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Article

Methanol-to-olefin induction reaction over SAPO-34

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ABSTRACT

The methanol-to-olefin induction reaction over the SAPO-34 was performed using a fluidized-bed system. We found that the whole induction period could be divided into three reaction stages. Further investigation of the reaction kinetics revealed that this induction reaction behavior was different from that over H-ZSM-5 catalyst. Compared with the H-ZSM-5, the generation of initial active centers is easier over SAPO-34 because of its limited diffusivity and the spatial confinement effect of the cages. However, the autocatalysis reaction stage is difficult over SAPO-34 because of the continuous formation of inactive methyladamantanes.

1. Introduction

The methanol-to-olefin (MTO) process, combined with the transformation of coal or natural gas to methanol, has been demonstrated to be a successful non-petrochemical route to produce ethylene and propylene [1]. Understanding the mechanism of the MTO reaction has drawn considerable interest over the past several decades because of its ability to produce C–C bonds from C1 reactants.

Previous studies have suggested that the MTO reaction occurs through a hydrocarbon pool (HCP) mechanism [2–8]. The reaction takes place over three periods: the induction period, the steady-state reaction period, and the deactivation period [9,10]. During the induction period, small amounts of polymethylbenzenes (PMBs) and their protonated analogues are formed and accumulated within the cages or channel intersections of the molecular sieves that act as the initial reaction intermediates [8,11–14]. After the induction period, methanol conversion is observed and increases autocatalytically. Eventually methanol conversion increases dramatically and polycyclic aromatic molecules and large coke fragments form at the same time, which leads to deactivation of the catalyst [8,15–17]. The time required for the formation of PMBs determines the induction period of the MTO reaction. In the case of ZSM-5 catalyst, we previously investigated reaction behavior and kinetics during the methanol conversion induction period [18]. Our results found that the induction period could be further broken down into three stages: an initial C–C bond formation stage, a HCP species formation stage and an autocatalysis reaction stage. A critical value of HCP species, $[HCP]_c$, that is required for starting the autocatalysis reaction (the third stage) was proposed and measured.

SAPO-34 (CHA type, containing chabazite cages and 8-member ring windows) offers excellent MTO activity and selectivity [19], and has been used for industrial applications with a fluidized-bed reactor and regenerator because of the

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rapid deactivation of the catalyst [20]. The aromatic-based cycle is the main reaction mechanism over the cage-type SAPO-34 catalyst. The catalytic performance of SAPO-34 is very different from that of ZSM-5. With larger channel sizes (10-member ring channels), the ZSM-5 catalyst shows less ethylene selectivity but better performance in methanol-to-gasoline, methanol-to-aromatics and methanol-to-propylene reactions than SAPO-34 [21–24]. It has been reported that with ZSM-5 catalyst, methanol conversion can proceed according to both the aromatic and the olefin-based cycles during the steady-state stage [25–28]. Based on the different zeolite framework structures, diffusivities, coking behavior and HCP mechanisms between SAPO-34 and ZSM-5 catalysts, it is important to compare the induction stage between SAPO-34 and ZSM-5. This study presents a kinetic investigation of the induction reaction at different temperatures. It is expected to gain more insight into the HCP mechanism.

2. Experimental

2.1. Materials

SAPO-34 ((Al + P)/Si = 16) was synthesized as described elsewhere [10]. The SAPO-34-based catalyst for fluidized reaction was prepared using the spray-drying method with an inert binder. Methanol (AR) was purchased from Xinxi Chemical Reagent Company of Shenyang, China.

