

Rational Design of Catalyst Support and Promoter in Methane Dehydroaromatization Reaction

Abstract

Methane dehydroaromatization (MDA) is the most promising route for direct valorization of natural gas producing value added aromatic hydrocarbons. Obstacles with MDA process are mainly associated to low methane conversion and fast catalyst deactivation. Mo/Zeolite based catalysts have been found to be highly selective towards MDA and suffer with rapid deactivation due to severe coking. These issues require more insights into functioning of the catalyst while developing effective catalytic formulation in view of upgrading the process. In this context, the present work covers theoretical investigations (DFT calculations) to understand methane transformation path into key intermediates (ethane and ethylene) and experimental studies for rational design of catalyst support and the promoter. As a first step, DFT calculations were performed to develop mechanistic path for methane to ethylene transformation over isolated Mo_4C_2 cluster (active Mo sites) analyzing dehydrogenation and coupling barriers. Calculations with variation in charge over the cluster suggested that lesser positive charged Mo cluster favors methane activation in MDA. Overall obtained results provided insights into ethane and ethylene formation in MDA route and guidelines towards tailoring the active sites via modification in electronic structure of Mo sites. In rational design of catalyst support, effect of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio (SAR) of MCM-22 zeolite was studied analyzing acidity variation, interaction of Mo species with zeolite framework and activity of Mo/HMCM-22 at different SAR (30, 40 and 55) towards MDA. Experimental results indicated that at low SAR (30), catalyst showed higher activity for MDA route exhibiting effective physiochemical properties. In parallel efforts, Mo/HMCM-22 catalyst was modified with Cr addition to improve the catalyst activity and stability. Investigations revealed that Cr added catalysts significantly improved the benzene yield and methane conversion with lower coke content over time on stream as compared to Mo/HMCM-22. Performed characterizations supported that Cr modified Mo/HMCM-22 possesses superior physiochemical and catalytic properties towards MDA path.

In addition, coke content was estimated over active Cr added catalyst at different time intervals for different temperatures and monolayer-multilayer coking model was applied to predict the coke formation rate over the catalyst. In kinetic results, observed higher activation energy for monolayer coking as compared to that for multilayer coking indicated that coke precursors in monolayer acts as an active site for multilayer coking. Moreover, obtained results supported the hypothesis of MDA path as carbide associated coke facilitates severe coking with the progress of reaction.