Applied Surface Science 511 (2020) 145398

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

Preparation of HZSM-5 catalysts with different ratios of structure directing agents and their effects on the decomposition of *exo*-tetrahydrodicyclopentadiene under supercritical conditions and coke formation

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ARTICLE INFO

Keywords:
Catalytic endothermic reaction
Exo-Tetrahydrodicyclopentadiene
Zeolite catalyst
Deactivation
Structure directing agent
Coke formation

ABSTRACT

Zeolite catalysts (ZSM-5) were synthesized using different ratios of structure directing agents (SDA) and Si/Al, and the synthesized ZSM-5 samples were used in the endothermic decomposition reaction of *exo*-tetrahydrodicyclopentadiene (*exo*-THDCP). The ZSM-5 synthesized with a 6.0:100 SDA/SiO_2 ratio and Si/Al ratio of 20 (S20/P6.0) showed higher mesoporosity than those of the other synthesized and commercial ZSM-5 catalysts. The decomposition reaction of *exo*-THDCP using the S20/P6.0 catalyst yielded the highest conversion of 58.4% after 65 min, whereas the commercial catalyst rapidly became deactivated and exhibited only 31.2% conversion, which was the same conversion obtained without the catalyst. The coke analysis results indicated that the ratio of mesopore to micropore volume of the catalyst was a major factor in determining the amount of internal and external coke produced in the catalyst. Moreover, the mesopore/micropore volume ratio affected the composition of soluble coke.

1. Introduction

In hypersonic aircraft, the engine temperature increases due to fuel combustion and friction with air. Therefore, aircraft engines require cooling technology to prevent deformation of the engine. Engine cooling technologies generally involve the use of air or cryogenic fuels such as liquefied methane and liquefied hydrogen. However, air cooling has a relatively low cooling efficiency due to friction with the aircraft body, and the storage of cryogenic fuel is problematic due to its bulky volume in the hypersonic aircraft applications [1]. In order to address these issues, a cooling technique using hydrocarbon-based endothermic fuels has been investigated [2,3]. Endothermic fuels decompose after absorbing heat from their surroundings under the high-temperature and high-pressure conditions of supersonic flight. The heat sink effect of the fuel is divided into sensible heat, which increases the temperature of the fuel/products, and endothermic heat, which is absorbed in the reaction [4]. Sensible heat is difficult to improve, because it depends only on the heat capacity and temperature of the fuel. On the other hand, the endothermic heat can be improved by controlling the chemical reaction to more efficiently decompose the endothermic fuel.

Various hydrocarbon-based compounds have been used as endothermic fuels, e.g., single-hydrocarbon combustibles such as methylcyclohexane [5], *n*-heptane [6,7], and *n*-dodecane [8] and mixed hydrocarbon combustibles such as Norpar 12 [9], JP-7, and JP-8 [10,11]. Among them, *exo*-tetrahydrodicyclopentadiene (*exo*-THDCP) is considered to be an excellent endothermic fuel with low freezing point, density, and price and high thermal stability, heat absorption, and energy density, which result from its cyclic structure [12]. *exo*-THDCP has been widely used as a propellant fuel for military missiles [13]. A number of investigations into the mechanisms of product formation in the thermal cracking and decomposition of *exo*-THDCP at atmospheric or high pressure have been conducted. Nageswara Rao and

Abbreviation: BET, Brunauer–Emmett–Teller; *exo*-THDCP, *exo*-tetrahydrodicyclopentadiene; FID, flame ionization detector; FT-IR, Fourier transform infrared; GC, gas chromatography; MS, mass spectrometry; NH_3-TPD, ammonia temperature-programmed desorption; SDA, structure directing agent; SEM, scanning electron microscopy; TCD, thermal conductivity detector; TMABr, tetramethylammonium bromide; TPABr, tetrapropylammonium bromide; XRD, X-ray diffraction

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https://doi.org/10.1016/j.apsusc.2020.145398
Received 21 September 2019; Received in revised form 1 January 2020; Accepted 13 January 2020
Available online 16 January 2020
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