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Insight into the side reactions in methanol-to-olefin process over HZSM-5: A kinetic study

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HIGHLIGHTS

- Aromatization of C_3–C_5 olefins occurs through oligomerization, cyclization and dehydrogenation successively.
- Paraffins are formed by hydrogenation of the corresponding olefins coupled with aromatization and coking.
- The generation of paraffin and aromatic increases with methanol concentration and decreases with temperature.
- An integrated kinetic model is developed including the side and the main reactions.

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ABSTRACT

The industrial methanol to olefin process over HZSM-5 zeolite is currently faced with a low propylene yield with one third of the products being paraffin and aromatic, implying the side reactions play an evident role. This work focused on the kinetic modeling of the side reactions in the methanol to propylene process over HZSM-5 (Si/Al = 200) following our previous works on the main reactions: methanol and olefin co-conversion and olefin interconversion. The experimental results show that C_2–C_5 paraffins are mainly produced from the hydrogenation of corresponding olefins and aromatics from C_3–C_5 olefins through oligomerization, cyclization and dehydrogenation in accordance with the hydride transfer mechanism. Methane comes from the cracking of both higher alkanes and methanol. A comprehensive kinetic model was then established by integrating the alkane and aromatic generation steps into our previous developed model for methanol and olefin conversion, and the calculated results agree well with the experimental data under the investigated feed composition and reaction temperature conditions. The further parameter studies show that the total yields of both paraffins and aromatics decrease with temperature but increase with the methanol concentration.

1. Introduction

Methanol to propylene (MTP) is a promising technology that converts coal, natural gas and biomass to petrochemicals via methanol as intermediate [1]. Nowadays, because of the growing market of propylene [2], MTP is attracting more and more attention from both academy and industry. The aluminosilicate zeolite HZSM-5 catalyst with a high Si/Al ratio is generally employed in a typical MTP process [3,4], since it exhibits a much higher propylene yield and stronger resistance to coking deactivation compared with SAPO-34 in a methanol to olefin process (MTO).

The commercial MTP process developed by Lurgi Company has been brought on line since 2010, in which the raw material methanol is first converted into an equilibrium mixture of methanol, dimethyl ether and water in a pre-reactor to remove partial reaction heat and then the MTP reactions are carried out in three parallel six-stage adiabatic fixed-bed reactors, with the oxygenates fed between stages to quench the hot reactants and the unwanted $C_2^=$ and $C_4^=$–$C_6^=$ recycled into the first stage. Unfortunately, the overall propylene yield turned out to be only about 61% with paraffins and aromatics as the main byproducts, lower than the expected value 65% [5], and much lower than the total yield of ethylene and propylene with a typical MTO process (generally over 80%) [6]. To increase the economic efficiency of MTP process, it is urgent to improve the propylene yield by all means.

A reliable kinetic model is vital for the optimization of the industrial reactors. It is widely accepted that the MTP process comprises several consecutive reaction steps starting by the dehydration of methanol to dimethyl ether, followed by the formation of

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Nomenclature

$A_{0,j}$	pre-exponential factor of jth reaction, mol kg^{-1} s^{-1} kPa^{-1} or mol kg^{-1} s^{-1} kPa^{-2}	P	pressure, kPa
$E_{a,j}$	activation energy of jth reaction, kJ mol^{-1}	p_i	partial pressure of ith component, kPa
$E_{a,j}^{app}$	apparent activation energy of jth reaction, kJ mol^{-1}	R_i	rate of ith component, mol kg^{-1} s^{-1}
F_T	total mole flow rate, mol h^{-1}	r_j	rate of jth reaction, mol kg^{-1} s^{-1}
k_j	kinetic constant of forward reaction rate of jth step, mol kg^{-1} s^{-1} kPa^{-1} or mol kg^{-1} s^{-1} kPa^{-2}	T	temperature, K
k_{sj}	kinetic constant of surface reaction rate of jth step, mol kg^{-1} s^{-1}	w_i	weight factor
		W_{cat}	catalyst weight, kg
		y_i	mole fraction of ith component
		ΔH_j	reaction heat of jth reaction, kJ mol^{-1}
OF	objective function for optimization	ϕ_i	total squares of difference

light and higher olefins together with their mutual transformation, and terminated by the formation of paraffin and aromatics [7,8], which can be represented by

$$2CH_3OH \xrightarrow{-H_2O} CH_3OCH_3 \rightarrow light\ olefin \rightarrow \begin{cases} paraffins \\ aromatics \end{cases}$$

In our previous two studies [9,10] we have investigated the mechanism of the co-reaction of methanol and C_3–C_6 olefins and the transformation of C_3–C_7 olefins over a high-silicon HZSM-5 under 400–490 °C, a typical reaction condition for MTP process. As shown in Fig. 1, it has been revealed that methanol is consumed through methylation reactions and the olefins take part in the methylation with methanol to make the chain grow to higher olefin and simultaneously the interconversion through mono-, bi- and trimolecular cracking reactions, which shows that the olefin methylation-cracking rather than the hydrocarbon pool mechanism is the dominant pathway of the MTP reactions under the practical operation conditions [11]. Furthermore, a rigorous kinetic model based on methylation-cracking mechanism has been established, which fits the experimental data excellently under various operation conditions. However, the generation of paraffin and aromatic has not been taken into account yet in the overall model since these side reactions obey different pathways from the main reactions, which is the main target of this work.

