FUEL PROCESSING TECHNOLOGY 89 (2008) 1281–1286

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Single-step synthesis of DME from syngas on Cu–ZnO–Al_2O_3/zeolite bifunctional catalysts: The superiority of ferrierite over the other zeolites

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ARTICLE DATA

Article history:
Received 17 January 2008
Received in revised form 24 July 2008
Accepted 25 July 2008

Keywords:
Dimethyl ether
Ferrierite zeolite
Cu-based catalyst
Bifunctional

ABSTRACT

Single-step synthesis of DME was studied on four different bifunctional catalysts containing Cu–ZnO–Al_2O_3 as the common methanol synthesis component and ferrierite, ZSM-5, NaY or HY, as the solid acid component. The catalysts were prepared by co-precipitation of the metallic component in the slurry of the zeolite, and were characterized by nitrogen adsorption, XRD and ammonia TPD. Cu–ZnO–Al_2O_3/ferrierite is found to be superior to the other catalysts in terms of better conversion and DME selectivity because of facile reducibility of the metal component, suitable topology, proper acidic property and resistance towards catalyst deactivation.

1. Introduction

Dimethyl ether (DME), a non-toxic, non-carcinogenic and non-corrosive compound, can be used as an excellent alternative to diesel fuel due to its high cetane number and the low emissions of CO, NO_x and particulates upon its combustion [1]. It has similar physical properties as that of LPG and hence can be used as an alternative fuel. As a multisource, multi-purpose clean fuel it is also projected as a chemical feedstock of the twenty-first century for the production of higher ethers and oxygenates. With high *H/C* ratio and intense energy density, DME can be used for hydrogen production, by either steam reforming or partial oxidation. DME has been increasingly used as an aerosol propellant to replace chlorofluorocarbons as well [2].

DME can be manufactured in large quantities from raw materials like natural gas and coal. The syngas produced as an intermediate from these sources is then converted to methanol which on dehydration gives DME. Of late, biomass is recognized as an extensive feedstock for syngas production, since it is a CO_2 neutral resource, distributed extensively in the world [3]. Methanol and/or DME synthesis from biomass syngas (biosyngas) is gaining attention with a few demonstration plants coming up in the world [1,4–6]. The biosyngas is produced from biomass-derived oil or char, using different gasifying agents like mixtures of CO_2 and N_2, H_2 and steam. However, the composition of biosyngas varies with the method of preparation and the nature of raw materials. It largely differs from the normal syngas by the presence of higher quantities of carbon dioxide and deficient amounts of hydrogen.

DME is originally produced by a two-step process involving synthesis of methanol from syngas in the first step and the dehydration of methanol in the second. However, the application of a bifunctional catalyst which performs both the functions in a single step, has gained considerable importance due to technological and economic advantages of DME production [7]. The bifunctional catalyst is a mixture of a metallic function component (composed of oxides such as CuO, ZnO,

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doi:10.1016/j.fuproc.2008.07.014

Al_2O_3 and/or Cr_2O_3) for the synthesis of methanol and an acid function component (such as γ-Al_2O_3, H-ZSM-5 or HY zeolites, SAPOs) for the transformation of methanol into DME. As the equilibrium limitations in DME synthesis via methanol could be easily overcome by the in situ dehydration of the methanol, the reactor can be operated at high temperatures and low pressures to achieve higher yields than the two-step process [8]. Furthermore, the incorporation of CO_2 in the syngas makes the process thermodynamically more favorable than without it. This is a positive feature for the large-scale utilization of CO_2, an environmentally objectionable compound because of its global warming potential.

A close scan of the literature reveals that in the case of development of the single-step DME synthesis much attention has been focused on the metallic component. Cu/ZnO is reported to be the best for methanol synthesis from syngas and hence extensive studies have been made to understand the reaction mechanism and the role of each component. The study on methanol dehydration, however, has received comparatively less attention. Among the various catalysts recommended for the dehydration functionality γ-Al_2O_3, silica-alumina and zeolites like H-ZSM-5 occupy prominent positions [9]. The activity of γ-Al_2O_3 for methanol dehydration is rather poor. It undergoes a fairly rapid, irreversible deactivation [10]. Several modifications like ion exchange have been made to make the zeolites suitable for the acid functionality. Besides, a new trend in the gas to liquids conversion is the selective synthesis of liquefied petroleum gas (LPG) from syngas via DME, for which several catalysts like ZSM-5 and Beta zeolite are again employed. Furthermore, when the solid acid component is mixed with the metallic component the acidic properties of the former are expected to change. Studies aimed at understanding these changes and the concomitant influence of these changes on the performance of the overall catalyst, are essential.

