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Impact of temporal and spatial distribution of hydrocarbon pool on methanol conversion over H-ZSM-5

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ABSTRACT

The hydrocarbon pool (HP) species in methanol-to-olefins (MTO) reactions over zeolite H-ZSM-5 were investigated by solid-state NMR spectroscopy and GC–MS. The distribution and reactivity of retained HP species such as carbocations and methylbenzenes (MBs) were found to evolve with reaction time and their positions in the catalyst bed. The underlying mechanism of the typical S-shaped methanol conversion curve was revealed, in which the dominating reaction route was found to be dependent on the formation and reactivity of different HP species that were varied at different reaction time. During the induction period, cyclopentenyl cations served as the precursor to MBs and exhibited higher reactivity than the latter. The reaction was accelerated by the accumulation of alkenes and further enhanced by consequent involvement of the cyclopentenyl cations and aromatics, which eventually led to a steady state reaction. The interconversions of the reaction cycles based on alkenes, cyclopentenyl cations, and MBs were proposed for the formation of light olefins. The co-catalysis of HP species in the MTO reactions showed that the cyclopentenyl cations and alkenes favored propene formation, while the light MBs such as xylene and triMB facilitated ethene formation. Within the catalyst bed, both cyclopentenyl cations and MBs were dominantly formed in the upper catalyst layers. The experiments indicated that both cyclopentenyl cations and alkenes maintained high reactivity throughout the catalytic bed, while MBs exhibited high reactivity only in the upper catalyst position.

1. Introduction

As a promising alternative for producing olefins such as ethene and propene, methanol-to-olefins (MTO) conversion over acidic zeolites has attracted significant attention [1–4]. Understanding the mechanism of the MTO reaction is essential in achieving selectivity control of specific olefins, which however, is a big challenge, due to the complex reaction network involved. Intensive experimental and theoretical efforts have been made to address this issue, but the exact mechanism underlying methanol conversion has remained not well understood over the past decades [2,5–8].

For olefin formation, direct route via key intermediates such as carbenium ions, carbenes, and free radicals was initially considered [2,9–11]. However, the direct route most likely operates at a relatively low rate, which does not contribute much to the formation of olefins, especially in the steady state stage [5,6]. Thus, the importance of the direct route is still under debate. On the other hand, an autocatalysis process existing in MTO reactions indicates that the indirect route can be responsible for the formation of olefins. In the indirect route, generally known as the "hydrocarbon pool mechanism," hydrocarbon pools (HPs) formed by aromatics, carbenium ions, and alkenes are sequentially methylated and cracked or dealkylated to form light alkenes on zeolites [3,4,12]. The working MTO catalyst can be considered as an organic–inorganic hybrid material and the active sites are defined as supramolecular reaction centers composed of the HP species and the inorganic zeolite framework [13,14]. The HP species are believed to have a co-catalytic role in the MTO reaction. On the basis of the methylbenzenes (MB) and their protonated counterparts (e.g., benzenium ions), two different HP routes have been proposed for the operation of the HP mechanism. One is side-chain methylation [15–19], which describes the formation of light olefins by elimination of the alkyl chain that is generated by repeated methylation of aromatics; the other, the paring route [20–22], featured by a ring contraction and expansion of a

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benzenium ion, leads to the formation of an alkyl chain followed by splitting off light olefins.

HP species display a vital role not only in the conversion of methanol/DME but also in controlling product selectivity [23]. It is well known that the MTO reaction is an autocatalyzed process and the conversion is increased with the accumulation of HP species in zeolite channels [24]. Haw et al. demonstrated that 1,3-dimethylcyclopentenyl cations were the main HP species in H-ZSM-5 that could shorten the induction period [25]. They later claimed that the carbocations could be transformed into toluene via ring expansion [26]. In our previous work, we found that the mean number of methyl groups in the methylbenzene HP species changes with the reaction, which affects the product selectivity [27]. The propene-to-ethene (P/E) ratio shows dependence on the distribution of the MBs at different reaction stages. It was also found that the HP species can lead to catalyst deactivation due to carbon deposition at long reaction times [28,29]. Thus, the evolution of HP species has a significant influence on aspects of the MTO reaction such as conversion, product selectivity, and catalyst lifetime.