2.2. Methanol conversion reaction

Methanol conversion was carried out in a fluidized-bed reactor, which guaranteed spatial uniformity of the catalytic reaction and coke deposition. Prior to the start of the experiment, 10 g of freshly calcinated catalyst was loaded into the reactor and pretreated at 550 °C under He flow (30 mL/min) for 40 min. The temperature was then adjusted to the desired value. By switching a four-port valve, the reactant (40% aqueous methanol solution), which was vaporized by a preheater, entered the reactor bottom through a distributor and contacted the catalyst. The space velocity (WHSV) of methanol was 1.5 h^{-1}. The product was detected using on-line gas chromatography (GC) (Agilent 7890A GC, USA) employing a CPPORAPLOT Q-HT (25 m × 0.32 mm) column and flame ionization detector.

3. Results and discussion

3.1. Methanol conversion reaction at different temperatures

Changes in methanol conversion with reaction time at different temperatures over SAPO-34 are presented in Fig. 1. At 290 °C, initial methanol conversion was low and almost no methanol conversion was observed, indicating that the initial HCP species were difficult to generate at a low reaction temperature. Methanol conversion (> 1%) was only observed after 100 min, after which the conversion increased more significantly. The highest methanol conversion (11.4%) occurred after 222 min and then decreased with gradual deactivation of the catalyst. At the higher temperature of 300 °C, the induction period was greatly shortened and the maximum methanol conversion increased to > 50%. The methanol conversion increased more rapidly during the autocatalytic reaction and was followed by faster deactivation compared with the reaction at 290 °C. Clearly, the MTO induction reaction is sensitive to the reaction temperature over the SAPO-34 catalyst. At higher reaction temperatures (310 and 320 °C), the induction period was further shortened and the maximum methanol conversion continuously increased, followed by more rapid catalyst deactivation. These phenomena are consistent with our previous studies on H-ZSM-5 in a fixed-bed reactor [18].

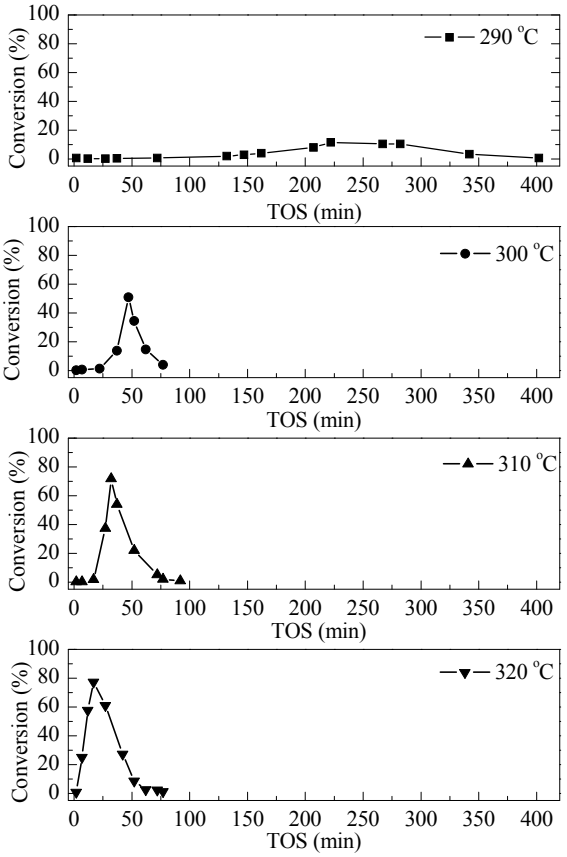

Fig. 1. Methanol conversion changes with reaction time at different temperatures over SAPO-34. TOS: time on stream.

3.2. Observation of three reaction stages

The MTO reaction is a typical autocatalytic process. The initially accumulated HCP species will promote and accelerate the generation of more HCP compounds. To gain deeper insight into how the fresh catalyst is transformed to the active one, detailed reaction stages that evolve during the induction period should be clearly differentiated. In our previous work, three reaction stages were observed over the MTO; induction period and the generation of initial HCP species were shown to occur during the second stage [18]. By plotting the methanol conversion on a logarithmic scale, as illustrated in Fig. 2, three reaction stages can also be distinguished during the induction period at 290 °C over SAPO-34. According to our previous results