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Effects of secondary mesoporosity and zeolite crystallinity on catalyst deactivation of ZSM-5 in propanal conversion

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ABSTRACT

Cooperative effects of secondary mesoporosity and zeolite crystallinity on the deactivation of ZSM-5 were investigated during propanal conversion. Varied secondary mesoporosities were introduced into a commercial ZSM-5 by alkaline desilication using solutions with different NaOH concentrations (0.1–0.5 M). The results showed that the mesoporosity gradually increased with the concentration of NaOH, while the intrinsic zeolitic microporosity decreased. This indicated that the alkaline desilication for mesopore generation is a destructive technique that sacrifices the zeolite crystallinity. In propanal conversion, ZSM-5 showed a longer catalyst lifetime as the external surface area increased (or as the zeolite framework thickness decreased) in the mild desilication regime (NaOH concentration \leq 0.3 M). The enhanced catalyst lifetime could be attributed to the facilitated diffusion of coke precursors out of the zeolite structure. However, when the zeolite crystallinity or microporosity of ZSM-5 was decreased too much from excessively severe alkaline treatments (NaOH concentration $>$ 0.3 M), deactivation of the catalyst became again faster. The result indicates that the crystallinity or the microporosity of ZSM-5 is also important in suppressing coke formation. This is in line with earlier reports showing that coke formation itself is a shape-selective reaction and significantly inhibited in the constrained space of the unique 10-membered micropore channels of ZSM-5. The present results imply that the generation of large mesoporosity (enhancing the diffusion of coke precursors) while keeping the zeolite crystallinity intact (suppressing coke formation by shape-selectivity) is highly desirable for designing a zeolite catalyst with an enhanced catalyst lifetime.

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1. Introduction

Zeolites are crystalline microporous aluminosilicates widely used as solid acid catalysts in a variety of chemical reactions in the petrochemical and refinery industry [1–4]. The success of zeolite catalysis can be partly attributed to the presence of strong acid sites on the zeolite frameworks with well-defined microporous structures that are responsible for the shape- and size-selectivity. Unfortunately, zeolite catalysts are generally known to deactivate due to coke formation during various acid catalysis, and thus, increasing coke resistance is very important in zeolite catalysis [5–8].

It has been repeatedly reported that ZSM-5 with a secondary mesoporosity (often called ‘hierarchical ZSM-5’) has a significantly

increased catalyst lifetime because of retarded coke formation due to the faster diffusion of coke precursors out of the zeolite structure [9–17]. For instance, M. Choi et al. showed that ultrathin ZSM-5 with a unit-cell thickness has a significantly enhanced deactivation in a methanol-to-gasoline (MTG) reaction [9]. It was shown that coke was mainly deposited on the external surface of the ultrathin ZSM-5, whereas an ordinary ZSM-5 mostly had internal coke formation. That result clearly indicated that coke precursors (i.e., alkylaromatics) can more readily diffuse out of the micropores in the case of ultra-thin zeolite. It was also reported that hierarchical ZSM-5 catalysts can generally show increased catalytic lifetime in MTG reaction, regardless of the synthesis methods used for generating secondary mesopores (e.g., post-synthesis desilication, carbon solid-templating, and soft-templating using an organosilane surfactant) [12]. R. Srivastava et al. reported that hierarchical ZSM-5 can also exhibit generally enhanced resistance to catalyst deactivation, regardless of the type of acid-catalyzed reactions [11]. More recently, J. Pérez-Ramírez and colleagues [13,14] showed that

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