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Direct observation of induction period of MTO process with consecutive pulse reaction system

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Abstract

The initial transformation of methanol over HZSM-5 catalyst was investigated by a consecutive pulse reaction system. The reactant–catalyst contact time influenced the initial methanol transformation and the performances implied methanol reaction in induction period or under steady-state condition. The induction period, in which an organic-free HZSM-5 catalyst could be transferred to a working catalyst, were directly observed. The analysis result of the product stream predicted hydrogen-deficient species deposition over catalyst surface at the beginning of MTO reaction. The hydrogen transfer level of steady-state MTO reaction also varied with reaction contact time.

Keywords: MTO; Pulse reaction; Contact time; Induction period

1. Introduction

Since its initial discovery by Chang and Silvestri [1], MTO process, regarded as a successful route for the conversion of natural gas or coal to light olefins, received significant research attention from industry and academia. For the mechanism study, more than 20 distinct mechanisms have been proposed concerning the first C–C bond formation [2]. Haw and Kolboe suggested that the reaction proceeds by a "hydrocarbon pool" mechanism with cyclic organic species as reaction center for light olefins production [3–8]. The previous findings indicated two reaction stages involved in MTO reaction, induction period reaction and steady-state reaction. During the induction period, carbonaceous species are initially formed and then in the steady-state reaction, reactants can be further added and alkenes products eliminate from the carbonaceous reaction center. Recent studies have verified that hydrocarbon pool mechanism is the dominating route in the MTO process under steady-state condition [6,9]. While in the induction period, the initial organic compounds formation is not very conclusive. Haw and coworkers claimed that the initial hydrocarbon pool is from the hydrocarbon contamination in methanol feed or over solid acid catalysts after calcinations [6,10]. On the other hand, IR and NMR investigations have provided evidences that surface methoxy species may act as a source of primary hydrocarbons during the induction period of methanol conversion on acidic zeolite catalysts [11–13].

Organic-free zeolite catalyst could be transferred to a working catalyst by contacting the catalysts with methanol or more reactive olefins [14,15]. In continuous-flow MTO process, direct observation of induction period is difficult since induction reaction is a very short-time reaction and once some cyclic species formation or some coke deposition on the catalyst surface, the conversion rate will increase to the steady-state level and the reaction will occur in a very quick way. A large amount of secondary reactions, especially the disproportionation of olefins products, from which aromatic and alkanes readily form over zeolite, also obstacle the determination of real reaction stage with product analysis. Clarifying the specific features of

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methanol conversion in induction period and steady-state period has been the main motivation for the present study. For the direct observation of the reaction behavior at the very beginning of methanol conversion, a consecutive pulse reaction system was designed and employed in the present study. The reaction could be performed at very high feeding rate to minimize secondary reactions as far as possible and thereby obtain clearer insight into the initial methanol conversion and primary product generation.

2. Experimental

HZSM-5 (Si/Al = 25, from NanKai University, China) was employed as catalyst in this work. Methanol was purchased from Xinxi Chemical Reagent Company (99.5%). The experiments were carried out on a pulse reaction system based on a VARIAN CP3800 gas chromatograph containing a 6-way valve and a 10-way valve, which are responsible for fixing the reactant quantity and injecting methanol vapor respectively. The methanol vapor stream was generated by passing He flow (1) through a methanol saturator at a certain temperature and then continuously passed through a quantitative loop connected to the 6-way valve. In this way, the sample loop was full of a certain amount of reactant. With the simultaneous switch of 6-way and 10-way valves, a fast He flow (2), with a set flow rate, injected the methanol vapor kept in the sample loop through the 10-way valve into the reactor. The two valves and all the tube were kept warm to ensure the volatile condition of reactants and products. The contact time could be calculated with the equation:

$$\text{Contact time} = V_{\text{cat}}/\text{Injecting flow rate}$$

where V_{cat} represents the volume of catalyst bed and injecting flow rate is the flow rate of He flow (2).

Series of methanol pulses delivered automatically in 30 min intervals were performed consecutively onto HZSM-5 catalyst beds at 400 °C. Before reaction, HZSM-5 catalyst was loaded in the quartz reactor with diameter of 3 mm and calcined at 600 °C in air for 6 h. Each injection contained 0.09 mg methanol vapor. By varying the rate of He flow (2), the contact time of methanol feed with catalyst bed is 3.9, 3.6 and 2.4 ms for the three series of pulse reactions which are named as Experiments A–C. Product stream from each injection entered the capillary column of VARIAN CP3800 gas chromatograph and analyzed with FID detector. The injections repeated for 4–11 times. The flow chart of the pulse reaction system is given in Fig. 1.

