

Improved Performance of W/HZSM-5 Catalysts for Dehydroaromatization of Methane

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Abstract: The dehydroaromatization of methane over W-supported ZSM-5 with varying degrees of Li^+ ion-exchanged catalysts was studied with and without oxygen at 1073 K and atmospheric pressure. Catalyst activity and stability were found to be influenced by the catalyst acidity related to Brønsted acid sites and by the presence of oxygen in the feed. The NH_3 -TPD and FTIR-pyridine results demonstrated that partially exchanged of H^+ ions by Li^+ into the W/HZSM-5 catalysts could be used to control the amount of strong acid sites on the catalyst surface. Without oxygen, the 3WHLi-Z (5:1) catalyst that has strong acid sites equal to nearly 74% of the original strong acid sites in the parent HZSM-5 exhibited the highest methane conversion and selectivity towards aromatics. However, the catalyst deactivated in a five hour period. In the presence of oxygen, the catalyst activity and stability could be improved further. The results of this study revealed that a suitable amount of strong Brønsted acid sites as well as oxygen addition in the feed increased the catalyst activity and stability. The 3WHLi-Z(5:1) catalyst exhibited improved performance in the dehydroaromatization of methane.

Key words: dehydroaromatization, methane, W-supported ZSM-5, partial ion exchange, H^+ ion, Li ion, catalyst activity, catalyst stability, catalyst acidity, oxygen presence, improved performance

1. Introduction

Natural gas has been used as a source for higher value hydrocarbons and fuels productions. However, the conversion of natural gas to higher hydrocarbons has been limited so far, as natural gas mostly consists of a stable molecule, methane. Currently, the commercialized technology to convert methane to the desirable chemical products and liquid fuels proceeds by an indirect route. In the indirect route, methane is converted to syngas ($\text{CO} + \text{H}_2$), an important raw material for petrochemical products, which is then converted to the desired chemical products either by Fischer-Tropsch or methanol synthesis (MTG) processes. The indirect route has high capital cost as

the formation of syngas is by steam reforming which operates at elevated temperature and pressure [1].

Extensive studies have been conducted on the direct conversion of methane to higher hydrocarbons thus, bypassing the syngas route. The catalytic conversion of methane to higher hydrocarbons such as aromatics has received much attention [1-18,20-25]. It is generally accepted that methane can be converted to aromatics in the absence of oxygen over bifunctional catalysts comprised of specific metal and zeolite in proton H^+ form. Earlier studies reported that metals such as Mo, W, and Re supported on zeolites (HZSM-5, HZSM-11, and MCM-22, whose pore diameters are equivalent to the dynamic diameter of a benzene molecule), were found to be active catalysts for the conversion of methane to aromatics [3,4].

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