Full Length Article

Isomerization of *endo*- to *exo*-tetrahydrotricyclopentadiene over alumino-silicate catalysts

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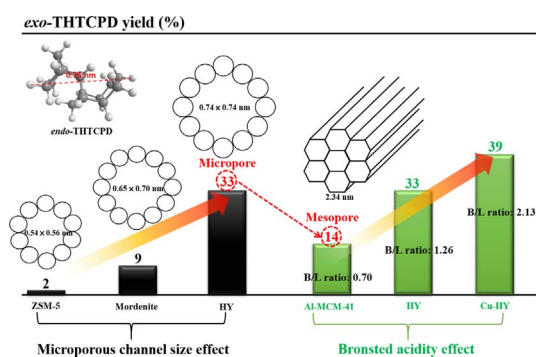[b] Super Ultra Low Energy and Emission Vehicle Center, Korea University, 145, Anam-ro, Seongbuk-gu, Seoul 136-701, Republic of Korea
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GRAPHICAL ABSTRACT

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ABSTRACT

Isomerization studies have been carried out to improve the physical properties of tetrahydrotricyclopentadiene (THTCPD), which has been attracting attention as a liquid fuel for aviation and military use. However, there have been few studies on heterogeneous catalysts for environmentally friendly process until now. In this study, the isomerization activities over various alumino-silicate catalysts (ZSM-5, MOR, HY, Cu-HY, Al-MCM-41) were evaluated using a batch reactor, and the catalytic properties suitable for the reaction were investigated. The catalytic performances were significantly affected by the microchannel or pore size, acid strength and acid type of each catalyst. N_2 adsorption-desorption, NH_3-temperature-programmed-desorption and pyridine Fourier-transform-infra-red analyses indicated that the pore size of the catalyst and the acid strength on the catalyst surface affected the conversion rate of *endo*-THTCPD, and the type of acid on the catalyst surface affected the *exo*-THTCPD selectivity. The HY catalyst showed the highest yield and productivity among all of the catalysts evaluated. The study of the time-on-stream reaction over the HY catalyst showed that some by-products continued to increase during the reaction time, and there was an optimum reaction time to obtain the highest yield.

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1. Introduction

With advances in aeronautical technology, aviation fuels are drawing great attention and have been developed over the last few decades to have higher energy densities in applications such as jets engine and other air-breathing propulsions. In addition to a high energy density, another characteristic of aviation fuel is that it must have low freezing point and viscosity for operability in harsh conditions [1].

The typical high-energy-density fuel (HEDF), JP-10, called *exo*-tetrahydrodicyclopentadiene (*exo*-THDCPD), which is mainly used in air-breathing-missile fuel, has a high enough mass density (0.94 g/ml), volumetric energy (39.6 MJ/L) and a low freezing point ($-79\,°C$) for use in HEDFs of aircrafts [2–5]. Since then, RJ-5, *endo-endo*-dihydrodinorbonadiene, which is synthesized from the selective dimerization and hydrogenation of norbornadiene (which can be synthesized from acetylene and cyclopentadiene) dimer, has been developed with a higher energy density (1.08 g/ml) and volumetric energy (44.9 MJ/L) than JP-10, but its use has been limited due to its high cost and difficult preparation procedures [2,6]. Until recently, efforts to develop high-performance HEDFs to meet next-generation aircraft fuel requirements have continued [7,8]. For example, *exo*-tetrahydrotricyclopentadiene (THTCPD) is one of such advanced HEDFs, which has a higher density and volumetric energy content (density: 1.04 g/ml, volumetric energy: 44.1 MJ/L) than those of JP-10 [6,9]. THTCPD is synthesized through several steps. First, tricyclopentadiene (TCPD) is synthesized from a Diels-Alder reaction between dicyclopentadiene (DCPD) and cyclopentadiene (CPD), and it is subsequently hydrogenated to THTCPD [10–14]. However the synthesized product is present as an *endo*-dominant isomer and cannot meet fuel requirements because it is solid at room temperature [15]. Therefore, *endo*-dominant THTCPD should be transformed to *exo*-dominant THTCPD (*exo*-THTCPD), a liquid form. Some studies of the isomerization of *endo*- to *exo*-THTCPD have been performed *via* an acid-catalyzed reaction [16–18]. All of the referenced works on the isomerization of THTCPD used AlCl₃ catalysts or AlCl₃-based ionic liquid (IL) catalysts, and their high performances were explained by Lewis acid properties of the catalysts. L. Wang et al. showed the isomerization pathway from *endo*-THTCPD to *exo*-THTCPD for the first time at a relatively low temperature range of 0–50 °C using AlCl₃ catalysts at various concentrations. In that study, the equilibrium conversion rate was 87% at reaction temperature of 15 °C [18]. In addition, in the same group, a study was made on other HEDFs called diamondoid fuels produced after the isomerization reaction of *endo*-THTCPD to *exo*-THTCPD using AlCl₃, CF₃SO₃H, and an ionic liquid catalyst [16]. S. G. Kim et al. reported that *endo*- to *exo*-THTCPD isomerization was carried out on a homogeneous system using an ionic liquid catalyst using three types of cation precursors with AlCl₃ as the base. A high *exo*-THTCPD yield of about 74% was achieved at a reaction temperature of 80 °C and the effect of Lewis acidity on reactivity was described [17]. However, these AlCl₃ or AlCl₃-based IL catalysts are toxic to the human body and cause environmental pollution [7]. In addition, AlCl₃-based IL catalytic processes pose a difficulty in separation and recycling because it is a homogeneous catalytic process. Alternatively, a heterogeneous catalytic system and non-AlCl₃-based catalytic system can offer a solution to such problems associated with *endo*- to *exo*-THTCPD isomerization. Several Chinese research groups have reported studies on the *endo*- to *exo*- isomerization of DCPD and THDCPD using commercial zeolites [10,16,19–23]. They claimed that the catalytic activity for the isomerization was strongly influenced by the characteristic acidities, pore channel shapes, and sizes of each zeolite. Similarly, there have been several reports of the acidic characteristics and pore size of zeolites affecting other isomerization reactions [24–26]. However, no studies have yet been made on the use of alumino-silicate catalysts such as zeolites and other heterogeneous acidic catalysts for *endo*- to *exo*-THTCPD isomerization.

