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Dimethyl ether conversion to light olefins over the SAPO-34/ZrO_2 composite catalysts with high lifetime

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ABSTRACT

The SAPO-34/ZrO_2 composite catalysts using ZrO_2 as a binder were prepared and their performance was investigated for the dimethyl ether to olefins (DTO) reaction. The composite catalysts showed higher catalytic lifetimes than the free SAPO-34 catalyst, while maintaining high selectivity toward light olefins. This suggests that the binder-filled space between the SAPO-34 crystals can provide additional diffusion paths for mass transfer. In the SAPO-34/ZrO_2 composite catalysts with different ZrO_2 contents, the SAPO-34(11 wt%)/ZrO_2 composite catalyst showed the highest catalytic lifetime. It can be concluded that ZrO_2 is one of the best binders for the preparation of SAPO-34/binder composite catalysts.

1. Introduction

Due to the increase in demand for light olefins and high crude oil prices, production methods that make light olefins from non-petroleum-based raw materials have attracted the attention of many researchers [1–4]. Specifically, the MTO/DTO (methanol to olefins/dimethyl ether to olefins) process is becoming more important because the starting materials are based on syngas, which can be produced from coal, natural gas and biomass [5–9]. The MTO/DTO process has been studied for many years, and some pilot plants are in operation [10–12].

The SAPO-34 catalyst, with its high selectivity toward light olefins such as ethylene and propylene, is known to be the most effective catalyst for the MTO/DTO process [1,13–22]. The SAPO-34 catalyst, which has a chabazite three-dimensional structure, shows shape-selectivity toward light olefins due to its small pore size of 0.38 nm. However, the catalyst is very easily deactivated due to this small pore size. Therefore, previous efforts to improve the performance of the MTO/DTO process focused on improving the catalytic lifetimes.

The mechanism proposed for the MTO/DTO reaction, using the SAPO-34 catalyst, has been reported as a hydrocarbon pool mechanism [13]. This mechanism is well-known, in that hexamethylbenzene (HMB) is a main intermediate in the reaction and is generated within the cages of the catalyst. Subsequently, the light olefins are produced via the combination of HMB and the reactants during the sequential cracking. The polyaromatic hydrocarbons (PAH), which are responsible for the deactivation of the catalyst, are produced at the same time. It was reported that the PAH were produced via additional condensation and cyclization reactions within the cages and that the diffusion of the reactants and products was inhibited due to these PAH-filled cages [23,24]. It was also reported that such deactivation of the SAPO-34 catalyst is strongly affected by the crystal size and acidity of the catalyst [25,26].

On the other hand, an industrial fluidized bed reactor has been developed for the MTO/DTO process that allows for the continuous regeneration of the deactivated catalyst and the uniform control of the temperature during a strong exothermic reaction. The use of the SAPO-34 catalyst in a fluidized bed reactor was developed by UOP/Hydro and the catalyst is often prepared by spray drying method [27]. An alumina sol is typically added to give increased mechanical strength during the preparation process. The existence of alumina in the composite catalyst causes the formation of additional acid sites, and thereby the formation of olefins is inhibited. Another method for preparing the catalyst in an industrial fluidized bed reactor was investigated, which involved growing micro-sized SAPO-34 crystals on the surface of the α-Al_2O_3 [28]. The activity and product selectivity of the composite catalyst showed similar results to those of the SAPO-34 catalyst.

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However, the composite catalyst has a lower SAPO-34 content, with a catalyst composition of 6–7%, compared to the industrial composites, which are usually in the range of 20–30%. Therefore, the development of new binder materials in the composite catalyst is required to provide a higher SAPO-34 content and improve the catalytic lifetimes. It is well known that using ZrO_2 as the binder could inhibit the sintering of the active components, due to its high mechanical strength and good thermal resistance; it is thus a good candidate to be a binder for fluidized bed catalysts [29–32].

In this study, SAPO-34/ZrO_2 composite catalysts, which can be utilized as catalysts in a fluidized bed reactor, were prepared with added ZrO_2 to give excellent catalytic lifetimes. The use of the ZrO_2 as the binder in the composite catalysts is previously unseen in the MTO/DTO process. For comparison, the SAPO-34/α-Al_2O_3 composite and free (unsupported) SAPO-34 catalysts were also prepared. The SAPO-34/ZrO_2 composite catalysts were prepared with different amounts of ZrO_2 to determine the appropriate amount of ZrO_2. The DTO reaction tests of the prepared catalysts were carried out using a fixed bed reactor. The catalytic lifetimes and the selectivity to light olefins were mainly confirmed. The crystal structure, morphology, pore structure and adsorption property of the prepared catalysts were characterized by XRD, SEM and BET.

