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Synthesis of high-energy-density fuel over mesoporous aluminosilicate catalysts

Jongjin Kim[a], Beomseok Shim[a], Gayoung Lee[a], Jeongsik Han[b], Ji Man Kim[c], Jong-Ki Jeon[a,*]

[a] Department of Chemical Engineering, Kongju National University, Cheonan, 31080, Republic of Korea
[b] Agency for Defense Development, Daejeon, 34188, Republic of Korea
[c] Department of Chemistry, Sungkyunkwan University, Suwon, 16419, Republic of Korea

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ABSTRACT

This study focused on the effect of the incorporation of aluminum on the catalytic performance of KIT-6 in the norbornadiene cyclodimerization reaction. An Al-KIT-6 material synthesized through Al grafting over siliceous KIT-6 was shown to have a well-ordered mesoporous structure and a large pore size. The grafting of Al onto siliceous KIT-6 generated weak acid sites consisting of Lewis acid sites and Brönsted acid sites. Cyclodimerization of norbornadiene was carried over Al-KIT-6 catalysts in a batch reactor in order to compare their activity with that of the Al-MCM-41 catalyst. The activity of norbornadiene cyclodimerization over the Al-KIT-6 catalyst was higher than that over the Al-MCM-41 catalyst, which could be attributed to the larger pore diameters of the Al-KIT-6 catalyst. The acidity and the catalytic activity of the Al-KIT-6 catalyst as used here could easily be recovered through filtering and calcination in an air atmosphere at 550 °C.

1. Introduction

High-energy-density fuels (HEDF) are liquid fuels that have higher density levels and higher volumetric energy contents than conventional liquid fuels. Cyclopentadiene and acetylene can be reacted to produce bicyclo[2.2.1]hepta-2,5-diene (norbornadiene). Norbornadiene dimer (NBDD) can be prepared through the cyclodimerization of norbornadiene [1,2]. The density and heat value of the hydrogenated norbornadiene dimers (H-NBDD) are 1.08 g/ml and 161,000 Btu/gal, respectively. Because these values are much higher than those of general aviation fuel, H-NBDD is attracting much attention as a candidate for ideal HDEFs [3,4].

It was reported that nearly 14 different types of NBDD isomers can be produced through the cyclodimerization of norbornadiene [5]. The pentacyclic exo-t-exo NBD dimer (Pxtx), the hexacyclic exo-endo NBD dimer (Hxn), and the hexacyclic endo-endo NBD dimer (Hnn) isomers are known to be the most commonly used HEDFs [5–7]. The cyclodimerization of norbornadiene can be carried out using expensive homogeneous catalysts, such as complexes of rhodium, iron, cobalt, and other transition metals [8,9]. Because it is very difficult to reuse these homogeneous catalysts after the cyclodimerization of norbornadiene, a heterogeneous catalyst that enables easy recovery and reuse is necessary for more economic NBDD manufacturing processes.

Several types of heterogeneous catalysts have been utilized in a norbornadiene dimerization reaction with a zeolitic catalyst in a batch-type process [10–12]. In particular, microporous zeolites such as HY, Hbeta, and HZSM-5 have been shown to be active during norbornadiene dimerization. However, microporous zeolites show low efficiency due to pore clogging during the synthesis of multi-cyclic hydrocarbons [13]. Recently, several studies have focused on catalysts with a large pore size in an effort to solve the clogging problem [14–16].

Mesoporous silica materials with well-ordered structures, such as MCM-41, MCM-48, SBA-15, and KIT-6, have received much attention due to the possibility of various application fields with them. They can be synthesized by a self-assembly method using long-chain anionic surfactants as a template [17–20]. Among mesoporous silica materials, KIT-6 has a three-dimensional cubic Ia3d symmetric structure with an interpenetrating bicontinuous network of channels. Due to the unique 3D channel networks in KIT-6, a large open space is formed, which allows direct access to intruding species without pore blocking [20]. This has a positive effect on the diffusion of large molecules such as norbornadiene and norbornadiene dimer. In order to improve the acidity of the pure silica KIT-6, aluminum atoms that can act as acid sites must be introduced through direct synthesis or post-synthetic routes [21]. To the best of our knowledge, Al-KIT-6 is utilized here for the first time in the norbornadiene cyclodimerization process. This study focused on the effect of the incorporation of aluminum on the catalytic performance of KIT-6 during the norbornadiene

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* Corresponding author.
E-mail address: jkjeon@kongju.ac.kr (J.-K. Jeon).

