Bifunctional Catalysis of W/HZSM-5 for Dehydroaromatization of Methane in the Absence of Oxygen

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Abstract

The direct conversion of methane to aromatics, mainly benzene without using oxygen, was studied. In prior, a comparison was conducted for the catalytic properties of W/USY, W/Al_2O_3, W/Hβ, W/HZSM-5. Among all the support used, the W/HZSM-5 catalyst showed the best activity and stability with highest methane conversion of 8.4%, corresponding to aromatics selectivity of 97.54% at 973 K and 1 atm. Meanwhile, almost ~ 7% of methane was converted on the other W-supported catalysts, which were drastically deactivated. Further study was performed to investigate the role of acidity of the W/HZSM-5 catalyst. The acidic properties of the catalysts undergone changes due to the introduction of Li ion. The catalytic properties for those catalysts with Li contents, including 3W/Li-HZSM-5(10), 3W/Li-HZSM-5(12), 3W/Li-HZSM-5(46), and 3WLi-ZSM-5 catalysts were tested at 1073 K and 1 atm. The results demonstrated that the introduction of a certain amount of Li into the ZSM-5 catalyst influences the catalytic performance of dehydroaromatization of methane under the non-oxidative condition. Over W/HZSM-5, a maximum methane conversion achieved was 16%, but decreased considerably to 8% over 320 min. of time on stream. Furthermore, the corresponding aromatic selectivity dropped rapidly from 93% to 56%. While, over the 3W/Li-HZSM-5(10) catalyst which contains 74% of strong acid sites of the parent HZSM-5, a slight decrease in methane conversion from 18% to 12%, corresponding to aromatics from 91% to 85%, was observed after 320 min. of time on stream. However, in the case of more Li content was added, the activity of the catalyst decreased as shown those on the 3W/Li-HZSM-5(12), 3W/Li-HZSM-5(46), and 3W/Li-ZSM-5 catalysts. Also it was found that the catalyst performance could be improved by reducing the amount of the strong acid sites, but considerable reduction in the amount of acidic sites, particularly the Brönsted acid sites, is unfavorable for the non-oxidative methane dehydroaromatization. The 3W/Li-HZSM-5(10) catalyst is found to be suitable catalyst as it has the optimum Brönsted acid sites and consequently, gives the maximum methane conversion and selectivity to aromatics. These results suggest that Li modified W/HZSM-5 catalysts is bifunctional catalyst in which both W active sites and Brönsted acid sites of HZSM-5 support are crucial factors for good catalytic performance.

Keywords: Bifunctional catalyst ; Methane dehydroaromatization ; W/HZSM-5 catalyst ; acidity.