For reactions occurring in a fixed bed reactor, the catalyst loading is a key factor affecting the catalytic performance. The work of Nishiyama and co-workers indicated that the selectivity for xylene increased with increasing contact time (increasing catalyst loading) in the methanol-to-aromatics (MTA) reaction [30]. Since the volume of the loaded catalyst is varied, the HP species could be formed with a spatial distribution in the catalyst bed, which would thus result in different reactivity of the HP species and different reaction routes. The investigation of catalyst deactivation by Haw et al. indicated that the time evolution of a catalyst bed was like a "cigar burn," in which the top part of the catalysts was faster deactivated than that on the bottom [13]. This could be due to the different reactivity of the HP species distributed in the catalyst, leading to catalyst deactivation to different extents. As indicated by Schulz [31], the retained species on zeolite leading to deactivation were different axially along the fixed-bed reactor in the MTO reaction over H-ZSM-5. The work of Svelle et al. showed that more coke was deposited in the topmost layers of ZSM-5 catalyst beds, and retained organics such as aromatics served as precursors to coke [32]. Moreover, in the elegant work of Lercher and co-workers [33], the reaction routes for the MTO reaction were identified as related to contact time. The aromatics-based cycle was found to be favored at lower conversion, namely shorter contact time, and less involved at longer contact time. These investigations imply that the distribution of HP species such as MBs along the catalytic bed is essential in the MTO reaction, which is related to the conversion of methanol and the catalyst lifetime. However, some important issues are still needed to be addressed. For example, although the cyclopentenyl cations have been considered as a type of important HP species involved in the MTO reaction [26,29,34,35], their distribution, reactivity, and influence on product selectivity and catalyst deactivation on a spatial scale are still unclear. Also, the reactivity of HP species along the catalytic bed in the early stage, especially in the induction period, which is related to the formation of initial C—C bonds of olefins, has not been fully explored. Thus, a systematic and comprehensive study of the HP species with regard to both time and spatial scale in the catalyst bed is critical for deeply understanding the HP chemistry in the MTO reaction.

The aim of this study is to explore the HP mechanism in the MTO reaction over H-ZSM-5 zeolite. Using solid-state NMR spectroscopy combined with GC–MS, the composition and nature of the HP species, particularly the retained organic species on zeolite, were studied in relation to reaction time and catalyst loading in the fixed bed reactor. In addition to alkenes, the formed MBs and carbocations were analyzed in depth. The reactivity of various HP species was assessed by $^{12}C/^{13}C$ isotopic switching experiments. Moreover, the impact of the HP species on product selectivity and catalyst deactivation was revealed.

2. Experimental

2.1. Materials and characterizations

H-ZSM-5 (Si/Al = 25) zeolites were obtained from the Catalyst Plant of Nankai University. Powder X-ray diffraction (XRD) was performed on a PANAlytical X'Pert^3 Powder X-ray diffraction diffractometer with Cu Kα (λ = 1.5406 Å), recording at 40 kV and 40 mA. The powder XRD pattern (Fig. S1 in the Supporting Information) confirms the well crystallized MFI phase. The ^{27}Al MAS NMR spectrum of H-ZSM-5 (Fig. S2) shows the presence of only tetrahedral framework Al atoms (54 ppm).

2.2. Catalysis experiments

The H-ZSM-5 powder was pressed into pellets at between 60 and 80 mesh. The pellets were activated at 400 °C in flowing helium for 1 h prior to the reaction. In the continuous-flow reaction, methanol with a partial pressure of 3.87 kPa was reacted over the H-ZSM-5 pellets (0.05 g) in a fixed bed reactor, leading to a WHSV of 12 g g^{-1} h^{-1}. For the study of the HP species at spatial scale in the catalyst bed, 0.15 g of H-ZSM-5 was equally divided into three parts (layers) by glass wool in the fixed bed reactor (Fig. 1) and the WHSV was 12, 5.9, and 4 g g^{-1} h^{-1} for 0.05, 0.10, and 0.15 g catalyst used, respectively. The total gas flow through the reactor was 200 sccm. Then the reaction was thermally quenched by pulsing liquid nitrogen onto the catalyst bed, and the temperature was cooled down from 623 K to ambient temperature within 0.2 s, which was achieved using high-speed valves controlled by a GC computer [25].

In the $^{12}C/^{13}C$ methanol isotope transient experiments, methanol at ^{13}C natural abundance was reacted at 325 and 350 °C for 15 min before switching to ^{13}C-methanol (99% ^{13}C) and was

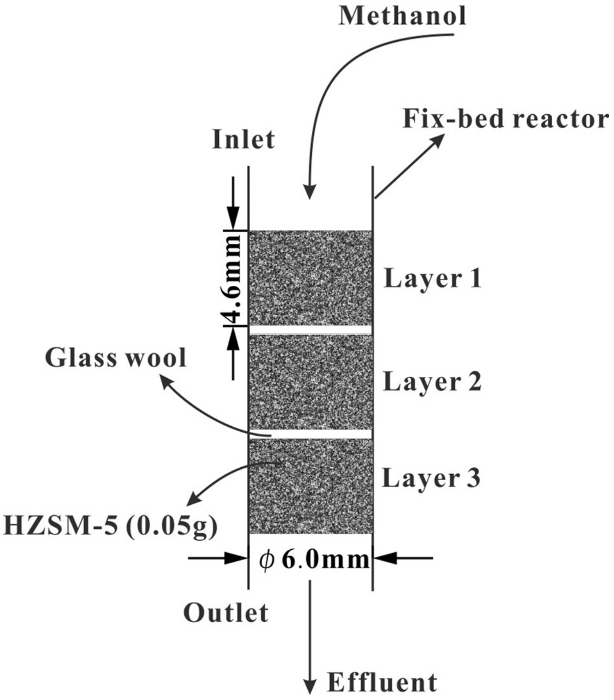

Fig. 1. The schematic illustration of the fixed bed reactor used in this work. The H-ZSM-5 catalysts were equally divided into three parts (layers) with glass wool.