



High-performance SS-fiber@HZSM-5 core–shell catalyst for methanol-to-propylene: A kinetic and modeling study



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ABSTRACT

For the methanol-to-propylene process, a lumped kinetic model was developed on the basis of dual-cycle reaction mechanism, which attempted to reflect the main reaction paths with a combination to show the evolution of mole fraction of individual light olefins ($C_2^=$, $C_3^=$ and $C_4^=$) with space time. The experiments were performed in a continuous flow fixed-bed reactor at 0.1 MPa as well as varied reaction temperature from 400 to 480 °C and space time from 0.3 to 32.0 $g_{catalyst} h mol^{-1}$, and the experimental data obtained on the structured SS-fiber@HZSM-5 and powdered HZSM-5 catalysts were fitted by MATLAB software based on the established model. The fitted results show that the lumped kinetic model well describes the product distribution and is identified to be suitable by model identification. Compared to the powdered HZSM-5, the SS-fiber@HZSM-5 shows higher diffusion efficiency and narrower residence time distribution, not only promoting the propylene formation but also improving the utilization efficiency of the structured HZSM-5.

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1. Introduction

Propylene is one of the most important raw materials in chemical industry and widely used for the production of polypropylene, acrylonitrile, and propylene oxide, as well as the synthesis of plastics, rubber and many other daily necessities [1,2]. In recent years, with the ever-increasing dilemma between the continuous consumption of the finite petroleum reserves and the sharply increased demands for propylene and its derivatives, the traditional petroleum-based production (such as steam thermal cracking of naphtha and refinery fluid catalytic cracking (FCC)) is difficult to meet the requirement of propylene. Therefore, it becomes urgent to develop economical and energy-efficient processes to replace the petroleum-based production of propylene [1,2].

Natural gas [3] and some gasifiable carbon-rich materials such as coal [4] and biomass [5] can be firstly transformed into syngas (mixture of H_2 and CO) and subsequently converted into methanol through the well-established technologies [6]. Methanol can be transformed into hydrocarbons (methanol-to-hydrocarbons,

namely MTH) in some acidic zeolite catalysts (e.g., HZSM-5 and HSAPO-34) under appropriate reaction conditions [7]. Depending on the desired product, MTH process is classified into the following types: methanol-to-gasoline (MTG, mainly producing gasoline) [8,9], methanol-to-aromatics (MTA, mainly aromatics) [10,11], methanol-to-olefins (MTO, mainly ethylene and propylene) [12,13] and methanol-to-propylene (MTP, mainly propylene) [14–16]. The global demand for propylene is growing faster than ethylene [6], and it is thus particularly desirable to develop catalysts preferable to MTP process.

Since the first discovery on MTH process by Mobil researchers in 1976 [17], its mechanism has become one of the most controversial topics in heterogeneous catalysis [2]. In the early 1990s, Dahl and Kolboe proposed the “hydrocarbon pool” mechanism over HSAPO-34 [18–20]. Subsequently, Svelle et al. investigated the MTH pathway over HZSM-5 by ^{13}C labeling strategy, which revealed that ^{13}C is divided into two groups in the products: one group of C_3 – C_6 olefins and the other group of ethylene and aromatics [21]. Accordingly, dual-cycle mechanism consisting of aromatic-based cycle (main products of ethylene and aromatics) and olefin-based cycle (main products of C_3 – C_6 olefins) were proposed and widely accepted as the dominant reaction mechanism of MTH process on HZSM-5 [22]. Notably, the general process of olefin-based cycle is methylating light olefins to higher olefins and higher olefins

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cracking into light olefins, and therefore the generation and consumption of propylene can be approximately regarded as a consecutive reaction.

Compared with other MTO catalysts such as SAPO-34, ZSM-5 favors competing formation of the propylene with relatively slow coke-induced deactivation, making it possible to use fixed bed reactor with excess catalysts [23]. In this context, most attention has focused on tuning the acidity (strength and density) [24–27], size- and/or morphology-controllable synthesis [28–31] and hierarchical design of the pore structure [32,33] of the ZSM-5 zeolite. In a case of ZSM-5 synthesized via the fluoride route [28], its low density of strong acid sites in combination with the long diffusion pathway and few crystal defects delivers a good propylene to ethylene ratio of ~5 with 66% selectivity toward C₂–C₄ olefins and complete methanol conversion at 350 °C. Moreover, very high propylene to ethylene ratio of above 10 is also reported to be obtainable over the ZSM-5 zeolite catalysts with additives (ZrO₂ and H₃PO₄) by using dimethyl ether (DME) and N₂ as feedstock (DME to N₂ mole ratio of 1:5) due to the depression of ethylene formation rather than promotion of the propylene selectivity [34].

