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# Effect of second metal on the selectivity of Mn/H-ZSM-5 catalyst in methanol to propylene process

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ABSTRACT

In order to attain to the higher selectivity of propylene in the process of methanol conversion to propylene (MTP) over H-ZSM-5, the bi element catalysts were prepared by Mn/H-ZSM-5 and each of Ce, Cr, Fe, P and Ni promoters. The results revealed that the Ce–Mn/H-ZSM-5 demonstrated the highest selectivity to propylene. Response surface methodology was applied to optimize the preparation parameters (second metal loading, calcination temperature and calcination time) of the bimetallic Ce–Mn/H-ZSM-5 catalyst. Kinetic modeling is performed in the reaction temperature range of 440–500 °C and in the different weight hourly space velocities of methanol (i.e., 2.51, 4.18 and 8.37 $h^{-1}$). A reaction mechanism based on the theory of hydrocarbon pool and conjugate methylation/cracking mechanisms is applied for the MTP. The hybrid genetic algorithm is employed to calculate the kinetic parameters.

## Introduction

Taking into account the restricted petroleum resources, the soaring price of the petroleum derivatives and to reduce the emissions of greenhouse gases of fossil fuels, finding alternatives to petroleum has engaged the investigators worldwide [1]. One of the best alternatives is biomass because it has renewable resources and it includes agricultural crops and wastes, forestry residues, etc. [2]. Biomass can be biochemically converted to the valuable materials such as methanol, ethanol, methane and hydrogen [3,4]. Among these materials, methanol is rather cheaper than the others are. Nowadays, methanol is usually used as an economic feedstock in gas conversion plants [5,6]. One of these appliances is the catalytic conversion of methanol into hydrocarbons (MTH) [7,8]. MTH process was developed widely by enhancing and modifying of the catalysts such as different types of silicoaluminophosphate (SAPO) and aluminosilicate (zeolite class) catalysts [9–12]. Subsequently the methanol to gasoline (MTG), methanol to olefins (MTO) and methanol to propylene (MTP) processes were developed [13–19]. In the MTO process, the main purpose is increasing the selectivity of ethylene while in the MTP the higher yield of propylene over ethylene is the outcome [20]. The request for propylene is growing much faster than that for ethylene and the MTP has been plotted as an exceptional and economical process for production of propylene [2,17,21,22]. Because of the extraordinary shape selectivity property of zeolites toward the production of propylene, the MTP process is usually carried out on the zeolite class catalysts [20]. Since the discovery of the MTO and the MTP processes, many investigators have endeavored to modify the activity of catalysts to enhance the selectivity of light olefins: ethylene and propylene. Dubois et al. [23] modified the SAPO-34 catalyst with Co, Mn, and Ni and investigated their activity, selectivity, and lifetime in the MTO reaction. MnSAPO-34 was found to be the best catalyst based on catalyst lifetime. Zhang [24] reported that the highest propylene selectivity and the best catalytic stability were gained over calcium (Ca) modified ZSM-5. Liu et al. [20] obtained the propylene selectivity to 55.6% over phosphorous modified H-ZSM5. They also added some promoters such as Ce, Mn, Fe, Cr, Mo, Ga, V and Ni to H-ZSM-5 with Si/Al ratio of 220. They

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**Nomenclature**

| | |
|---|---|
| $E$ | activation energy (kJ mol$^{-1}$) |
| $k_j$ | kinetic parameter for the $j$th chemical reaction (h$^{-1}$) |
| $k_o$ | frequency factor of the kinetic parameters (h$^{-1}$) |
| $m$ | number of chemical species |
| OF | objective function |
| $p$ | number of experimental data related to a specified space time and temperature |
| $R$ | universal constant of gases, 8.314 (J mol$^{-1}$ K$^{-1}$) |
| $T$ | reaction temperature (K) |
| $T_m$ | reference temperature (K) |
| $W$ | catalyst weight (g) |
| $\omega_i$ | weight fraction of the $i$th chemical species ($g_i\ g_{Total}^{-1}$) |

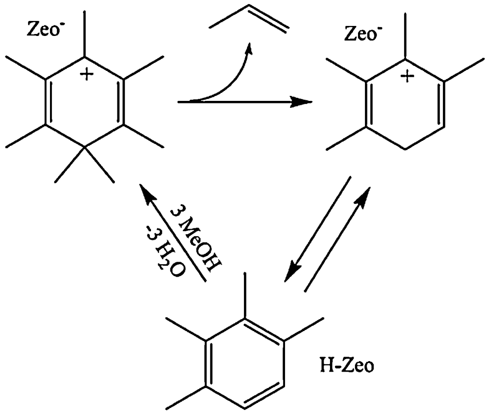

**Fig. 1.** The mechanism of hydrocarbon pool for propylene formation from the cation of hepta-methyl-benzenium over zeolite (H-ZSM-5) proposed by Bjørgen et al.

