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Improved methanol-to-olefin reaction selectivity and catalyst life by CeO_2 coating of ferrierite zeolite

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ABSTRACT

The catalytic performance of the methanol-to-olefin (MTO) reaction over ferrierite zeolite was improved greatly by introduction of a CeO_2 coating that selectively masked the acid sites on the external surface of the catalyst. In the absence of this coating, significant deterioration of the catalytic performance was observed owing to coke formation on the external surface and resultant blockage of the portals. Selective coating of CeO_2 on the external surface was investigated using transmission electron microscopy, temperature-programmed desorption of NH_3, N_2 adsorption–desorption isotherms, and xenon adsorption measurements to reveal the structure–activity relationship. The resulting catalytic performance of CeO_2-coated ferrierite zeolite in the MTO reaction was similar to that of MFI or high-silica CHA zeolite. The observed preferential formation of $C4,^{=}$ and $C6,^{=}$, ~90% free of aromatics was obtained because of the negligible deposition of heavy coke. This work shows that selective CeO_2 coating on ferrierite zeolite was effective during catalyst regeneration and hydrothermal aging, leading to extended catalyst life and improved selectivity for catalytic applications.

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1. Introduction

The methanol-to-olefin (MTO) or methanol-to-hydrocarbon (MTH) reaction is of importance in both fundamental research and industrial applications because of the increasing demand for lower olefins, such as ethylene, propylene, and butenes, from alternative carbon sources instead of from thermal cracking of naphtha [1–5]. Among MTO processes, both the INEOS MTO process using SAPO-34 zeolite and Lurgi MTP process using high-silica ZSM-5 zeolite are well known, and corresponding commercial MTO plants are operating in China [2].

The methanol transformation reaction mechanism has been investigated extensively. Among the various proposed mechanisms, the dual-cycle mechanism, consisting of aromatic and olefin cycles, has been widely accepted [2,5–7]. SAPO-34 zeolite, which contains a large cage with an 8 membered ring (MR), has shown excellent catalytic performance for methanol conversion, consistent with the known mechanism [8,9]. The use of ZSM-5 zeolite, with a three-dimensional structure containing the cage at the intersection between a straight channel and a sinusoidal channel, realizes a similar product distribution in the MTO reaction, which has been explained based on the reaction mechanism of dual aromatic and olefin cycles [10,11]. Depending on the reaction conditions, the aromatic cycle mainly plays a role at low reaction temperatures, whereas the olefin cycle is prevalent at high temperatures, resulting in increased production of propylene or butane. In contrast, the use of ZSM-23 and ZSM-22 zeolites, each containing a one-dimensional 10MR, gives a product distribution that is consistent with a reaction mechanism based on the olefin cycle only [12,13].

In the MTO reaction, in addition to the presence of a cage structure, the catalytic performance is also influenced by acidity and the pore size [14–16]. The Svelle group conducted MTH reactions at 673 K using various zeolites with different pore structures [14]. The catalytic activity was found to decrease in the following order, MFI » MFS » CHA, MTT, TON, *MRE > EUO > SZR, FER. MFI, EUO, *MRE, MFS, TON, MTT, and FER zeolites, consisting of 10MR, mainly produce C_{4+} hydrocarbons, whereas MFI, EUO, *MRE, and MFS zeolites also produced aromatic compounds, which can lead to significant deterioration of the catalytic performance. Furthermore, SZR and CHA exhibited high selectivity (>60%) for ethylene and propylene. However, even though preferential

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