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cyclodimerization reaction. We report the textural and structural properties of synthesized materials using X-ray diffraction, nitrogen adsorption, and high-resolution transmission electron microscopy techniques. The nature and strength of the active sites present in the catalyst were also determined by means of the temperature-programmed desorption of ammonia and pyridine-adsorbed IR. The cyclodimerization of norbornadiene was carried out over Al-KIT-6 catalysts in a batch reactor in order to compare their activity levels with those of the Al-MCM-41 catalyst. In addition, the catalytic performance of the regenerated Al-KIT-6 catalyst was investigated in comparison with a fresh catalyst sample.

2. Experimental details

2.1. Catalyst preparation

The Si-KIT-6 material used here was prepared with an aqueous solution of amphiphilic polymer P123 (Aldrich) mixed with 1-butanol (Aldrich) as a template. Tetraethyl orthosilicate (TEOS, Aldrich,) was used as a silicon source. The molar composition of the raw materials used to synthesize Si-KIT-6 was as follows: TEOS: P123: BuOH: HCl: H_2O = 1.000: 0.017: 1.307: 0.527: 194.45. First, 30 g of P123 was dissolved in 30 g of 1-butanol and 1085 g of distilled water with 59 g of hydrochloric acid (35–37%). The mixture was then stirred in a bath while holding the temperature at 35 °C and was subsequently mixed with 64.5 g of TEOS. After stirring at 35 °C for 24 h and hydrothermal synthesis at 100 °C for 24 h, filtration was conducted. The white powder thus obtained was dried at 100 °C. The mixture of ethanol and hydrochloric acid (40:1) was then added while stirring. After washing and drying at 100 °C, the final product was calcined at 550 °C for 3 h in an air atmosphere.

The alumination of siliceous KIT-6 was conducted by a post-synthetic route. First, an appropriate amount of $AlCl_3$ was dissolved in ethanol (100 ml). To the resulting solution was added 10 g of Si-KIT-6, followed by stirring at room temperature for 12 h. The mixture was washed with ethanol and then filtered. The obtained powder was dried at 100 °C for 12 h and calcined at 550 °C for 3 h. The prepared material was denoted as Al-KIT-6(number), with the value in parentheses denoting the molar ratio of Si/Al. X-ray fluorescence (XRF) spectroscopy of the prepared Al-KIT-6 catalyst showed that the molar ratio of Si/Al was 57.

A mesoporous MCM-41 material was synthesized via a hydrothermal synthesis method described in the literature [22,23]. An Al-MCM-41 catalyst was prepared via a post-grafting method similar to that mentioned in the previous section. The Si/Al mole ratio of the Al-MCM-41 determined by XRF spectroscopy was 60.

2.2. Catalyst characterization

The powder XRD pattern of the catalyst was determined using an X-ray diffractometer (Rigaku D/MAX-III) with Cu-Kα radiation. The structure of the catalyst was examined by means of transmission electron microscopy (TEM). Each sample for the TEM measurement was suspended in ethanol and supported on a carbon-coated copper grid. The JEOL JEM-2011F (22 kV) model was utilized for the TEM analysis. The N_2 adsorption-desorption isotherm was analyzed at −196 °C using a BELSORP-Mini II device by BEL JAPAN. Prior to each measurement, all samples were degassed at 300 °C for 4 h. The specific surface areas were calculated using the Brunauer–Emmett–Teller (BET) equation based on the adsorption data obtained in the pressure (P/P_0) range of 0.05–0.3. The pore size distributions were determined from the entire desorption branch based on the Barrett–Joyner–Halenda (BJH) algorithm.

