Observation of the “Two Sides” of Hydrocarbon Pool Species during Methanol to Hydrocarbons Reaction over HZSM-5 Catalyst

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Abstract: A temperature-programmed methanol to hydrocarbon (TP-MTH) reactions were performed over HZSM-5 zeolite. With gradual increase of reaction temperature, the MTH reaction evolved from induction period with low methanol conversion to the state with 100% methanol conversion. Interestingly, after the initial reaction stage and auto-catalysis reaction stage, an unusual deactivation behavior was observed. Further investigations revealed that there exist “two sides” for the aromatic hydrocarbon pool (HCP) species and it is their “overloading” effect resulted in this phenomenon, *i.e.* despite its high intrinsic reactivity, too quick accumulation of poorly mobile methylbenzenes will lead to the occupation of most catalyst internal space and cause the deactivation .

Keywords: Methanol to hydrocarbons, Hydrocarbon pool, Overloading effect.

1. Introduction

With the change of the world energy situation, the methanol-to-hydrocarbon (MTH) process has received increasing attention as a perfect alternative for production of gasoline or basic chemicals from non-oil route. In recent years, the hydrocarbon pool (HCP) mechanism has made great contribution for understanding of the MTH reaction behaviors, according to which the real working MTH catalyst is actually the composite of the zeolite framework and the retained HCP compounds in it.[1,2] Generally speaking, the whole MTH process can be divided into three stages： induction period, high activity period and deactivation period considering the change of catalyst activity. The existence of these three stages can be reasonably understood according to the HCP mechanism.[2,3] It is the initially generation and accumulation of HCP compounds that bring about the induction period and the high activity period. After that, since the formation of enough active species, a certain amount of inactive and poorly mobile retained species and coke species will be unavoidably generated and strongly adsorb on Brønsted and Lewis acid sites and block pore entrances, leading to the final catalyst deactivation. As a result, it is traditionally accepted that, it is the active HCP species that bring about the high activity while the inactive retained species cause the final catalyst deactivation.

However, in this contribution we found that there existed “two sides” for the aromatic HCP species over HZSM-5 catalyst: despite its high intrinsic reactivity, too quick accumulation of aromatic HCP compounds will lead to the occupation of most catalyst internal space and can also cause the deactivation. This phenomenon can also be understood as the “overloading” effect of HCP species. Further study demonstrated that the “overloading” effect could be alleviated or eliminated by enhancing the catalyst diffusivity or decreasing the acid site density of the zeolite catalyst.

2. Experimental

The reactions were performed in a fixed-bed reactor, the methanol was fed by passing helium through a saturation evaporator or directly with a pump. For the TP-MTH reaction, the reaction temperature was increased at a heating rate of 0.5 °C·min^{-1}. The reaction products were analyzed by on-line gas chromatography (Agilent GC 7890A). The total amount of retained species on the catalysts was determined using TGA method. Organic compounds trapped in the catalyst were obtained by dissolving the catalyst in 1.0 mL of 15% HF and the organic phase was extracted by CH_2Cl_2. In the $^{12}C/^{13}C$-methanol switch experiments, after the reaction temperature reached predetermined time or temperature with ^{12}C-methanol, the feeding line was switched to ^{13}C-methanol for a certain period. The isotopic distribution of the materials confined in the catalyst were determined by GC-MS after extraction.

3. Results and discussion

During the whole TP-MTH reaction from low to high temperatures, four different reaction stages could be clearly observed (Figure 1 (a)): the initial reaction stage, the auto-catalysis reaction stage, the deactivation stage and the activity recovering stage. The amount of organic species deposited on catalyst firstly increased from 277 to 297 °C and then decreased when temperature was higher than 317 °C (Figure 1 (b)). As shown in Figure 1 (c), at 277 °C tetramethylbenzenes and pentamethylbenzene appeared as the first retained organics. Their amounts, especially for tetramethylbenzene, increase gradually with the rose of temperature and reached to a maximum until 297 °C.