In this study, various alumino-silicate catalysts (HY, ZSM-5, Mordenite, Cu exchanged HY and Al-MCM-41) were examined for the isomerization of THTCPD to develop aeronautical HEDFs. Through the comparison of test results over different Si/Al ratios of microporous zeolites (HY, ZSM-5, Mordenite, Cu modified HY) and synthesized mesoporous Al-MCM-41, we investigated the correlation between the characteristics of the catalysts (acidity, acid type, pore channel size) and their catalytic activities on THTCPD isomerization. Additionally, we tried to identify reaction pathways based on time-on-stream tests with the best catalyst.

2. Experimental

2.1. Catalyst preparation

Commercial Y zeolites (Si/Al = 30, hydrogen form), ZSM-5 (Si/Al = 40, ammonium form), Mordenite (Si/Al = 10, ammonium form) were purchased from *Zeolyst International*. Each zeolite has different initial cation forms (Y zeolite: hydrogen form; ZSM-5 and Mordenite: ammonium form). All of these catalysts were calcined at 550 °C for 6 h to remove template residue and at the same time convert the form of an ammonium to a hydrogen along with hydrogen forming on the zeolite, with the water removed during heat treatment.

The Al-MCM-41 (Si/Al = 15) was synthesized based on a method described in a previous article [27]. Cetyl-trimethyl-ammonium bromide (CTAB, Aldrich, 98%) was used as a template surfactant, and tetraethyl orthosilicate (TEOS, Aldrich, 98%) as well as aluminum sulfate hydrate (Aldrich, 98%) were used as Si and Al precursors. First, 2.4 g of CTAB was dissolved in deionized water, and aluminum sulfate (0.146 M) was added. A stoichiometric amount of TEOS was added to the mixture, and the mixture was stirred for 1 h at room temperature, followed by the addition of 30 ml of ammonium hydroxide (25%) until a pH value of 10.5 was reached, followed by additional stirring for 1 h. The precipitates were washed with DI water and filtered. The precipitate was dried at 70 °C overnight and calcined at 550 °C for 6 h.

The copper (Cu)-modified HY(30) was synthesized from these steps. 15 g of HY(30) was prepared and Cu(NO₃)₂·2.5 H₂O (Sigma-Aldrich) was adjusted so that Cu content of the finally prepared catalyst was equal to 2 wt% of the total catalyst mass. Next, 500 ml of DI water added and stirred for 2 h at room temperature, followed by the removal of excess water using a rotary evaporator. As-synthesized catalyst was calcined at 550 °C for 6 h.

The nomenclature for each catalyst is as follow: Y zeolite (Si/Al = 30, hydrogen-form) is denoted by HY(30), Al-MCM-41 (Si/Al = 15) by Al-MCM-41, ZSM-5 (Si/Al = 40, NH₄-form) by ZSM-5(40), Mordenite (Si/Al = 10) by MOR and copper-modified HY(30) by 2Cu-HY(30).

2.2. Catalyst characterization

The nitrogen adsorption-desorption analysis was carried out with a BELCAT-M-77 (BEL Japan Inc.) to measure the specific physical properties of each catalyst such as the surface area, pore volume, and pore size. The specific surface area and pore volume were measured by the BET method, the average micropore size (zeolites) distribution was calculated by the HK method, and the mesopore size (Al-MCM-41) was calculated by the BJH method. Before measurements, each sample was degassed at 4 mmHg and heated to 100 °C overnight.

NH₃ temperature-programmed desorption (NH₃-TPD) was performed on a BELCAT-M-77 (BEL Japan Inc.) to measure the acid amount and the strength of the catalysts. Each catalyst was pretreated at 400 °C for 1 h under a 50 ml helium gas environment. Afterwards, the catalyst was cooled to 100 °C, followed by NH₃ adsorption for 30 min using a 5% NH₃/He gas mixture. The physisorbed NH₃ was purged with helium gas at 100 °C. The NH₃-TPD measurement was taken in a temperature range from 100 °C to 600 °C at a ramping rate of 10 °C/min.

The pyridine adsorbed FT-IR spectra (Perkin Elmer, Spectrum GX) were collected to determine the nature of acidic sites of the catalysts.