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Review

Methanol-to-propylene process: Perspective of the most important catalysts and their behavior

M. Khanmohammadi [a,*], Sh. Amani [a], A. Bagheri Garmarudi [a], A. Niaei [b]

[a] *Department of Chemistry, Faculty of Science, Imam Khomeini International University, Qazvin, Iran*
[b] *Department of Chemical Engineering and Applied Chemistry, University of Tabriz, 51666-16471, Tabriz, Iran*

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ABSTRACT

The methanol-to-propylene (MTP) process is a route of methanol conversion to hydrocarbons, which is in high demand because of limited oil resources. The present paper discusses the effect of catalyst structure on the MTP process conditions, and the role of different zeolite factors, such as acidity, crystal size, mesoporosity, and topology, on the activity and selectivity of the MTP reaction.

1. Introduction

Propylene is one of the key building blocks of petrochemicals used as a feedstock for a variety of polymer and chemical intermediates, such as polypropylene, acrylonitrile, propylene oxide, and many other commodity chemicals that are consumed as substitutes for non-plastic materials (e.g., paper, steel, and wood). Recent developments in the production of propylene derivatives, especially polypropylene, which requires a major fraction (about 60%) of the total propylene, have led to growing global demand for propylene at an annual rate of approximately 5%–6% [1,2]. Fluid catalytic cracking and steam cracking are two major commercial methods of propylene production, and both are dependent on crude oil resources [3]. Considering the increasing consumption of propylene and the expected shortage of petroleum resources in the future, the petrochemical industry is presently facing a crisis in propylene availability, and the lack of novel processes for the production of propylene is becoming clear [4]. The methanol-to-olefins (MTO) process developed by UOP/Norsk Hydro [5] and the methanol-to-propylene (MTP) process developed by Lurgi [6] are promising alternative approaches for the production of propylene. Because methanol can be easily produced from natural gas, coal, and biomass with lower prices and more availability than crude oil, these two routes have attracted significant attention [7–10]. The Dalian Institute of Chemical Physics, Chinese Academy of Sciences, has developed an MTO technology, known as dimethyl ether or methanol-to-olefin, which has been used in the world's first coal-to-olefin plant [11,12]. The MTO process uses small-pore silicoaluminophosphate molecular sieves (SAPO-34) as catalysts, and the main product is ethylene [13,14]. Lurgi's MTP process has optimized the propylene yield in the MTO process using MFI-type framework high silica zeolite catalysts (H-ZSM-5), and the high propylene to ethylene ratio (P/E) was a criterion, enabling higher selectivity for propylene in the recirculation process [6]. In the MTO process, methanol is first dehydrated to dimethyl ether to form an equilibrium mixture of methanol, dimethyl ether, and

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* Corresponding author. Tel/Fax: +98-28-3378 0040; E-mail: m.khanmohammadi@sci.ikiu.ac.ir

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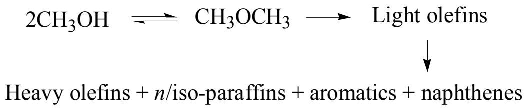


Scheme 1. Reaction path of methanol during the MTO process [14].

water. The equilibrium mixture is then converted to light olefins, which can further react to form paraffin, aromatics, naphthenes, and higher olefins via hydrogen transfer, alkylation, or polycondensation (Scheme 1) [1,14].

