On methanol to hydrocarbons reactions in a hierarchically structured ZSM-5 zeolite catalyst

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ARTICLE INFO

ABSTRACT

Two type ZSM-5 catalysts (Si/Al ratio of ∼30) with different mesoporosity were synthesized by using a structure directing agent of tetra-n-butylphosphonium hydroxide. In particular, the molar compositions of ethanol and water in the synthetic precursor were changed in order to acquire the two type ZSM-5 catalysts. The resulting ZSM-5 catalysts were formed via the interconnection of very thin pillars or lamellae; (1) ∼6 nm thick with marked mesoporosity (H_30; high mesoporous ZSM-5) and (2) ∼13 nm thick without any considerable mesoporosity (L_30; low mesoporous ZSM-5). The pyridine-based acid titration reveals that H_30 had internal Brønsted acid sites similar to those in the commercially available ZSM-5 with a Si/Al ratio of 75 (referred to as C_75), though H_30 contained a large amount of external Brønsted acid sites. The methanol to hydrocarbons (MTH) reaction performance of these two ZSM-5 catalysts demonstrates that H_30 preferred to produce propene over ethene compared to C_75, while L_30 showed a very poor MTH performance mainly due to the lower amount of internal Brønsted acid sites. More desirably, a very short diffusional length (∼18,600 times lower than that in C_75) in H_30 considerably disfavored the aromatic dealkylation that is known to produce ethene. With this, H_30 allowed for achieving the ratio of propene to ethene as high as ∼9.1, which is, to the best of our knowledge, a highest value among the MTH results on ZSM-5 catalysts without any co-feed. Furthermore, ceria-doped H_30 not only enhanced the stability for the MTH reaction via a passivation of the external Brønsted acid sites, but also improved a propene to ethene ratio up to ∼15.0.

1. Introduction

Since the degree of the depletion of petroleum has been pronounced, there have been numerous researches to seek for alternative energy resources. In a way to secure industrially demanding chemicals from other resources, an upgrading reaction from methanol to hydrocarbons (MTH) holds promise, as it produces not only the liquid oil part of fossil fuel but also the industrially important chemical building blocks (e.g., olefin) [1]. In particular, recent advent of resources such as shale gas and biomass enhances feasibility of the methanol-based upgrading [2–4]. Mainly constituted of methane, shale gas can be easily converted to methanol via the synthesis gas.

The MTH reaction over ZSM-5 has been intensively studied by many researchers [1,5–24]. Although the origin of the initial hydrocarbon species is still unclear [25], the product distribution of the MTH reaction is known to abide by the dual-cycle mechanism [9,10]. According

to the dual-cycle mechanism, hydrocarbons undergo methylation and dealkylation reaction to grow and break down in two separate cycles, while affecting each other. The yields for propene and higher alkenes are governed by the olefin cycle, while those for ethene and aromatic products are controlled by the aromatic cycle. Methylcyclopentenyl ion (MCP$^+$) or polymethyl-benzenium ion (MB$^+$) in the aromatic cycle generates lower olefins (mainly, ethene and propene) through the dealkylation reaction. Consequently, the selectivity of the MTH reaction can be tuned and controlled by activating one cycle over the other [16,21,23,24,26].

Many researches on ZSM-5-based MTH reactions demonstrated that adjusting the properties of ZSM-5 catalysts (e.g., acidity and effective diffusional length) allows for controlling and desirably, maximizing the selectivity toward a wanted product [1,5,7,11,12,15–17,20–22,27–30]. For example, a high Si/Al ratio, inversely proportional to the acid sites, accommodated the enhanced selectivity of olefin compounds including

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