In spite of these promising results, their practical application in a fixed bed reactor is still significantly challenging, as macroscopic shape of microgranules or extruded pellets a few millimeters in size are required in the real-world forms rather than as-made powders. Therefore, some problems emerge in these cases of mass/heat transfer limitations, high pressure drop, non-regular flow pattern and adverse effects of the used binders, which will reduce the intrinsic catalyst selectivity and activity. Recently, microfibrillar structured catalysts and reactors (MSCRs), as one primary kind of structured catalysts or catalytic reactors (SCRs), have been developed and applied in order to achieve the aim of process intensification in chemical industry, because MSCRs and other SCRs can be precisely designed in full detail up to the local surroundings of the catalyst, and the exact shape and size of all column internals are determined by pre-design and calculation rather than trial and error [35,36]. Therefore, these MSCRs exhibit great flexibility with respect to different length scales (e.g., diffusion lengths and voidage) and allow exceptionally large rates and selectivities [36,37], and have many significant functional advantages over the conventional catalysts and reactors, providing broad prospects in desulfuration [38,39], air filtration [40,41], H₂ fuel generation and cleanup [42–45], selective oxidation [46–52] and other fields [53–56], especially providing a new way of designing efficient catalysts and reactors for mass and/or heat transfer limited reactions [57]. In our previous studies [16,58], a new standing-free microfibrillar-structured ZSM-5 zeolite catalyst was developed, being obtainable in a macroscopic scale by direct growth of the ZSM-5 zeolite crystals onto a three-dimensional (3D) porous network of sinter-locked metal microfibers. Thanks to the above beneficial properties, our structured SS-fiber@HZSM-5 core-shell catalyst demonstrated visible promotion on the selectivity to C₂–C₄ olefins especially to propylene with obviously prolonged lifetime in stream, compared to the corresponding pure powdered HZSM-5 catalyst. However, deep insight into such selectivity/stability promoting effect of the microfibrillar-structured design is particularly desirable to further improve the catalyst performance or design next-generation catalyst with more advanced performance. This work attempts to carry out kinetic and modeling study of MTP reaction over our structured SS-fiber@HZSM-5 catalyst as well as powdered HZSM-5 catalyst for contrastive study, because it is a useful and helpful tool for us to accomplish this goal.

Due to the early rudimentary understanding of the complexity of reaction mechanism, rigorous kinetic treatments may neither be practicable nor have much practical justification [59]. Subsequently, some progress has been made in kinetic studies, but the

kinetic models suffer either from severe complexity or from oversimplification. For example, Park [60,61] formulated detailed kinetic models at the elementary step level, including 726 elementary steps, 142 olefins and 83 carbenium ions, which is so complex that it is difficult to apply; while, in contrast, Aguayo [62] established a very simple kinetic model, only containing seven lumps (oxygenates, n-butane, C₂–C₄ olefins, C₂–C₄ paraffins (without n-butane), C₅–C₁₀ fraction and methane), with regarding the C₂–C₄ olefins as a lump, being unable to meet the requirements of separately describing ethylene and propylene formation. It is thus necessary to further improve the model to study MTP reaction kinetics. Xiao [63,64] proposed a lumped kinetic model consisting of 17 reactions among 15 species, in which light olefins are described separately, which could be applied to describe their monolith reactor behavior of MTP.

In the present work, we established a reaction network based on the dual-cycle mechanism (olefin-based cycle and aromatic-based cycle). This network not only simply described the rapid equilibrium, olefin-based cycle, aromatic-based cycle, methanation, and the generation of other alkanes and high-carbon hydrocarbons, but also particularly described the individual formations of C₂⁺, C₃⁺ and C₄⁺. Accordingly, a kinetic model (consisting of 19 reactions involving 10 lumps: methanol, dimethyl ether, ethylene, propylene, butene, pentene, hexene, methane, C₂–C₆ alkane and C₇⁺) was developed. The experimental kinetic data obtained from our structured and powdered catalysts were fitted in our kinetic model by MATLAB software, and the pre-exponential factors and activation energies were obtained, indicating that the active center utilization efficiency and hexene cracking into propylene apparent reaction rate of the structured catalyst are higher than of the powdered one. Therefore, the structured SS-fiber@HZSM-5 core-shell catalyst exhibited longer lifetime and higher propylene selectivity [16,58].

2. Experimental

2.1. Synthesis of the structured SS-fiber@HZSM-5 core-shell catalyst

The structured SS-fiber@HZSM-5 core-shell catalyst was synthesized, as described elsewhere [58], by direct growth of ZSM-5 crystals on macroscopic thin-sheet sinter-locked microfiber of stainless steel 316-L fibers consisting of 15 vol% SS-fiber and 85 vol% voidage (SS-fiber, 20 μm in dia., purchased from Western Metal Material Co. Ltd., China). Firstly, circular chips (16.1 mm in dia.) of SS-fiber substrate were soaked in HCl (1 wt%) aqueous solution for 0.5 h, sonicated in acetone for 5 min, thoroughly washed using deionized water, and then dried at 80 °C in air. Secondly, the SS-fiber substrate chips were seeded with the ZSM-5 nanocrystals using dip-coating method. The dip-coating suspension was prepared by adding 1 wt% ZSM-5 seeds (SiO₂/Al₂O₃ ratio = 180; crystal size: 100–200 nm) into a silica sol-gel (1 wt% SiO₂) and its pH was adjusted to 2.3 using HCl (1 wt%) aqueous solution prior to the dip coating. Seeding of the ZSM-5 was performed by slowly dipping the SS-fiber substrates into the above suspension for 10 s, followed by drying at 25 °C for 14 h and calcining at 450 °C for 2 h in air. Thirdly, the seeded SS-fiber circular chips (3 g) were placed in a Teflon-lined steel autoclave (100 mL) filled with 70 mL synthesis gel consisting of tetraethylorthosilicate (TEOS, A.R.)/tetrapropylammonium (TPAOH)/NaOH (C.P.)/NaAlO₂ (C.P.)/H₂O with a mole ratio of 1/0.25/0.4/0.010/250 (corresponding to the gel SiO₂/Al₂O₃ mole ratio of 200), followed by gel-aging at room temperature for 4 h. After hydrothermal synthesis at 180 °C for 48 h, the resulting samples were washed thoroughly, dried at 100 °C overnight, and directly calcined in air at 550 °C for 5 h to remove the organic template.

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