For the temperature-programmed desorption of ammonia (NH_3-TPD), a BEL-CAT-B device manufactured by BEL JAPAN was used to analyze the acid strength in the catalyst and the number of acid sites. Prior to the NH_3-TPD analysis, outgassing of the sample was conducted under a helium flow (50 ml/min) at 550 °C for one hour. After the adsorption of ammonia for 30 min at 100 °C, physically adsorbed ammonia was removed by flowing helium for 2 h. Temperature-programmed desorption of ammonia was then carried out from 100 °C to 550 °C at a heating rate of 10 °C min^{-1} under a flow of He gas. The desorbed NH_3 was monitored with a thermal conductivity detector.

In order to analyze the types of acid sites over the catalysts, the FT-IR spectra of the adsorbed pyridine were obtained with a Spectrum GX tool equipped with a MCT detector (Perkin Elmer) and an *in situ* cell containing CaF_2 windows [24]. After degassing of the disk-type catalyst (0.013 g) for 2 h in a vacuum below 1.0×10^{-2} torr and at 350 °C, pyridine was allowed to absorb onto the catalyst for 30 min at room temperature. The IR spectrum was collected in a temperature range of room temperature to 300 °C under a vacuum below 1.0×10^{-2} torr.

2.3. Cyclodimerization of norbornadiene

Cyclodimerization of norbornadiene was conducted in a mechanically stirred autoclave with a capacity of 160 ml. A mixture of 90.0 g of norbornadiene and 32.6 ml of toluene as a solvent was mixed with 3.3 g of the catalyst. After ensuring that the inside of the reactor had a nitrogen atmosphere, the temperature of the reactor was increased to 250 °C and the agitation speed was set to 300 rpm to start the reaction. The reaction proceeded for 6 h, and products were collected at a predetermined time interval. The collected samples were analyzed using a gas chromatograph (YL 6100 GC) equipped with a CP-Sil5 column (capillary 30 m × 0.32 mm × 0.25 μm) and a FID detector. A qualitative composition of the products was performed via a gas chromatograph (Agilent 6890 N, columns: CP-Sil5, 30 m × 0.32 mm × 0.25 μm) coupled to a mass spectrometer using a mass selective detector (Agilent MSD 5973). The conversion of norbornadiene, the degree of selectivity to NBDD, and the yield of NBDD were determined based on Eqs. (1)–(3), respectively.

$$\text{Conversion of norbornadiene (\%)} = \left[1 - \frac{\text{Concentration of residual norbornadiene}}{\text{Concentration of initial norbornadiene}}\right] \times 100 \quad (1)$$

$$\text{Selectivity to NBDD (\%)} = \left[1 - \frac{\text{Concentration of NBDD}}{\text{Concentration of products}}\right] \times 100 \quad (2)$$

$$\text{Yield of NBDD (\%)} = \text{Conversion of norbornadiene} \times \text{Selectivity to NBDD}/100 \quad (3)$$

3. Results and discussion

3.1. Structural characterization of catalysts

Fig. 1 shows small-angle XRD patterns which confirm the mesoporous structure of the catalysts. With regard to the XRD patterns of the Al-KIT-6 catalysts, peaks that appeared in the (211), (220) and (332) reflections showed a bicontinuous cubic $Ia\bar{3}d$ symmetrical structure [21,25]. This indicates no changes of the basic mesoporous structure of siliceous KIT-6 after Al grafting. In addition, a weaker peak corresponding to the (211) reflection of Al-KIT-6 in comparison with that of Si-KIT-6 can be described as a structural instability due to the fact that the Si atoms in the well-arranged framework are replaced by Al. Small-angle powder XRD patterns of the Al-MCM-41 prepared in this work are also shown in Fig. 1. The Al-MCM-41 had three obvious peaks corresponding to the (100), (110) and (200) diffractions of hexagonal symmetry [26,27].

An HR-TEM image of the calcined Al-KIT-6 is shown in Fig. 2. The HR-TEM images showed the presence of well-ordered cubic 3D