In the MTP process developed by Lurgi, apart from propylene as main product, ethylene and other olefins, also fuel gas, gasoline range hydrocarbons, and liquefied petroleum gas can be produced, depending on the reaction conditions and operating parameters used [6]. The important key step in the effective conversion of MTP is to control the reaction during olefin formation, where the acidity of the catalyst plays an essential role. Various acidic catalysts, mostly zeolites, have been evaluated for methanol conversion to light olefins [15–18]. Zeolites (microporous crystalline aluminosilicates) are widely used in petrochemical and fine chemical syntheses because of their strong acidic sites within the uniform micropores, as size- and shape-selective catalysts [7,8]. These frameworks are three-dimensional networks composed of TO_4 tetrahedra (T = Si, Al) linked by oxygen ions. When some of the Si_4^+ ions in the SiO_4 tetrahedra are replaced by Al_3^+ ions, an excess negative charge is generated. Mobile alkali metal ions are considered as a compensating source of positive charge, which can be exchanged with other cations (nonframework cations). Numerous reports have been presented supporting Lurgi's process, indicating aluminosilicate H-ZSM-5 as the appropriate candidate catalyst for the MTP reaction [1–3,5–10]. This topology has a medium size pore system with two channels, both including 10-ring channels. Straight channels (5.1–5.5 Å) are intersected by zigzag channels (5.3–5.6 Å), creating a three-dimensional network [19]. In the MTP process developed by Lurgi, at least 35% of one-pass propylene selectivity has been achieved at atmospheric or nearly atmospheric pressure at a reaction temperature range of 350–500 °C using a fixed bed reactor and ZSM-5 (MFI) zeolite catalyst [20,21]. Commercial use of the MTP process involves fixed-bed reactors, and numerous patents have discussed their design, obtaining higher selectivity by recycling the formed olefins, after propylene extraction, into the reactor [22–26]. However, propylene selectivity and the P/E ratio are still low, and the improvement of one-pass selectivity to propylene has been regarded as the major challenge and emphasis of current research on the MTP reaction. Among all of the parameters, the catalyst plays effective and important roles in determining the process features and efficiency [16]. To develop a commercial catalyst for the MTP reaction, stable and high methanol conversion and propylene selectivity are critical [27]. Physical and chemical properties of ZSM-5 zeolite (e.g., channel structure, total acidity, and crystal size) and operating conditions affect the selectivity for propylene [28–30].

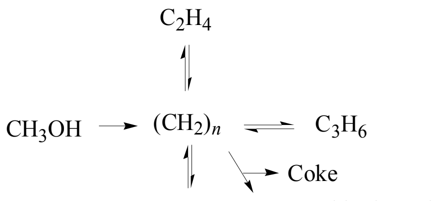
The present contribution reviews the effect of catalyst structure on the MTP process conditions and yield. Catalysts are classified into two categories: ZSM-5 and non-ZSM-5 with other topologies, and recent advances regarding the improvements in utilizing catalysts with higher propylene selectivity and more stability in the MTP process are investigated. The roles of different factors such as acidity, crystal size, mesoporosity, and topology of zeolite on the activity and selectivity of the catalyst toward the MTP reaction are studied. This review covers articles published within the past decade reporting different methods of improving the propylene selectivity and catalyst stability in the MTP reaction.

2. Mechanism and pathways of the reaction

Due to the complexity in product distribution and the difficulty in reaction intermediate identification, understanding the MTP reaction mechanism is still challenging [31]. To date, more than 20 distinct mechanisms have been proposed to elucidate the MTO reaction and how C–C forms from C1 through various processes, which can be broadly divided into direct (consecutive) and indirect (parallel) processes. Some of these mechanisms can be grouped into classes based on whether the key intermediates are oxonium ylides, carbenes, carbocations, free radicals or surface-bound alkoxy species [32,33]. Currently, the direct C–C coupling mechanism is an unfavorable route because it operates at a rate near zero; an indirect route is widely accepted [33].

The basic feature of this indirect route is that the organic reaction centers act as scaffolds for producing light olefins (i.e., ethene and propene) within the pores of molecular sieves to avoid high-energy intermediates required by the direct mechanisms [32]. An indirect reaction cycle known as the hydrocarbon pool mechanism has been adopted as the dominant reaction mechanism and is presented in Scheme 2. This mechanism consists of a cycle of reactions in which methanol successively reacts with the organic hydrocarbon pool via methylation leading to C–C bond formation. Subsequently, the cracking of higher olefins through an autocatalytic reaction [14] produces light olefins such as ethylene and propene, which regenerate the initial hydrocarbon pool species and completes the catalytic cycle [14,34–37].

Pathway of successive methylation/cracking of methanol and reaction intermediates have been demonstrated by nuclear magnetic resonance (NMR) studies [38]. Several studies have shown that alkylaromatic intermediates (methylbenzenes) may form in the hydrocarbon pool [39,40]. The nature and concentration of alkylaromatic intermediates formed in the zeolite



Scheme 2. Proposed hydrocarbon pool mechanism by Dahl et al. [36].