



Research paper

Synthesis of light olefins from CO₂ hydrogenation over (CuO-ZnO)-kaolin/SAPO-34 molecular sieves

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ARTICLE INFO

Keywords:

SAPO-34

CuO-ZnO

Kaolin

Bifunctional catalyst

Light olefins

ABSTRACT

Cu–Zn oxide/SAPO-34 molecular sieves was used as bifunctional catalyst for the direct synthesis of light olefins from CO₂ and H₂, but the production of SAPO-34 molecular sieves required high cost and the Cu–Zn oxide (CuO-ZnO) particles were prone to sintering, which severely restricted its industrial application. Herein, kaolin was used as raw material to prepare SAPO-34 molecular sieves and as supports to prepare kaolin-supported CuO-ZnO catalysts. The samples were characterized by X-ray diffraction, Scanning Electron Microscope, Energy Dispersive Spectroscopy, N₂ sorption, H₂ temperature programmed reduction, NH₃ temperature programmed desorption and Fourier Transforms Infrared spectra techniques. The results showed that the SAPO-34 molecular sieves presented lamellar structure and the CuO-ZnO particles were well dispersed on the surface of kaolin. The results of catalytic reaction for the direct synthesis of light olefins from CO₂ and H₂ indicated that the (CuO-ZnO)-kaolin/SAPO-34 molecular sieves could enhance not only the yield of light olefins, but also the lifetime.

1. Introduction

The utilization of carbon dioxide has recently become attractively due to the increasing attention on the effects of green house gas accumulation in the atmosphere (Zoundi, 2017). Additionally, the potential of CO₂ as a carbon source for synthesizing chemicals, fuels and materials are of importance (Dai et al., 2001). Among various transformation routes, the chemical conversion of CO₂ hydrogenation to produce renewable fuels, such as methanol, higher alcohols and dimethyl ether, have been considered to be one of the most promising processes (Bian et al., 2009; Centi and Perathoner, 2009; Jiang et al., 2010; Wu and Zhou, 2016). Especially, synthesis of light olefins from the viewpoint of converting CO₂ to building blocks for chemicals and polymers are particularly important and have progressed in recent years (Sattawong et al., 2015). There are two main routes to produce light olefins from CO₂ and H₂. The first route is a two-step process, including a methanol synthesis step from CO₂ hydrogenation, followed by a methanol dehydration step to produce light olefins. The second route is a one-step process, integrating the methanol synthesis and methanol dehydration into a single step. At present, the research is focusing on developing the one-step conversion process for two reasons. First of all, synchronous production of methanol and light olefins in one step can eliminate the accumulation of methanol in the reactor which usually impedes the conversion of CO₂ due to reaching the thermodynamic equilibrium.

Moreover, from the perspective of economy, one-step conversion is more advantageous, because the methanol synthesis and methanol dehydration requires only one reactor (An et al., 2008; Zhou et al., 2016).

The one-step conversion of CO₂ hydrogenation to light olefins can be catalyzed by bifunctional catalysts. Presently, bifunctional catalysts for the synthesis of light olefins have relied on copper-based catalysts or noble metal catalysts as the hydrogenation component and solid acid catalysts such as HZSM-5, HZSM-22, SAPO-34, SAPO-57, SAPO-59 and HSSZ-13 for the dehydration component (Ahn et al., 2016; Li et al., 2011; Oyola-Rivera et al., 2015; Wang et al., 2015; Xiao et al., 2015). Copper-based catalysts have been widely used for the CO₂ hydrogenation to methanol process due to they can be used at relatively high temperature and pressure (Chen et al., 1999; Fan and Wu, 2016). In Cu–Zn oxide-based catalysts, ZnO is regarded to provide active sites for hydrogen spillover, or as a structure-directing support controlling the dispersion of metallic copper particles (Ren et al., 2015). Moreover, the interaction between Cu and Zn oxide causes an electron transfer from Zn oxide to Cu metal that occurs as Cu⁰ and Cu(I) species, which are crucial for CO₂ hydrogenation to methanol (Deerattrakul et al., 2016; Donphai et al., 2016). Among these solid acid catalysts, SAPO-34 is of particular importance. Its framework contains chabazite (CHA) cages, which can be accessed via an eight-membered ring (8R) window with a pore diameter of ~0.38 nm. SAPO-34 molecular sieves have shown

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Received 25 March 2018; Received in revised form 23 June 2018; Accepted 26 June 2018

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potentials for several applications including gas separation and water adsorption. Perhaps, the most important use of this material is to catalyze the methanol to light olefin (MTO) reaction, because of its moderate acid strength, high selectivity and hydrothermal stability (Kim et al., 2011; Tian et al., 2015; Zhang et al., 2011).

