



4TH National Conference of Iran Chemistry, Chemical Engineering And Nano

PROMOTION OF SELECTIVE CONVERSION OF METHANOL TO XYLENES OVER TRIMETALLIC & ALKALINE-LOW-Si/Al ZSM-5

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Abstract: In the current communication, the catalytic conversion of methanol to gasoline range hydrocarbons has been studied over mesoporous low-silica ZSM-5 (Si/Al = 11) catalysts while the promotional effect of Zn and Fe was also explored. The catalyst was prepared by employing alkaline treatment of the parent ZSM-5 (alk-ZSM-5) prior to impregnation with Fe and Zn. The catalyst samples were characterized by using XRD, XRF, NH₃-TPD, SEM, TGA, FT-IR techniques. On the basis of TPD analysis, the incorporation of Zn into ZSM-5 adjusted the acidity to notable strong/weak ratio of 2.1. The parent ZSM-5 and [Fe, Zn]-alk-ZSM-5 catalysts were hired for the conversion of methanol to gasoline (MTG) process. The dehydration of methanol over catalysts carried out in a fixed-bed tubular reactor at 375 °C and WHSV of 1.9 h⁻¹ under ambient pressure. The trimetallic catalyst [Fe, Zn]-alk-ZSM-5 exhibited great improvement in selectivity for aromatic hydrocarbons on the basis of GC and GC-MS results. [Fe, Zn]-alk-ZSM-5 catalyst was capable to promote the formation of 86.8 wt.% aromatics with highly selective for xylenes selectivity (44.7 %) having very low content of benzene (0.1 %). Both of the catalysts enjoy of long-term activity, e.g. keeping ~96% of their activity after 8 h.

Keywords: ZSM-5, alkali treatment, low-Si/Al, iron, zinc, MTG.

1. INTRODUCTION

Nowadays, fossil fuels are the most reliable world's energy resources. Petroleum products cover more than 90% of transportation fuel among which gasoline is a vital product extensively [1-3]. At the present rate of production, the established reserves of crude oil are estimated to survive merely about a few more decades. Hence, the concern of energy resources leads the scientists to search for future energy sources as substitutes for petroleum [4]. Methanol is one of the candidate for the production of gasoline range hydrocarbons [2,5], namely gasoline cut [1]. Practically, any gasifiable carbon-based feedstock as natural gas, biomass and coal are significant resources by which methanol can produce via a syngas intermediate. In the 1970's, the first report on the conversion of methanol to hydrocarbons (MTH) was published by Chang and Silvestri, researchers at Mobil Central Research [6]. They showed the production of synthetic gasoline over acidic zeolite. Furthermore, one of the broadly applied technologies for production of high-octane gasoline was found to be methanol-to-gasoline (MTG) process [7]. Numerous types of zeolites have been tested as the catalyst for the MTG process [8-10]. One of the most potential catalysts industrially applicable to MTG process is ZSM-5 which enjoys of having acidic nature within its pores, shape-selectivity specification and high surface area [10,11]. Basically, two types of pores, both formed by 10-membered oxygen rings could be found in ZSM-5 structure [12]. These types of pores together with the zigzag pores intersecting them are crucial to the formation of desirable components in gasoline during MTG process. One of the noticeable restrictions on the applicability of this catalyst in MTG process, however, is the diffusion limitation. Therefore, the modifications of ZSM-5 catalyst and its subsequent improvements of the diffusion properties could enrich the catalyst performance [13]. A well-known method for this aim is known as the modification of ZSM-5 by selective removal of framework Si controlled by employing desilication method using NaOH. During the application for this method,