

Dealuminated ZSM-5 Zeolite Catalyst for Ethylene Oligomerization to Liquid Fuels

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Abstract: Ethylene oligomerization using ZSM-5 zeolite was investigated to study the role of Brönsted acid sites in the formation of higher hydrocarbons. The oligomerization of olefins, dependent on the acidity of ZSM-5 zeolite, is an important step in the conversion of natural gas to liquid fuels. The framework Si/Al ratio reflects the number of potential acid sites and the acid strength of the ZSM-5 catalyst. ZSM-5 with the mole ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ equal to 30 was dealuminated for different periods of time according to the acidic ion-exchange method to produce ZSM-5 with various Si/Al ratios. The FT-IR analysis revealed that the integrated framework aluminum band, non-framework aluminum band, and silanol groups areas of the ZSM-5 zeolites decreased after being dealuminated. The performance of the dealuminated zeolite was tested for ethylene oligomerization. The results demonstrated that the dealumination of ZSM-5 led to higher ethylene conversion, but the gasoline selectivity was reduced compared to the performance of a ZSM-5 zeolite. The characterization results revealed the amount of aluminum in the zeolitic framework, the crystallinity of the ZSM-5 zeolite, and the Si/Al ratio affected the formation of Brönsted acid sites. The number of the Brönsted acid sites on the catalyst active sites is important in the olefin conversion to liquid hydrocarbons.

Key words: ethylene, liquid fuels, oligomerization, dealumination, ZSM-5

1. Introduction

The conversion of natural gas to liquid fuels can be carried out over bifunctional catalysts that are acidic and oxidative [1-3]. Normally, the dominant component of natural gas is methane (CH_4). The mechanism of the reaction between methane and oxygen to produce liquid hydrocarbons over acidic zeolites is postulated to start from the formation of methyl radicals (CH_3^*) from CH_4 [4]. The methyl radicals combine to form ethane which dehydrogenates to ethylene. Ethylene will oligomerize further into higher hydrocarbons to form oxygenates, aromatics, and liquid fuels or be involved in deep oxidation to produce CO_2 and H_2O .

The strength of oligomerization depends, among others factors, on the acidic sites of the zeolite [5-7]. For ethylene oligomerization over ZSM-5, both Brönsted and Lewis acid sites were observed to be active although Lewis sites have a small advantage in suppressing the coke formation [8]. The strong Brönsted acid sites eliminated coke or aromatic formation and allowed only oligomerization to proceed [8]. The amount of framework aluminum is related to the number of Brönsted acid sites [9].

The framework Si/Al ratio is a reflection of the number of potential acid sites [10]. For each particular zeolite structure the acidity per active site reached a maximum value at a particular Si/Al ratio, which determines the acidic strength of the zeo-

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