Ph.D. Thesis Technical Summary

Ion-exchanged Metal–Organic Frameworks for Industrially Relevant Catalysis Applications

by

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The inorganic clusters of metal–organic frameworks (MOFs) offer a unique combination of synthetic tunability, structural uniformity, and site accessibility uncommon in conventional heterogeneous catalysts. As such, the inorganic nodes of MOFs provide a promising platform that can be engineered to promote challenging chemical transformations for which no adequate solid catalysts exist. This thesis focuses on the postsynthetic ion exchange behavior of the inorganic nodes in MOFs and its use in the preparation of ion-exchanged MOF catalysts for industrially relevant chemical transformations. Chapter 1 introduces the characteristics of MOFs relevant to heterogeneous catalysis and highlights their structural tunability with an emphasis on their node ion exchange behavior. Chapter 2 details the application of the postsynthetic ion exchange strategy in the preparation of $Co(CO)_4^-$-incorporated Cr-MIL-101 ($Co(CO)_4$⊂Cr-MIL-101, Cr-MIL-101 = $Cr_3O(BDC)_3F$, H_2BDC = 1,4-benzenedicarboxylic acid), the first heterogeneous catalyst for epoxide carbonylation. Chapters 3 and 4 outline the use of $Co(CO)_4$⊂Cr-MIL-101 in a fixed-bed reactor process for the continuous-flow carbonylative production of β-lactone and succinic anhydride, respectively. Chapter 5 describes the use of Cr^{3+}-exchanged MFU-4*l* (Cr-MFU-4*l*, MFU-4*l* = $Zn_5Cl_4(BTDD)_3$, H_2BTDD = bis(1*H*-1,2,3,-triazolo[4,5-*b*],[4',5'-*i*])dibenzo[1,4]dioxin)) as an exemplary system to demonstrate pre-reaction treatment with alkylaluminum species as a simple method to isolate a MOF catalyst for gas phase ethylene polymerization.

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Publications:

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