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On reaction pathways in the conversion of methanol to hydrocarbons on HZSM-5

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ABSTRACT

The underlying mechanisms of the two distinct catalytic cycles operating during conversion of methanol to olefins (MTO) on HZSM-5 have been elucidated under industrially relevant conditions. The co-existence of olefins and aromatic molecules in the zeolite pores leads to competition between the two cycles. Therefore, their importance depends on the local chemical potential of specific carbon species and the methanol conversion. Due to a faster, "autocatalytic" reaction pathway in the olefin based cycle, olefin homologation/cracking is dominant under MTO conditions, irrespective of whether aromatic molecules or olefins are co-fed with methanol. Another hydrogen transfer pathway, faster than the usual route, has been identified, which is directly linked to methanol. In agreement with that, the co-feeding of olefins resulted in a remarkable longer lifetime of the catalyst under MTO conditions, because the high rate methylation competes with the formation of more deactivating coke – presumably oxygenates- through methanol derivatives.

1. Introduction

The catalytic conversion of methanol to olefins (MTO) has drawn particular attention in recent years, as this process is believed to provide an alternative pathway for the production of ethene and propene [1–4]. One of the key issues of the MTO chemistry, the control of product selectivity, necessitates a fundamental understanding of the reaction mechanism. The extremely complex reaction network makes this, however, a very challenging task [5–7].

The initial debate was mainly focused on how the first C–C bond was formed. Over 20 direct coupling mechanisms were suggested in spite of little experimental evidence [2,8,9]. Recent experimental and theoretical investigations suggested, however, that direct C–C coupling is not the dominating pathway due to unstable intermediates and prohibitively high activation barriers [8–10]. Several mechanisms involving impurities in the feedstock appear to offer more plausible reaction routes for the formation of initial hydrocarbons.

In 1979, Chen and Reagan originally proposed that MTH is an autocatalytic reaction [11]. Consistent with this proposal, an olefin homologation/cracking route was suggested by Dessau and co-workers as the main reaction pathway on HZSM-5 at steady-state conditions [12,13]. After the initial olefins are formed during the induction period, these olefins are consecutively methylated to form higher olefin homologues, which in turn crack into lighter olefins such as ethene and propene. Hydrogen transfer and cyclization reactions lead to the formation of alkanes and aromatics as end products. In parallel with the proposal of this olefin based cycle, the important role of aromatics and unsaturated cyclic species in the methanol reaction has also been proposed. Langner et al. for example reported that co-feeding 36 ppm of cyclohexanol significantly reduced the duration of the induction period [14]. In a parallel study, experiments of co-feeding toluene or *p*-xylene with methanol led Mole et al. to postulate a co-catalytic effect of methylbenzenes on methanol conversion [15,16]. As the conversion of methanol produces aromatic molecules, one could also identify the aromatics based reaction routes as another form of autocatalysis. These early investigations were very insightful and embodied already the concept of aromatics based cycle. However, these findings remained largely ignored.

It was the invention of SAPO-34 material in the 80s that stimulated again the investigations in the early 1990s of the role of aromatics in the MTH reaction and subsequently the proposal of the "hydrocarbon pool" concept by Kolboe et al. [17–19]. In the original proposal, the active center was a "coke-like" organic species adsorbed on the surface [17–19]. The active site for MTO was later defined as a supramolecular inorganic–organic hybrid (zeolite-

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hydrocarbon species), which acts as a scaffold for light olefin formation [20,7]. The unique structure of SAPO-34 material provided the possibility of trapping carbon intermediate species and, thus, stimulated intensive investigations in parallel by groups of Kolboe and Haw, respectively. This established the role of aromatics, especially polymethylbenzenes and their protonated forms, as the active hydrocarbon pool species in SAPO-34, H-BEA, and H-MOR catalysts have large pores or cages [20,7,21–30]. Recent experimental and theoretical work proposed that olefins may act as another kind of active hydrocarbon pool species, particularly in medium-pore zeolites, such as the ZSM-22 zeolite with 1-D 10-ring channels, in which the internal spaces are too small to form polymethylbenzenes [31–34].

In retrospect, the MTO history clearly demonstrated that the actual course of the mechanistic understanding developed in loops, and the key mechanistic aspects that are generally accepted today were reported already in the very early literature [5]. Both, the olefin-based cycle and the aromatic-based route are well accepted at present by researchers favoring either the early "autocatalysis" proposal or the later "hydrocarbon pool" concept [5,6]. However, further insights into the dynamic course of the interactions of zeolite (acid sites), hydrocarbon species, and methanol are yet to be developed, some of which we try to address in the present work.

Although a general rationale of the zeolite-specific product distribution has been achieved through understanding the kinetic consequences of the zeolite topology and the identity of the active hydrocarbon species, for zeolites such as H-BEA, SAPO-34 or HZSM-5, where probably both catalytic cycles work, a quantitative relationship between these cycles and the product distribution has not been unequivocally established [5,6]. For instance, although several reports have shown that aromatics, especially higher polymethylbenzenes, are active hydrocarbon pool species in H-BEA zeolite at 623 K [29,30], recent investigations by Ahn et al. and Simonetti et al. [35,36] demonstrated that, over H-BEA, the olefin based cycle can be selectively favored over the aromatics based cycle, and the carbenium-ion chemistry dictates the formation of a product pool rich in highly branched C_4 and C_7 alkanes by using low temperatures (473 K) and moderate DME partial pressures (>50 kPa). Therefore, the reaction conditions, in addition to zeolite topology, play a remarkable role in evolvement of the active hydrocarbon species and the product selectivity.

