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Prevention of deactivation of HZSM-5 by mixing with NaZSM-5 in catalytic reaction of methylcyclohexane

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ABSTRACT

In this study, Zeolite Socony Mobil-5 (ZSM-5) was modified by ion exchange with sodium ion to control the strong acid sites of catalyst, and the specific control of strong acid sites was carried out by mixing HZSM-5 and NaZSM-5. The characteristics of the catalyst were analyzed using X-ray diffraction, NH₃-temperature programmed desorption, pyridine adsorption Fourier transform infrared spectroscopy, and nitrogen adsorption-desorption analysis. The catalysts were used for the catalytic reaction with methylcyclohexane under supercritical condition (500 °C and 5.0 MPa). After reaction, the liquid product was analyzed using gas chromatography-mass spectrometry, and the spent catalyst was analyzed using thermogravimetric analysis to measure coke formation. In the catalytic reaction, conventional HZSM-5 was deactivated quickly with time (59.6 % of deactivation rate), but the mixed catalyst with NaZSM-5 was deactivated more slowly than HZSM-5. In addition, the mixed catalyst having the same mass ratio for HZSM-5 and NaZSM-5 showed the lowest deactivation rate of 37.4 % after 60 min. The mixed catalyst produced 10.1 wt% coke and it was lower than HZSM-5 (12.5 wt%). The catalytic robustness of HZSM-5 could be enhanced by mixing with NaZSM-5.

1. Introduction

Cooling technology for the supersonic flight is necessary to prevent the deformation of the internal structure or the failure of the engine as the temperature rises rapidly due to friction with the air. Cryogenic fuels such as liquid methane or liquid hydrogen can provide an efficient cooling performance. However, they require large storage volume and accompanying cost, and operational and safety problems because of the low density of the cryogenic fuels. In addition, cryogenic fuels can contribute only to sensible heat because chemical decomposition rarely occurs during the endothermic process that can be classified as sensible heat (physical endotherms) and chemical endotherms. On the other hand, liquid hydrocarbon fuels are free from the above problems and are decomposed after absorbing heat from their surroundings under the high-temperature and high-pressure conditions [1–5].

JP-7, JP-9, JP-10, Jet A, and Norpar 12 are examples of liquid hydrocarbon fuels used as endothermic fuels [6,7]. Most of these fuels consist of n-paraffin, cycloparaffin, and aromatics [8–10]. Fuels composed of mixtures are difficult to analyze and characterize after reaction

because of their complicated composition. For this reason, various researches selected a single compound as the representative substance and conducted pyrolysis reaction. Among the representative substances, methylcyclohexane (MCH) has been mainly used as the representative substance of cycloparaffin compound due to its simple structure. Liu et al. selected MCH as a representative substance and observed the heat absorption and coke inhibition of the decomposition reaction under supercritical conditions using beta zeolite modified with lanthanum as a catalyst [11]. Narayanaswamy et al. studied the oxidation reaction mechanism of MCH as a representative substance of naphthene molecules for the kinetic model of jet fuel and other surrogates [12]. Vasu and his co-workers selected MCH as the representative substance of JP-8 and measured the ignition delay time of MCH in a wide range condition (1–50 at m, 520–1300 °C, and 0.5–2.0 equivalence ratio condition of N₂ and Ar) [13].

As mentioned briefly in the first paragraph, the heat absorbed by the endothermic fuel is roughly classified into sensible heat and chemical endotherms. Sensible heat is hard to improve because it depends only on the heat capacity and temperature of the fuel. On the other hand,

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