concluded that the performance of P, Ce, Mn, Fe and Cr were the best in propylene selectivity, respectively. Jin et al. [25] synthesized zeolites with MFI structure by hydrothermal method. Among the MFI-metallosilicate catalysts, aluminous H-ZSM-5 (H-AlMFI) disclosed the highest methanol conversion but low selectivity toward light olefins. The H-Fe-AlMFI zeolite showed high selectively to propylene and improved stability compared to the H-ZSM-5. The H-Fe-Ga-AlMFI zeolite showed the best MTO reaction activity among the MFI-metallosilicates. Kaarsholm et al. [26] investigated deactivation and product distribution of the MTO/MTP process over phosphorous modified H-ZSM-5 catalyst, on which propylene selectivity reached about 40%. Qi et al. [27] investigated coke deposition on SAPO-34 during the MTO reaction. A model relating the coke content over SAPO-34 to cumulative amount of methanol fed to the catalysts was proposed. Hadi et al. [28] improved the activity of H-ZSM-5 by addition of Ca, Mn, Cr, Fe, Ni, Ag, Ce and P. The maximum selectivity of propylene was obtained over the Mn/H-ZSM-5 catalyst which was about 45.21%.

Because of the complexity in mechanism of the MTH reactions, many investigators have employed their equipment to interpret the chemistry of the MTH series of reactions [29–39]. As a simplified mechanism of the MTH reactions, methanol is dehydrated to form dimethyl ether (DME) and water, subsequently the formation of alkenes from this equilibrium mixture was the outcome. For instance, Bos [36] and Gayubo [37] believed that the light olefins, higher olefins and paraffins are produced directly from methanol. But there exist strong evidences that disapprove direct mechanisms of the MTH [40–42]. Nuclear magnetic resonance (NMR) studies demonstrated that the complex molecules are formed initially that in the later stages of the process undergo cracking to produce the light olefins [43]. Another indirect pathway for the MTH is identified as “Hydrocarbon pool” mechanism [38,39]. This mechanism mainly contains a central complex chemical species. According to this mechanism over the zeolite, the hepta-methyl-benzenium cation is divided into propylene and butene, accompanying formation of the tetra and tri-methyl-benzenium ions, respectively. The hepta-methyl-benzenium cation is then regenerated by methylation of these lower poly-methyl-benzenium ions after deprotonation. A representation of this reaction cycle is indicated in Fig. 1 [39].

Kaarsholm et al. [44] carried out some experiments in a small scale fluidized bed reactor for the MTO reaction over a phosphorous modified H-ZSM-5 catalyst. Their kinetic model was based on the mechanism of hydrocarbon pool. Wu et al. [45] investigated the reaction scheme for propylene formation over a high silica H-ZSM-5 catalyst in a fixed bed reactor. In their reaction scheme methylation-cracking was dominated as the reaction mechanism of the MTP process. The proposed reaction scheme includes a cycle of a consecutive methylation from butene through pentene to hexene and further to heptene and cracking of hexene and heptene for generation of propylene and ethylene.

Guo et al. [46,47] accepted the reaction scheme proposed by Wu et al. [45] and carried out some experiments using the monolithic and packed bed reactors for the methanol conversion to propylene. Simulation results demonstrated that the monolithic catalyst enhanced significantly the methanol conversion and the propylene selectivity, compared with the randomly packed catalyst pellets. More recently Hadi et al. [28] proposed a reaction mechanism for the MTP process based on the theory of the hydrocarbon pool and the conjugate methylation/cracking mechanisms. This mechanism contained 17 reactions and 14 chemical species in which initially methanol was dehydrated to form higher olefins. The higher olefins underwent the methylation reactions. The more complex components: hexene and heptene cracked to form light olefins: ethylene and propylene. Finally, heptene, the most complex component in the reaction, generated the paraffins and the aromatics.

In our previous work [28] the H-ZSM-5 catalyst was modified by Ca, Ce, Mn, Cr, Fe, Ni, Ag and P. The best selectivity of propylene was obtained over the Mn/H-ZSM-5 catalyst. At the present work, in order to reach to the higher amount of propylene selectivity, the bi element catalysts were prepared by Mn and each of the Fe, Cr, Ce, P and Ni promoters. To our knowledge, there is not any report of using bi element modification of catalyst for the MTP process in the open literatures. Therefore, the preparation and optimization of bi element catalysts with support of H-ZSM-5 and investigation on their selectivity to propylene was carried out first time in this work. Among the bi element catalysts the Ce–Mn/H-ZSM-5 was selected as the best catalyst according to the highest propylene selectivity.

Response surface methodology (RSM) was applied to optimize the preparation parameters of the Ce–Mn/H-ZSM-5 catalyst. The selected preparation parameters were: second metal loading, calcination temperature and calcination time. It should be noted that the process parameters such as reaction temperature, the weight hourly space velocity (WHSV) of the feed and the methanol molar ratio in the feed were considered at their optimal values according to Liu et al. and Hadi et al. [20,28]. The Ce–Mn/H-ZSM-5 with the optimized preparation conditions obtained was used for kinetic modeling.