The same situation applies to HZSM-5. The archetypical catalyst for methanol conversion to gasoline – and in recent years light olefins – has attracted tremendous efforts to elucidate the mechanism (e.g. [1–2,5–6]). A more recent study of the group of Olsbye summarized the proposals for a dual-cycle mechanism on HZSM-5 [5]. An aromatics-based cycle involved ethene and methylbenzenes, and the olefin-based methylation/cracking cycle produces C_{3+} olefins [37,38]. This has been a seminal contribution to the interpretation of HZSM-5 specific product distributions. However, compared to the typically chosen temperatures ($\leqslant$623 K) for these mechanistic studies, higher reaction temperatures ($\geqslant$723 K) are used in the case of HZSM-5 based industrial processes [5], such as the Air Liquide's MTP process, for which a recycling operation of the aliphatic products other than propene is incorporated [39–42]. As a result, tailoring product distributions requires insight into the reaction mechanism under realistic reaction conditions and specific operation modes.

Thus, we report here the elucidation of the kinetic aspects of the mechanism under reaction conditions closely related to the practical operations, i.e., the intrinsic selectivities toward ethene and propene formation of the aromatics- or olefins-based cycles, and how the dominant reaction pathways are influenced by feed composition, how they change during the reaction course, and, ultimately, how each cycle contributes to methanol conversion and the specific product distributions.

2. Experimental

The employed catalyst and other reagents are identical with the materials used in the previous paper [43]. The zeolite powder has a Si/Al ratio of 90 and crystal size of 500 nm. The catalytic tests were performed on either a bench-scale plug flow reaction unit (with nitrogen dilution) or 10-fold parallel reaction unit (using water as diluent). The pressed, crushed, and then fractionized zeolite pellets are diluted, loaded and processed with the identical procedures as reported in Ref. [43].

In the experiment addressing the MTO reaction cycles, a fixed catalyst amount of 20 mg was loaded into the reactor. The methanol partial pressure in the flow is held constant at 10 kPa by maintaining the temperature of methanol saturator at 299 K. The total flow rate was systematically changed to achieve different space velocities. After the reaction temperature was stabilized under 50 ml/min N_2 flow at 723 K for 1 h, the N_2 flow was passed through the methanol saturator to achieve 10 kPa methanol. After 5 min on stream, the GC was started to measure the reactor effluent composition, and subsequently the valve for the feed control was switched to pure N_2 flow and the N_2 flow rate was set to the target value. This procedure was repeated for a series of space velocities.

The experiments for the aromatics co-feeding were conducted as previously described [43]. The methanol partial pressure was 10 kPa, while the *para*-xylene partial pressure was 0.2 kPa, both diluted by N_2. The total flow rate was maintained, as the catalyst charged was changed to reach different levels of conversions. In the experiments for the conversion of pure olefins (120 C%), i.e., 1-pentene, 1-hexene or 1-heptene, experiments were performed under reaction conditions as close as possible to those applied in the MTO reaction of a feed containing 10 kPa methanol (100 C%) and 0.4 kPa 1-pentene (20 C%). 10 kPa water vapor was introduced with the olefin, to mimic the water concentration formed during the MTO reaction (i.e., the outlet partial pressure of water at 100% conversion of 10 kPa methanol). Identical to the experiments of toluene co-feeding, the total flow rate was unchanged, while the catalyst weight was systematically changed to reach different levels of conversions.

In the experiment addressing the impact of the carbon ratio of methanol to co-feed (butene or 0-pentene), experiments were performed in the 10-fold parallel reaction unit at 748 K with water dilution. 2-butanol or 2-pentanol were used as co-feed, as they were expected to be fully dehydrated on acidic zeolite to butenes and pentenes, respectively. Defining the carbon based concentration in a mixture of methanol and water (weight ratio 1:2) as 100%, different compositions of the same carbon based concentration were used: (a) 100 C% from methanol, methanol partial pressure 0.22 kPa, (b) 90 C% from methanol with 10 C% from co-feed (2-butanol or 2-pentanol), (c) 83 C% from methanol with 17 C% from co-feed (2-butanol or 2-pentanol), (d) 73 C% from methanol with 27 C% from co-feed (2-butanol or 2-pentanol), (e) 63 C% from methanol with 37 C% from co-feed (2-butanol or 2-pentanol), (f) 37 C% from methanol with 63 C% from co-feed 2-butanol. Thus, identical carbon concentrations were used in all experiments with alcohol co-feeds.

3. Results and discussions

3.1. Autocatalysis versus hydrocarbon pool proposal

Fig. 1 depicts the effect of repeated variations of the methanol contact time on the catalytic performance of a fixed catalyst loading. When a methanol conversion of 93% was reached at a contact time of 0.11 min $kg_{cat}\ mol^{-1}_{MeOH}$, the subsequent increase of flow rate led to a decrease of contact time to 0.03 min $kg_{cat}\ mol^{-1}_{MeOH}$,