It is generally acknowledged that paraffin formation involves the saturation of double C–C bond by hydrogenation reactions [12,13], in which the olefin molecular is firstly adsorbed on the acid site to form a carbonium ion, undergoes hydrogen transfer reaction with the hydride abstraction, such as cycloalkanes and other paraffins, and then desorbs into the bulk phase. The alkane molecular can further participate in isomerization, dehydration and cracking reactions on the acid site [13–16], resulting in complex product distribution. Methane, the smallest hydrocarbon with no carbon–carbon bond, is one of the primary cracking products of alkanes higher than ethane [16] with the reactivity increasing with the carbon number and a selectivity up to 5% in the cracking of hexane [17]. Besides, it is also reported that the methoxyl generated from the reaction of methanol and Brönsted acid site of the zeolite can also pyrolyze into methane [18,19].

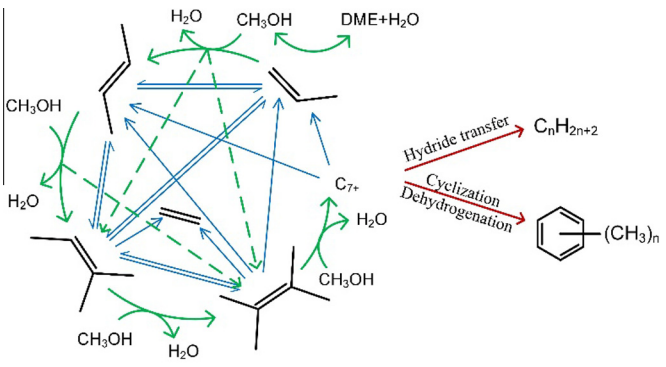

Fig. 1. The overall reaction network in the co-reaction of methanol and olefins.

In the generation of aromatics, C_6–C_9 carbocation from the adsorption or the dimerization of olefins first cyclizes to a hexatomic ring and then dehydrogenates to form the benzene ring [20–23]. The aromatic hydrocarbons in MTP process are mainly toluene, *m*-, *p*-, *o*-xylene and 1,2,3-, 1,2,4-, 1,3,5-trimethylbenzene, together with a small amount of benzene [24]. Aromatics with long side chain such as ethylbenzene, however, can barely be generated. Moreover, the aromatics can also participate in disproportion and isomerization over the acid zeolite [25–27].

In most of the other published MTP kinetic models [19,28–31], though the generation of paraffins or aromatics is usually included, they are lumped as one component directly produced from methanol or olefin by a first order kinetic step. Nevertheless, the hydrogen transfer is essentially a complex process [32] and such a simple kinetic step may fail to predict the product distribution under various conditions. Consequently, a detailed study on the mechanism and kinetic of paraffin and aromatic formation is required for the development of a kinetic model.

In this work, we performed the co-reaction of methanol and C_3–C_6 olefins and the individual transformation of C_3–C_6 olefins over a high silica HZSM-5 at 400–490 °C. Long space time was employed so that the yield of byproduct was significant. The features of paraffin and aromatic generation under different feed composition and temperature were investigated. Based on our previous developed kinetic model for methanol and olefin conversion, a more comprehensive model with byproduct formation was then established for the MTP process.

2. Experiment

2.1. Catalyst and reagents

The HZSM-5 catalyst with Si/Al ratio of 200 used for kinetic study has been described in our previous work [9,10,33]. It was received from Fuyu New Material Company in extrudes measuring 3–5 mm in length and 3 mm in diameter. The catalyst was supplied in ammonium form and calcined at 550 °C for 5 h to obtain the acid form. Then the zeolite pellets were grinded and sieved into particles measuring 100–120 mesh, small enough to eliminate the effects of inner diffusion resistance, before being used for catalytic reactions [34].

The n-alcohol of C_3–C_7 was used to substitute the corresponding olefin, as performed in our previous work [9,10], because it is more convenient to obtain and control, especially for olefins higher than butene. At the tested reaction temperature, the instantaneous dehydration of alcohols to alkenes over HZSM-5 catalyst was