2. Experimental

2.1. Catalyst preparation

The SAPO-34 catalyst was prepared based on a previous report [33]. LUDOX AS-40 (Sigma–Aldrich, 40%), aluminum isopropoxide (Junsei, 99%) and phosphoric acid (Samchun chemicals, 85%) were used as the starting materials for silica, alumina and phosphorous sources. Tetraethylammonium hydroxide (TEAOH, Samchun chemicals, 25%) and diethylamine (DEA, Junsei, 99%) were used as the structure directing agents, and α-aluminum oxide (α-Al_2O_3, Sigma–Aldrich, 99+%) and zirconium oxide (ZrO_2, Kanto chemical, 99%) were used as binders. The molar composition for synthesis of the catalysts was 1.0 Al_2O_3:1.0 P_2O_5:0.3 SiO_2:1.0 TEAOH:1.0 DEA:52 H_2O (mol).

The SAPO-34 catalyst was prepared through hydrothermal synthesis in an autoclave. DEA, water and aluminum isopropoxide were sequentially added into a beaker, and phosphoric acid was added dropwise over 2 h to the solution with stirring. The solution of LUDOX AS-40 and TEAOH was subsequently added to the mixture and stirred for 1 h. For the SAPO-34 composite catalysts, α-Al_2O_3 or ZrO_2 was added as the binder to the mixture for 1 h. The final gel was transferred into an autoclave and heated at 200 °C for 72 h. After crystallization, the prepared sample was filtered, washed, dried at 100 °C and calcined at 600 °C for 6 h to obtain the final catalyst. The weight of the SAPO-34 in the synthesized composite was confirmed based on the weight ratio of the final catalyst, and all catalysts were named by their SAPO-34 content in the final composite catalyst.

The crystallinity and composition of the catalysts were characterized using powder X-ray diffraction (XRD, Rigaku D/max III-B) with Cu Kα radiation. XRD measurements were recorded in the angle range of $5 < 2\theta < 80^\circ$ at a voltage of 40 kV and an electric current of 30 mA. The particle size and morphology of the catalysts were observed by scanning electron microscopy (SEM, Hitachi Japan, S-5500). The BET surface areas of calcined catalysts were measured at 77 K from the isotherm data of a N_2 adsorption–desorption experiment obtained using a Micromeritics ASAP-2400 analyzer.

2.2. DTO reaction

A schematic diagram of the experimental apparatus used for the DTO reaction is shown in Fig. 1. The catalytic reaction was carried out using a fixed bed reactor under atmospheric pressure, and the

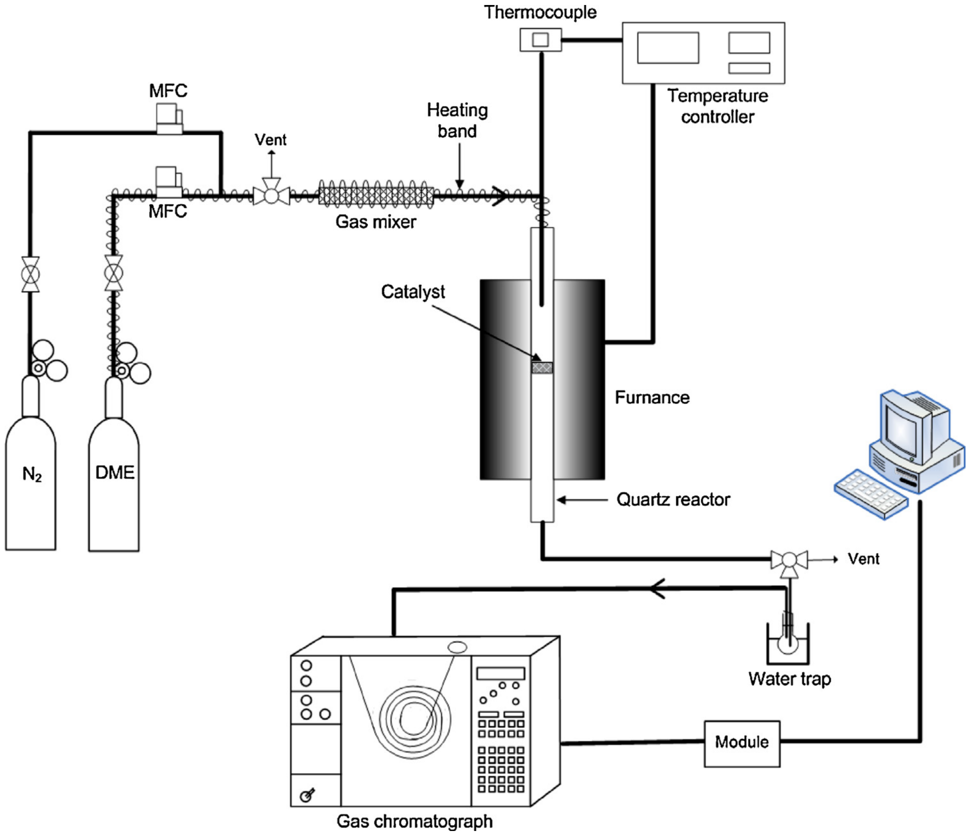

Fig. 1. Schematic diagram of the experimental apparatus for the DTO process.