In the present investigation four different zeolites are selected for studying the acid functionality of the bifunctional catalyst, whereas Cu–ZnO–Al_2O_3 (CZA) is chosen to impart the metallic function. The aim of this investigation is to understand the influence of the nature of zeolite used on the overall activity and selectivity of the bifunctional catalyst in the one-step synthesis of DME from the syngas derived from biomass, and to explain the reason for the superiority of ferrierite zeolite over the other zeolites.

2. Experimental

2.1. Catalyst preparation

Different commercial zeolites namely, H–Ferrierite (Si/Al=25), H-ZSM-5 (Si/Al=50), H–Y (Si/Al=2.3) and Na–Y (Si/Al=2.3) provided by Zeolyst were used in the preparation of bifunctional catalysts. The bifunctional catalyst, Cu–ZnO–Al_2O_3/zeolite, was prepared by co-precipitation in the slurry of zeolite powder. In the present study, a metal oxide composition of 50 wt.% CuO, 40 wt.% ZnO, and 10 wt.% Al_2O_3 was selected for the metallic component.

The weight ratio of methanol synthesis catalyst (Cu–ZnO–Al_2O_3) to solid–acid catalyst (zeolite) was kept as 2.3. The pH of the mixed metal solution was found to be in the range of 5.5. An aqueous solution of sodium carbonate was used to raise the final pH of precipitation to 10.5–11.0.

The required quantity of previously synthesized zeolite powder was added to a 200 ml of deionized water taken in a 2 L flask while stirring at around 70 °C. Then, the metal precursor solutions containing copper acetate, zinc acetate, and aluminum nitrate and sodium carbonate solution were added separately through a syringe pump with precise control of the feeding rate. The temperature was maintained at around 70 °C during the precipitation, and the pH measured after precipitation was found to be in the range of 7.5–8.0. The slurry was further digested at around 70 °C for 3 h. The precipitates were filtered, washed with hot deionized water, and extruded to the size of 2 mm before drying for 16 h at room temperature. The material was then dried in an oven at 110 °C for 12 h and subsequently calcined at 350 °C for 5 h in air.

2.2. Catalyst characterization

The BET surface areas were estimated from nitrogen adsorption isotherm data obtained at −196 °C on a Micromeritics, ASAP-2400 equipment. The calcined samples were degassed at 300 °C in an He flow for 4 h before the measurements. The pore volumes and pore size distributions of the samples were determined by the BJH (Barett-Joyner-Halenda) model from the data of the desorption branch of the nitrogen isotherms. The pore volumes were determined at a relative pressure (P/P_0) of 0.99.

The powder X-ray diffraction (XRD) patterns were obtained with a Rigaku diffractometer using Cu–K_α radiation to identify the phases of CZA-Zeolite catalysts and their crystallinity. The temperature-programmed reduction (TPR) experiments were performed to determine the reducibility of the surface oxides. Prior to the TPR experiments, the samples were treated in an He flow up to 350 °C and kept for 2 h to remove the adsorbed water and other contaminants followed by cooling to 50 °C. The reducing gas containing 5% H_2/Ar mixture was passed over the samples at a flow rate of 30 ml/min with the heating rate of 10 °C/min upto the 600 °C and kept at that temperature for 30 min. The effluent gas was passed over a molecular sieve trap to remove the generated water and analyzed by GC equipped with thermal conductivity detector (TCD).

The temperature-programmed desorption of ammonia (NH_3–TPD) experiments were performed to determine the surface acidity of various bifunctional catalysts. About 0.1 g of the sample was flushed initially with an He flow at 250 °C for 2 h, cooled to 100 °C, and saturated with NH_3. After NH_3 exposure, the sample was purged with an He flow until equilibrium, and then, TPD experiments were carried out from 100 to 600 °C at a heating rate of 10 °C/min.

2.3. Catalytic activity tests

The catalytic activity measurements were conducted in a fixed-bed stainless-steel reactor with a diameter of 12.7 mm using 1.0 g of pellet-form bifunctional catalysts. Prior to evaluation, all the catalysts were reduced by using a 5% H_2/N_2 flow at 250 °C for 4 h under atmospheric pressure. On the basis of the results of other researchers on biomass gasification, a mixed