3. Results and discussion

Fig. 2 depicts the GC analysis results of product stream after injecting methanol onto HZSM-5 catalyst. Even the reactions were carried out under almost the same condition, just varying the contact time, we can observe the different performances of pulse reactions (Fig. 2a–c). The total hydrocarbon yields of the three series of consecutive pulse reactions are compared in Fig. 3.

In Experiment A with contact time of 3.9 ms (Fig. 2a), four methanol injections performed onto HZSM-5 catalyst give rise to quite close conversion and product distribution. Just a slight increase of the total hydrocarbon products yield could be observed from pulse 1 (62.33%) to 2 (67.52%). Light olefins (ethylene, propylene and butenes) are the dominating products and about 50% of products in the effluent stream are attributed to the light olefins. Propylene forms with higher initial selectivity than other olefins. For the first pulse, the total light olefins yield attains to 30.45%, with ethylene yield of 7.37%, propylene yield of 15.80% and butenes yield of 7.28%. The following three methanol pulses upon the catalyst generate light olefins with similar yield to pulse 1. Propane also appears in a relative large amount in the product stream, accompanied by aromatics generation, which stems from the secondary reactions of light olefins products. High hydrocarbon yield and high light olefins yield from the first injection means the induction period ends during the first pulse reaction and its value is <3.9 ms, the contact time of Experimental A. We can just see methanol transformation under steady-state condition.

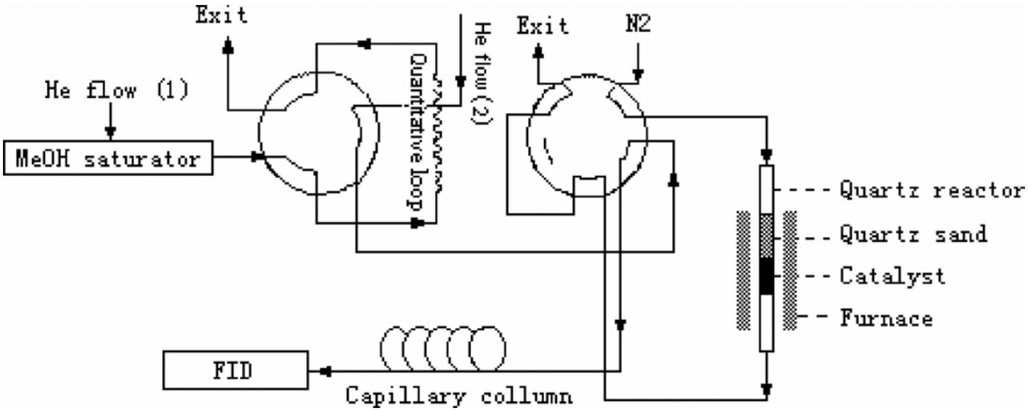

Fig. 1. Flow chart of pulse reaction system.

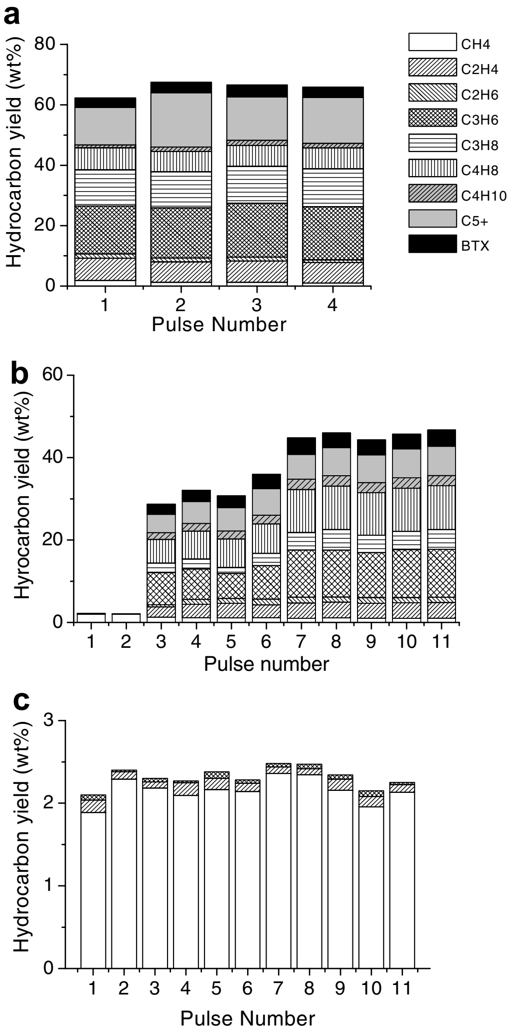

Fig. 2. Detailed hydrocarbon yield of methanol pulse reaction over HZSM-5 with contact time of 3.9 ms (a), 3.6 ms (b) and 2.4 ms (c).

