrO_2 catalysts prepared by impregnating of various sulfur contents (i.e. 0.1, 0.25, 0.5 and 0.75 wt%) over ZrO_2 and denoted as w%SZ (ZrO_2 -N) and w%SZ (ZrO_2 -Cl).

3.1. Catalyst characterization

3.1.1. X-ray diffraction (XRD) and scanning electron microscopy (SEM)

The XRD patterns of ZrO_2 and sulfated zirconia (SO_4 - ZrO_2) catalysts synthesized from $ZrOCl_2$ are shown in Fig. 1, whereas those synthesized from $ZrO(NO_3)_2$ are shown in Fig. 2. Clearly, both ZrO_2 and SO_4 - ZrO_2 catalysts exhibited the similar XRD peaks at $2\theta = 28.2^\circ$ and 31.5° , indicating the presence of the monoclinic phase. Besides the monoclinic characteristic peaks, they also exhibited the XRD characteristic peaks at 2θ of 30.2° , 35.3° , 50.2° and 60.2° , which indicate the presence of tetragonal crystalline

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