Conventionally, SAPO-34 molecular sieves were prepared by a hydrothermal method from traditional chemicals (containing individual Si, Al, and P) or aluminophosphate fabricated from related chemicals, which result in high cost (Zhu et al., 2009). Kaolin, a typical phyllosilicate with a 1:1 layer structure consisted of a $[\text{SiO}_4]$ tetrahedral sheet and a $[\text{AlO}_6]$ octahedral sheet in the layer unit (Ayele et al., 2016; Shu et al., 2016). It consists of high SiO_2 and Al_2O_3 content that is beneficial for aluminosilicate synthesis (Mohiuddin et al., 2016; Qoniah et al., 2015). Herein, kaolin is used in the synthesis of SAPO-34, in which all of the SiO_2 and a portion of Al_2O_3 elements are supplied by kaolin to reduce the cost of SAPO-34. In addition, the copper-based catalyst usually exhibits inferior activity and stability for the hydrogenation of CO_2 due to Cu sintering accelerated from the presence of the water vapor byproduct (Zhang et al., 2017). To solve the problem of Cu sintering, many attempts have been made such as immobilizing metal oxides onto a suitable support to improve Cu dispersion has been found to be an effective way. Hence, kaolin can be used as supports to prepare kaolin-supported CuO-ZnO catalysts to restrain sintering of Cu metal particles due to their strong interaction with the supports.

2. Experimental

2.1. Chemicals and materials

$\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Na_2CO_3 , phosphoric acid and triethylamine (TEA) are all of analytical grade. Kaolin, pseudoboehmite (Al_2O_3 , 70 wt%) and silica sol (SiO_2 , 30 wt%) are all of industrial grade.

2.2. Catalyst preparation

2.2.1. Preparation of kaolin-supported CuO-ZnO

Kaolin-supported CuO-ZnO (CZ-k) was prepared by a deposition-precipitation method using Na_2CO_3 as precipitation agent and kaolin as supports (Zhang et al., 2017). The aqueous solution (containing 3.2 g of $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 2.0 g of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 30 mL of deionized water) was impregnated into 1.5 g of kaolin sample at 353 K. After stirring for 2 h, the impregnated sample was precipitated with an aqueous solution of Na_2CO_3 (2.1 g of Na_2CO_3 dissolved in 30 mL of deionized water) and stirred for 1 h at the same temperature. Aged for 2 h, the solid was filtrated and dried at 383 K over night. It was calcined at 623 K for 2 h to obtain CZ-k. The CuO-ZnO (CZ) was prepared under the same condition.

2.2.2. Preparation of SAPO-34

The SAPO-34 molecular sieves were synthesized by temperature-programmed methods in the presence of triethylamine as structure directing agent. In details, 2.5 g of phosphoric acid was dissolved into 10.8 g of distilled water and was vigorous stirred for 0.5 h at room temperature. After adding in 1.4 g of kaolin and 0.7 g of pseudoboehmite in turn, the mixture was stirred for 2 h, and then 4.0 g of triethylamine was added in and was continually stirred for 4 h. The synthesis gel was transferred into a stainless-steel autoclave and was heated at 403 K for 4 h, followed by 473 K for 24 h. The solid product was separated by centrifugation, washed with distilled water, and dried at 383 K. Finally, the sample was calcined at 823 K for 5 h to remove organic template to produce SAPO-34 (Sk). For comparison, the SAPO-34 molecular sieve obtained from pseudoboehmite and silica sol was operated under the same condition, and it was denoted as S (Rahimi et al., 2016; Wang et al., 2016; Wang et al., 2013).

