Effect of CeO_2 coating on MTO reaction over ferrierite zeolite: Increased catalyst life

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Methanol to olefin (MTO) process has drawn much attention because of its practical importance for the production of $C2^=$ and $C3^=$ olefins from various renewable C1 resources. In general, the most suitable catalyst for MTO process is believed to be SAPO-34 zeolite of chabazite (CHA) topology.[1] The topology contains the interconnecting cage in three dimensional framework structure. Therefore, the carbon accumulation in the cage during the MTO reaction leads the pore blockage, which consequently deteriorates the catalytic performance.

Ferrierite (FER) zeolite contains two dimensional intersection of 10MR (5.4×4.2 Å) and 8MR (4.8×3.5 Å) channels. The catalyst has been considered as a promising catalyst for skeletal isomerization of *n*-butene.[2] However, FER zeolite can be deactivated for MTO reaction because the portal of the 10MR channel can be blocked readily with the coke and subsequently the significant deactivation occurs.

In this work, the selective CeO_2 coating over the zeolite surface has been employed to suppress the coke formation at the pore entrance at the external acid site, thereby extending the catalyst life. The commercial FER zeolite (Zeolyst) with the Si/Al ratio of 11.7 was ion exchanged with NH_4^+ cation and calcined to provide the acid site. The CeO_2 coating was performed up to 30 wt% by employing the impregnation of cerium salts and subsequent calcination. For MTO reaction, the weight hourly space velocity (WHSV) of the methanol (Daejung, 99%) was controlled at 2.4 h^{-1}, and the reaction temperature was 673 K.

The CeO_2 was found to be deposited selectively on to the external surface of zeolite to inhibit the formation of coke at the pore entrance. The distribution of cerium was found mostly at the external surface from the elemental mapping, which was consistent with TEM observation. Further, the results of the xenon adsorption measurement on the ceria coated samples suggested that the two dimensional channels were accessible for xenon of diameter, 4.3 Å and there was no pore blockage by the impregnated CeO_2.

Fig. 1 shows the effect of selective CeO_2 coating of 30 wt% on FER zeolites on regeneration and hydrothermal treatment during MTO reaction at 673 K. Before the CeO_2 coating, the conversion of methanol was decreased rapidly within 1 h while the catalytic performance was maintained for more than 2 h, implying the increase of catalyst life upon selective CeO_2 coating. The selectivity of the MTO reaction over the 30 wt% on FER zeolite indicated that $C_4^=$, $C_5^=$ and $C_6^=$ were major products, > 90%.

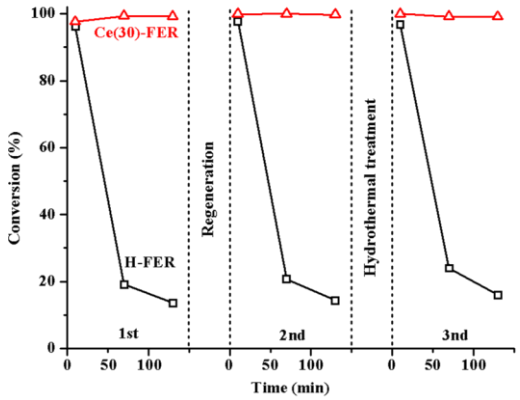

Fig.1 Catalytic performance of MTO reaction over CeO_2 coating FER zeolites at 673 K, 2.4 h^{-1} WHSV.

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