Catalyst design for controlled methanol-to-olefin reaction selectivity and catalyst life of high silica zeolites, FER and CHA by selective CeO_2 coating

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Abstract: The catalytic performance of the methanol-to-olefin (MTO) reaction on high silica FER and CHA zeolites was improved greatly by selective CeO_2 coating on the external surface of the catalyst to inhibit the blockage at the portal. Further the proper combination of two zeolites, FER and CHA resulted in the different selectivity to olefins, $C_3^=$ or higher. It has been demonstrated that selective CeO_2 coating on zeolites led an extended catalyst life and improved selectivity for catalytic applications and also selectivity control over olefins.

Keywords: MTO, Zeolite, Selective CeO_2 coating

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 [1,2]. 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]. Recently, we demonstrated that the FER zeolite was selectively coated with up to 30 wt% CeO_2 to mask preferentially the acid sites in the portals or on the external surfaces, which would extend the life of the selectively coated zeolite catalyst and realize a preferential product distribution through the olefin cycle mechanism [3].

In this work, the engineered zeolite catalysts incorporating two zeolites (FER and CHA) were designed to control the olefin selectivity with enhanced catalytic performance. Therefore, the selectively CeO_2-coated zeolites were mixed physically to control the olefin selectivity to $C_3^=$ or higher.

2. Experimental

In brief, FER zeolite with a SiO_2/Al_2O_3 molar ratio of 20 was obtained from Zeolyst International (CP914C). Cerium nitrate hexahydrate (Yakuri, 98%) was impregnated into FER zeolite using an incipient wetness method by varying the amount of the impregnation material within the range of 10–30 wt%. The CeO_2-coated FER catalysts [denoted as Ce(x)-FER (x = 10, 20, and 30)] were obtained by drying the impregnated samples, followed by calcination at 823 K for 4 h. The same procedure was applied to CHA zeolite with a SiO_2/Al_2O_3 molar ratio of 26. The MTO reaction was performed using a packed bed flow reactor at ambient pressure. The reactant flow was controlled using a mass flow controller (MFC, Bronkhorst, F-201CL). Methanol vapor diluted in a He flow of 30 mL min^{-1} was supplied to the reactor by passing the flow through a methanol evaporator set in a constant-temperature bath (Daewon Science, DS-250WL2). The weight hourly space velocity (WHSV) of methanol (Aldrich, 99.8%) was controlled to 1.2 h^{-1} WHSV at 673 K. The product stream was analyzed using an on-line gas chromatograph (Agilent, HP6890) equipped with a flame ionization detector and a capillary column (Agilent, HP-PLOT Q, 30 m × 0.32 mm).

3. Results and discussion

Figure 1 shows the transmission electron microscopy of CeO_2-coated FER zeolite. Further, the elemental distributions of Si, Al, Ce, and O were recorded to examine the presence of CeO_2 or Ce^{3+}/Ce^{4+} in the pores of FER zeolite. The elemental distribution of Si and Al suggested a uniform distribution of acid sites over the entire FER zeolite. However, the elemental distribution of Ce over the entire FER zeolite was not uniform, as shown in Figure 1. The density of Ce was relatively low in the interior of the FER zeolite, and it increased significantly at the exterior of the FER zeolite, implying CeO_2 is located on the external surface of the FER zeolite. The other supporting evidence from N_2 adsorption-desorption and xenon adsorption indicated that there was no pore blockage. The same is true for the selective CeO_2 coating on CHA zeolite.

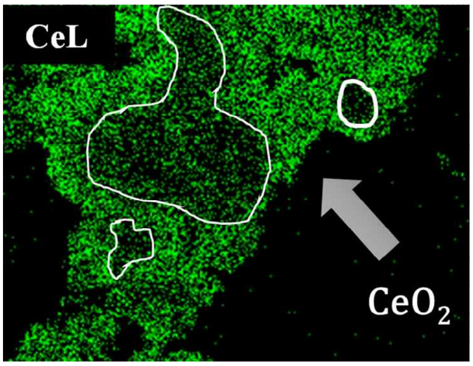

Figure 1. Elemental mapping of Ce in Ce(30)-FER showing preferential CeO_2 coating on the external surface.

Figure 2 shows the catalytic performance of MTO reaction over CeO_2-coated zeolites and the corresponding zeolite mixture of 1:1. The activity of the individual zeolite can be combined to express the different olefin selectivity in which the formation of $C_4^=$ was favored. The results indicated the progressive change of olefin selectivity through proper design of the catalyst with similar end of life.

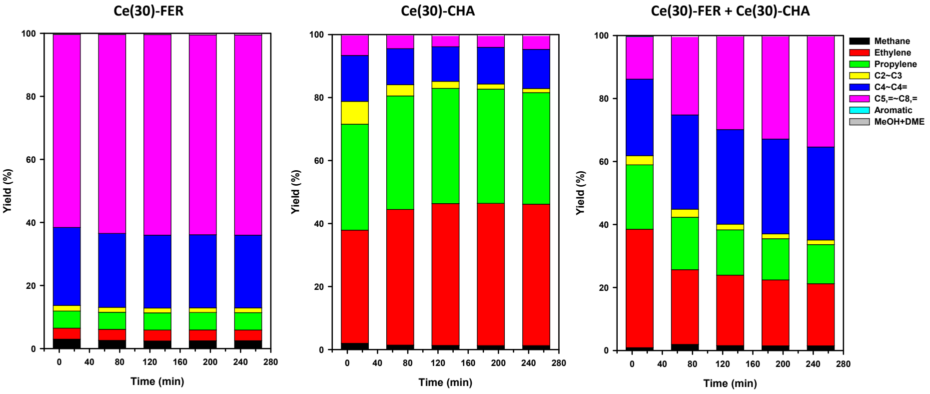

Figure 2. Product yields for the MTO reaction at 673 K and 1.2 h^{-1} WHSV over CeO_2-coated zeolite catalysts.

4. Conclusions

In the present work, it has been shown that the proper combination of two zeolites, FER and CHA resulted in the different selectivity to olefins, $C_3^=$ or higher. Such catalyst design provides the flexible olefin production using a single reactor.

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References

1. M. Stöcker, Micropor. Mesopor. Mater. 29 (1999) 3.
2. U. Olsbye, S. Svelle, M. Bjørgen, P. Neato, T.V.W. Janssens, F. Joensen, S. Bordiga, K.P. Lillerud, Angew. Chem. Int. Ed. 51 (2012) 5810.
3. S.J. Park, H.-G. Jang, K.-Y. Lee, S.J. Cho, Micropor. Mesopor. Mater. 256 (2018) 155.