2.2.3. Preparation of bifunctional catalyst

CZ and CZ-k were physical mixed with S and Sk (by the mass ratio of CuO-ZnO: SAPO-34 = 1: 1) to prepare bifunctional catalysts of CZ/S, CZ/Sk, CZ-k/S and CZ-k/Sk, respectively.

2.3. Characterization of the catalysts

The purity and crystallinity of samples were identified by using powder X-ray diffraction patterns (XRD) recorded on a Rigaku D/Max-2400 ($\lambda = 0.1542 \text{ \AA}$) with Cu K α radiation source operating at 40 KV and 60 mA. Relative crystallinity of the samples was calculated by the following equation (Elamin et al., 2015):

$$\% \text{crystallinity} = \frac{\sum I}{\sum I_r}$$

where I is the line intensity of the sample and I_r is the line intensity of the reference sample, using the products having the highest crystallinity, as identified by XRD. The line intensity of the XRD pattern at 2θ equal to 9.5° , 12.9° , 16.0° , 17.7° , 20.6° , 24.9° , 25.9° , 30.6° and 31.0° were employed for calculations (Aghaei and Haghighi, 2014). The morphology and elemental composition of samples were analyzed by JEOL JSM-5600 scanning electron microscope (SEM) equipped with Noran System Six energy dispersive spectroscopy (EDS). The Brunauer-Emmett-Teller (BET) surface area, pore volume and pore size of samples were determined by N_2 sorption using Quantachrome Autosorb-1 apparatus. The pore volume was determined at a relative pressure (P/P_0) of 0.99. The samples were degassed at 473 K before analysis.

The H_2 temperature programmed reduction (H_2 -TPR) and NH_3 temperature programmed desorption (NH_3 -TPD) of samples were taken in a Baidewo MFTP3060 multifunction catalyst analysis system (Xiamen, China). For H_2 -TPR, 150 mg of sample was pretreated with Ar ($50 \text{ mL} \cdot \text{min}^{-1}$) at 453 K for 2 h, and then cooled down to room temperature. After that, sample was reduced by a reducing gas ($30 \text{ mL} \cdot \text{min}^{-1}$) composed of 5% H_2 and 95% Ar heated from room temperature to 873 K at a rate of $10 \text{ K} \cdot \text{min}^{-1}$ (Kang et al., 2009). For NH_3 -TPD, 150 mg of sample was pretreated with Ar ($50 \text{ mL} \cdot \text{min}^{-1}$) at 723 K for 2 h, and then saturated with 5% NH_3 and 95% N_2 ($30 \text{ mL} \cdot \text{min}^{-1}$) at 353 K for 1 h. After purging with hydrogen at 363 K for 1 h, the analysis was carried out at a heating rate of $10 \text{ K} \cdot \text{min}^{-1}$ from room temperature to 873 K (Cui et al., 2013; Izadbakhsh et al., 2009). Fourier transforms infrared (FT-IR) spectra was conducted using a Digilab-FTS3000 photometer.

2.4. Catalytic reaction tests

The investigation of the catalytic activities for CO_2 hydrogenation to light olefins was carried out at 673 K in a stainless steel fix-bed reactor at 3.0 MPa. Before the test, 1.0 g of the bifunctional catalysts were pretreated in a H_2/N_2 stream with a ratio of 1:9 for 4 h and immediately replaced by pure hydrogen flow for 2 h at the same temperature. Then the gas mixture composed of 25% CO_2 and 75% H_2 was flowing through the catalyst bed with a space velocity of $1800 \text{ mL} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$. The reaction products were analyzed by an online Shimadzu GC-2010A gas chromatograph with a thermal conductivity detector (TCD) and a capillary column (CB-PLOT Q) to separate the products. The CO_2 conversion and product distribution were calculated using the area normalization method (Liu et al., 2015; Zha et al., 2012). The total process was shown in Fig. 1.

3. Results and discussion

3.1. Catalyst characterization

3.1.1. XRD analysis

The XRD patterns of the samples are shown in Fig. 2. The diffraction of kaolin exhibits a classic kaolinite phase with two broad diffractions peaks at $2\theta = 20\text{--}40^\circ$. The peaks at $2\theta = 20.8^\circ$ and 26.6° are related to

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