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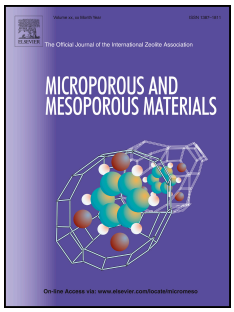

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Xin Li, Fateme Rezaei, Ali Rownaghi

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Methanol-to-Olefin Conversion on 3D-printed ZSM-5 Monolith Catalysts: Effects of Metal doping, Mesoporosity and Acid Strength

*Xin Li, Fateme Rezaei, Ali Rownaghi**

Department of Chemical and Biochemical Engineering, Missouri University of Science and Technology, 1101 N State St., Rolla, MO 65409, United States

Abstract

In this study, activity and selectivity in methanol-to-olefins (MTO) reaction of Cr, Cu, Ga, La, Mg, Y, and Zn-doped 3D-printed ZSM-5 zeolite monoliths were evaluated and the appropriate dopants were screened through various analysis. These 3D-printed ZSM-5 zeolite monoliths were doped with the above metals by direct addition of metal nitrate precursors into the 3D printing paste thus the metal doping procedure was integrated with the 3D printing fabrication. The effect of dopants on physical and chemical characteristics of the doped monoliths was studied through XRD, XRF, N_2 physisorption, FTIR, SEM-EDX, H_2-TPR, and NH_3-TPD. The performance of these printed metal–doped zeolite monoliths in MTO reaction was systematically evaluated and compared with their non-doped counterparts at 673 K for 24 h of reaction time. It was found that doping of Cr, Mg, and Y into 3D-printed ZSM-5 zeolite monoliths leads to enhanced methanol conversion, whereas doping of Ce, Cu, Ga and Y has little or no effect on catalysts reactivity. The olefins selectivity followed the sequence Zn >Mg >La >Y >Cr >Cu >Ga at 10 wt% dopant contents, in line with the relative amount of moderated acid sites in the monoliths. The results indicated that among all the investigated metal dopants, 3D-printed ZSM-5 zeolite monolith doped with 10 wt.% Mg exhibited the favorable effect on the light olefins production and showed ethylene and propylene selectivity of 24% and 33%, respectively with methanol conversion approaching 95% at 673 K. The increased