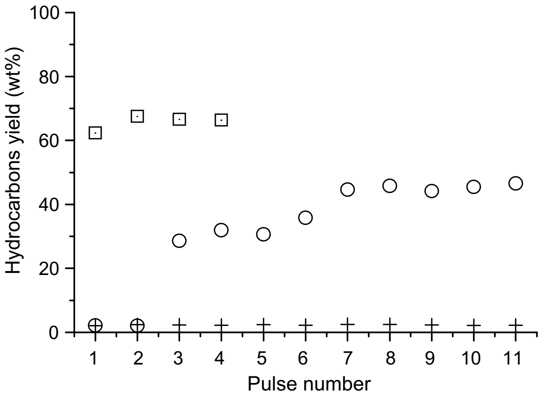

Fig. 3. Comparison of total hydrocarbon yield with contact time of 3.9 ms (□), 3.6 ms (○) and 2.4 ms (+).

Compared to Experiment A, methanol was conducted upon catalyst in Experiment B with slightly lowered contact time (3.6 ms) for each injection. The performances detailed in Figs. 2b and 3 present that the first and the second pulses show very low hydrocarbon yield (2.18% and 2.10%) and methane is extremely predominant in the product stream. While from the third pulse, total hydrocarbon yield increases significantly with the appearance of ethylene, propylene and butenes as the main products. This performance evolution is quite different from Experiment A. The first and the second pulse reactions clearly present the induction period performance of methanol conversion. Following the two injections, consecutive pulses 3–11 are fed into the reactor. Methanol transfers with steady-state character and the total hydrocarbons yield increases from 28.58% (pulse 3) to 46.55% (pulse 11) with large amount of light olefins generation, responsible for 56% of hydrocarbons in the effluent stream.

Methanol is very reactive on HZSM-5 in Experiments A and B. When the contact time is lowered to 2.4 ms, pulse reactions of Experiment C just present very low hydrocarbons yield, 2.10% for the first methanol pulse, and about 2.30% for the following injections. Methanol injection repeated 11 times, we just observe low conversion and predominant formation of methane as the beginning two injections of Experiment B, indicating that the reaction is still in the induction period. Low-contact time may influence the efficient formation of primary organic compounds and subsequent assembly of initial hydrocarbon pool cannot be realized.

Previous studies have suggested that some facile reactions proceed by way of Eley–Rideal mechanism [16,17] with the occurrence of gas-phase reagent striking an adsorbate and a followed possible abstraction. Methanol conversion on catalysts resembles the Eley–Rideal reactions in some respects. Methanol and dimethyl ether react on cyclic carbonaceous species trapped in the channel of the catalysts. These deposited organic species act as the scaffolds for the assembly of light olefins. Reactants add to these organic species and products split off. If the formation rate of this cyclic organic intermediate is low, the short duration pulse does not allow its formation efficiently and the followed step of the reaction will not perform. As is observed in Experiment C with short pulse duration of 2.4 ms, conversion and hydrocarbon yield remain low. The period for initial reaction center formation, during which the conversion degree increases to a steady and high level is thought to be the induction period of MTO reaction.

Induction period reaction in MTO process will transform an organic-free catalyst to a working catalyst for light olefins production [14,15]. During this period, methanol dehydration to form dimethyl ether (DME) is rapid. As is seen in Fig. 4, long contact time reactions (3.9 or 3.6 ms) present relatively low DME yield caused by DME consumption in the followed conversion to light olefins. In the low-contact time reaction, the highest DME yield and the lowest hydrocarbon yield in the final products implies the further transformation of DME to hydrocarbons is difficult. Slow kinetics is the character of the

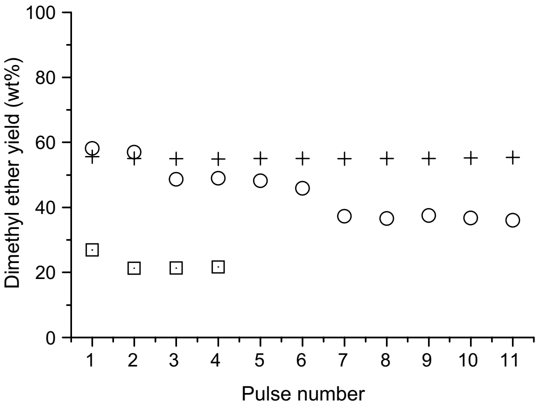

Fig. 4. Dimethyl ether yield with contact time of 3.9 ms (□), 3.6 ms (○) and 2.4 ms (+).

