Different Induction and Deactivation Reaction behavior over HZSM-5 and HSAPO-34 Catalysts during Methanol to Hydrocarbon Reaction under low Temperature

1st Liang Qi\(^{a,b}\), 2nd Zhongmin Liu*\(^{a}\)

\(^{a}\)National Engineering Laboratory for Methanol to Olefins, Dalian National Laboratory for Clean Energy, iChEM (Collaborative Innovation Center of Chemistry for Energy Materials), Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, People's Republic of China;

\(^{b}\)University of Chinese Academy of Sciences, Beijing 100049, P. R. China;

*Corresponding author: liuzm@dicp.ac.cn

Keywords: HZSM-5, HSAPO-34, methanol to hydrocarbons, zeolite, mechanism

1. Introduction

As an important acid-catalyzed and shape-selective process, the methanol to hydrocarbon (MTH) reaction deactivation has made great contribution to the world chemical industry. Detailed investigation of the reaction mechanism has ignited great enthusiasm in recent years.[1,2] Nowadays the “hydrocarbon pool” (HCP) mechanism is the most acceptable one: the organic compound retained in the catalyst channels and/or intersections can act as reactive center (namely HCP species).[3]

Mechanistic studies are always performed under low temperature since capture and identification of the active and deactivating species is relatively easier under that conditions. We recently found that, at low temperature, there exist an obvious induction period over HZSM-5 and HSAPO-34 catalyst, during which sufficient amount of HCP species should be accumulated to initiate the autocatalysis reaction. Moreover, a quick deactivation behavior was observed immediately at the end of the autocatalysis reaction indicating that there may also exist an intimate relationship between the autocatalysis and deactivation stage during the whole process. Considering the different topologies, the evolution of mechanism from the autocatalysis stage to the deactivation stage maybe not the same over these two catalysts.

In the present work, methanol conversion over HZSM-5 and HSAPO-34 catalyst under low reaction temperature was both investigated. After the autocatalysis stage, a two-staged deactivation behavior over HZSM-5. While for HSAPO-34 catalyst, the increasing rate of methanol conversion was retarded before deactivation and an exponential-type deactivation behavior were clearly observed. Combined with detailed characterization, these two different reaction phenomena were clearly explained.

2. Experimental Part

Methanol conversion was performed in a fixed-bed quartz tubular reactor at atmospheric pressure. Change of the amount of retained species was in situ monitored with the intelligent gravimetric analyzer (IGA) instrument. Pore volume of the catalyst was obtained from BET analysis

3. Results and discussion

It can be seen from Figure 1 that there existed an obvious induction period for both catalysts. The methanol conversion was plotted against TOS in a logarithmic scale. For HZSM-5 catalyst, the initial two stages was clearly presented and after the very initial stage, the autocatalysis reaction can be observed—a perfect straight line before deactivation. The MTH reaction seemed to be initiated much easier over the HSAPO-34 sample. Consequently, the initial two stages was not presented and the autocatalysis stage can be observed since the very beginning of the induction reaction. It should be noted that, the increase of the methanol conversion was quite different for the HSAPO-34 catalyst. The real autocatalytic reaction can only be observed before 40 min and after that the increasing rate of methanol conversion lowered down gradually.

Although the deactivation behavior started soon after the autocatalysis stage on both catalyst, the deactivation phenomenon was quite different for the two catalysts under current conditions. For HZSM-5 catalyst, the deactivation reaction can be divided into two stages: an initial quick deactivation stage and then a slowly linear deactivation stage, during which the HZSM-5 catalyst can sustain a low but relatively stable activity even after 10 hours reaction. While for HSAPO-34 catalyst, the deactivation cure seems like an exponential function and the catalyst almost totally lost activity after 6 hours.

As is shown in Figure 2, for HZSM-5, the pore volume decreased rapidly during the autocatalysis stage. However, it is interesting to see that the pore
Figure 1. Methanol conversion as a function of time on stream (TOS) over HZSM-5 (a) and HSAPo-34 (b) catalyst.

Figure 2. Change of the catalyst volume and the amount of retained species with TOS at 270 °C for HZSM-5 (top) and HSAPo-34 (down). Volume and the amount of the retained species kept constant since the beginning of the deactivation stage. For HSAPo-34 catalyst, the changing trend was obviously different. The pore volume decreased during the autocatalysis stage and after that, the coke amount increased rapidly during the initial deactivation stage, the increasing rate of the coke amount slowed down later but the amount of retained species still increased continuously until the catalyst was completely deactivated. As a result, it can be seen that although the deactivation started suddenly and rapidly at the end of the autocatalysis reaction for both catalysts, the coking behavior seems “accelerating” for HSAPo-34 but “stopped” during the deactivation stage for HZSM-5 catalyst.

The GC-MS analysis showed that, the dominated retained species were tetramethylbenzenes (tetraMBs), and pentamethylbenzene (pentaMB) over HZSM-5 catalyst, which have been proved to be the major active HCP species. However, for HSAPo-34 catalyst, both the active and inactive species were simultaneously generated during the induction reaction and the inactive species was the major constituent which can slow down the increasing rate of methanol conversion.

From the isotopic switching experiment, it can be seen clearly that the reactivity of the retained aromatics started to decrease since the beginning of the deactivation stage and the reactivity of triMBs and tetraMBs (as the main retained species) was very low during the initial rapid deactivation stage. For HSAPo-34, the retained higher methylbenzenes were still very active and continued working to generate olefin products. However, the olefin products were difficult to diffuse out due to the reduced catalyst diffusion property. Consequently, the generation and accumulation of methyladamantanes would be accelerated in the initial deactivation stage.

4. Conclusions
The MTH induction reaction over HZSM-5 catalyst was a well-defined autocatalysis reaction while the increase of methanol conversion was retarded at the latter stage over HSAPo-34 catalyst due to the accumulation of methyladamantanes. The two-staged deactivation behavior over HZSM-5 originated from the “overloading” effect of lower methylbenzenes while the deactivation of HSAPo-34 was caused by accumulation of the inactive methyladamantanes.

References