Selective formation of propylene from methanol over high-silica nanosheets of MFI zeolite

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A high-silica nanosheet MFI zeolite was successfully assembled by low-cost raw materials and a special bifunctional organic surfactant. It showed high propylene selectivity (51.0%) and high propylene/ethylene (P/E) ratio (12.1), as well as long catalytic lifetime in methanol to propylene (MTP) reaction under the operating condition of T = 450 °C, P = 0.1 MPa (P_\text{methanol} = 20 kPa) and WHSV = 1.5 h^{-1}. The excellent catalytic performance of MFI nanosheets could mainly be ascribed to its unique morphology and textural properties. The ultrathin nanosheets enormously shorten the diffusion path length and thus remarkably improve the molecular diffusion. As a result, the product molecules could easily escape from zeolite channels, and the secondary reactions like aromatization and hydrogen transfer are inhibited dramatically, leading to a high propylene selectivity and a low deactivation rate. Moreover, the considerably large specific surface area and high mesoporosity of the nanosheet MFI zeolite enable it to accommodate a lot more coke deposition, which also gives a good contribution to the notable improvement in the catalytic lifetime.

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1. Introduction

As the sustained increase in oil price and growing global demand for light olefins, methanol to olefins (MTO) and methanol to propylene (MTP) process have attracted a lot of interest from both scientific and commercial viewpoints [1–5]. In a post-oil society, MTP process is highly desired due to the sharply increasing demand for propylene [6,7], and much more efforts have been devoted for practical applications of MTP reaction, including process studies and optimization of the catalyst properties [7–16].

Among all the factors in MTP process, the catalyst plays a pivotal role in determining the process feature and efficiency [7,8,14,17], thus more and more attention and interest have been focused on developing highly efficient catalysts for MTP reaction. Over the past decades, many researchers have investigated the product distribution of methanol conversion over ZSM-5 (MFI) zeolite with different SiO_2/Al_2O_3 ratio [1.12–16,18], and concluded that high-silica H-ZSM-5 zeolite with the SiO_2/Al_2O_3 ratio of up to 400 might be a promising catalyst for MTP. However, the further improvement of propylene selectivity and catalytic lifetime over H-ZSM-5 catalyst for MTP reaction remains a challenge due to the inherent feature of MFI zeolites. Recently, Firouzi et al. [19] observed that H-ZSM-5 with nanoparticle size exhibited higher catalytic activity and propylene selectivity in MTP reaction as compared to its microporous counterpart because of its lower diffusion resistance. Moreover, H-ZSM-5 with high mesoporosity was also found to exhibit high propylene selectivity and long catalytic lifetime during the catalytic conversion of methanol to propylene [14,20,21]. This indicated further that the improvement of diffusivity of H-ZSM-5 catalyst would be a favorable way to enhance its MTP catalytic properties.

In theory, a maximized molecular diffusion would be achieved if the thickness of the zeolite crystal is reduced to the single unit cell dimension [22]. Recently, a nanosheet MFI zeolite with only 2 nm thick (corresponding to the b-axis dimension of a single MFI unit cell) was successfully synthesized by Choi et al. [22–25], and this material was expected to be an efficient catalyst with high propylene selectivity and long catalytic lifetime in MTP reaction because of its excellent diffusivity. The present study was undertaken to investigate the catalytic performance of the high-silica MFI nanosheets (SiO_2/Al_2O_3 = ~400) during the catalytic conversion of methanol to propylene. To get a better understanding of catalytic implications of the textural properties and crystal morphology of the nanosheets material, a conventional particle type MFI zeolite was employed for comparison.

2. Experimental

2.1. Catalyst preparation

The high-silica nanosheets of MFI zeolite were synthesized after Choi et al. [22,23], using another kind of bromination alkane, \[\text{[C}_18\text{H}_{37}^-\text{N}^+\text{(CH}_3)_2^-\text{-(CH}_2)_6^-\text{N}^+\text{(CH}_3)_2^-\text{C}_6\text{H}_{13}^-]\] Br_2 (designated as