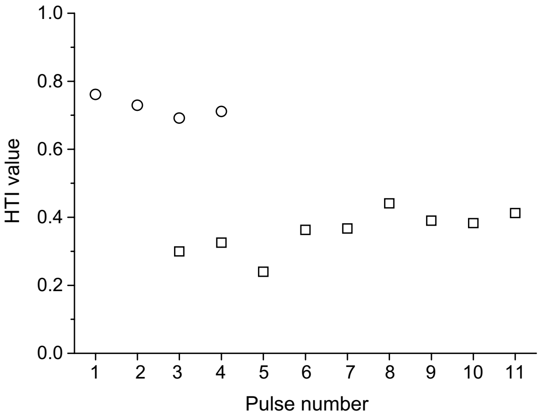

Fig. 5. HTI value ($C_3^0/(C_3^= + C_3^0)$) of methanol conversion under steady-state condition with contact time of 3.9 ms (□) and 3.6 ms (○).

induction period reaction with low-contact time. As is shown in (1):

$$CH_3OH \rightarrow CH_3OCH_3 \rightarrow CH_4 + (C_2^= + C_3^=, \text{ trace amount}) + (\text{H-deficient}(CH_x)_n, 0 < x < 2, \text{ coke deposition}) \quad (1)$$

methanol or dimethyl ether transfers with a very low hydrocarbon yield and the products consist of methane and a trace amount of ethylene and propylene. The work of Haw and coworkers also indicated very low methanol conversion and CH_4 formation over HZSM-5 in the initial conversion of methanol [6]. Methane is more hydrogen-rich than the reactant, while no a lot of hydrogen-deficient products are tested in the product stream, so methane formation is therefore more likely accompanied by unsaturated hydrocarbon restrained in the channel of HZSM-5 for H-balance. Previous study proposed multi-substituted benzene or cyclopentenyl cations as hydrocarbon pool, which persist in the catalyst and serve as the reaction center [9,18]. These large-scale cyclic organic species in our present study are responsible for the trace amount of ethylene and propylene production in pulses 1 and 2 of reaction B and pulses 1–11 of reaction C. Further reaction of these olefins would cause more unsaturated hydrocarbon deposition. A self-acceleration of methanol transformation to light olefins in reaction B starts from the third pulse, meaning that the first two pulse reactions contribute to the formation and aggregation of enough hydrocarbon pools for transferring an organic-free catalyst to a working catalyst. The followed pulse reactions 3–11 present the steady-state character as the performance of reaction A. For reaction C with lowest contact time, the shortened pulse duration obstacles the effective generation of cycle-organic reaction centers. The further reactants addition and olefins products elimination from these centers also could not be realized effectively in so short residence time.

Under steady-state condition, light olefins can be produced from methanol conversion over a working catalyst. Propylene mainly forms over HZSM-5 among MTO products. The secondary reactions of olefins, which are very reactive over zeolite catalysts, such as oligomerization and hydrogen transfer, determine the final products different from the primary products in MTO process. Hydrogen transfer reaction of olefins products, $(CH_2)_n$, gives rise to alkanes and hydrogen-poor compounds, such as aromatics or even more hydrogen-unsaturated species, coke. Hydrogen transfer index (HTI), which has been proposed by Tsang [19], is a useful parameter to discuss these reactions. For different catalysts, pore dimensions and acid site density affect the hydrogen transfer ability [20]. For a given catalyst, the residence time influences HTI [21]. The HTI values of steady-state MTO reaction, with the definition of $C_3^0/(C_3^= + C_3^0)$, are compared in Fig. 5. The result indicates that hydrogen transfer reaction could be depressed to some extent by shortening the reaction contact time.

4. Conclusion

Two reaction stages of MTO process, induction period reaction and steady-state reaction, were observed clearly by means of a consecutive pulse reaction system. Varying the reactant–catalyst contact time gave rise to the difference of initial catalytic performance. Methanol conversion with low-contact time presented induction period characters. Low hydrocarbon yield proved the slow kinetics of induction period reaction. Predominant methane formation predicted H-deficient hydrocarbons deposition as hydrocarbon pool over catalyst. Self-acceleration of methanol conversion may stem from the aggregation of enough reaction centers during the induction period. Prolonged reaction contact time favored the reaction center formation, which could end the induction period in one pulse duration. Under steady-state condition, light olefins were the primary products from methanol conversion over HZSM-5 and propylene mainly formed among the olefins products. Elimination of secondary reactions in MTO process by varying the contact time gave more clear insight of the initial transformation of methanol and primary products generation.

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