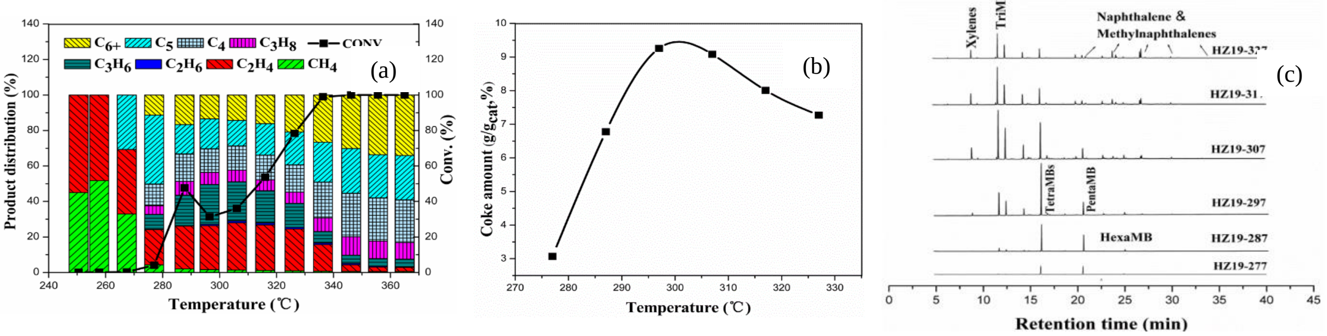

Figure 1. Methanol conversion and product distribution (a), change of total coke amount (b) and change of composition of retained species (c) as a function of temperature during the TP-MTH reaction.

To follow the reactivity change of the retained species, additional ^{12}C/^{13}C switch experiments were carried out at 287, 297 and 327 °C (one of the autocatalytic, deactivating and activity recovering points) (Table 1). In comparison, it can be seen that the active aromatic HCP compounds suddenly lost most of its reactivityt 297 °C, and xylenes and triMBs almost totally changed to inactive species. Interestingly, during the activity recovering stage (> 320 ^{o}C), all the tested retained species became active again.

Table 1. The total ^{13}C content of the retained organics and the effluent products after the ^{12}C/^{13}C switch experiment over HZSM-5 at 287, 297 and 327 °C with ^{12}C-methanol feeding during the TP-MTH reaction, followed by 1.5 min of ^{13}C-methanol feeding.

Retained Species	Xylenes	TriMBs	TetraMBs	PentaMB	HexaMB
287 ^{o}C	40.2	38.8	47	58.5	21.4
297 ^{o}C	0.55	1.15	12.76	48.66	29.60
327 ^{o}C	45.73	47.82	59.97	60.39	27.66

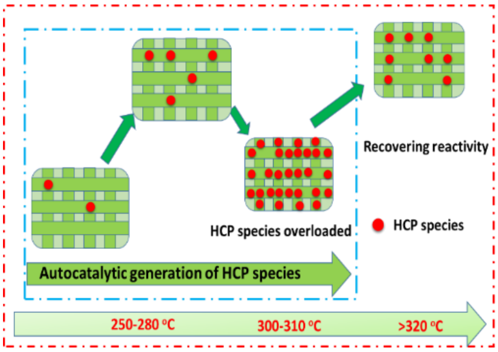

Figure 2. Illustration of the HCP species "overloading" effect.

4. Conclusions

Taking all the analysis above into consideration, we propose an assumption that there may exist an "overloading" effect for the HCP species. As illustrated in Figure 2, after generation of initial HCP species, more HCP species will be generated in an autocatalytic way. When adequate amount of HCP compounds were accumulated, they can act as reactive centers and accelerate the MTH reaction. However, due to the too rapid generation of aromatic species and the poor diffusivity of primary olefins at relatively low temperature, too many poorly mobile compounds would be generated, retain and occupy most of the catalyst internal space and thereafter, cause the following deactivation behavior.

References

1. I. M. Dahl and S. Kolboe, J Catal. 149 (1994), 458-464.
2. P. Tian, Y. X. Wei, M. Ye and Z. M. Liu, Acs Catal, 5, (2015), 1922-1938.
3. J. F. Haw, W. G. Song, D. M. Marcus and J. B. Nicholas, Accounts Chem Res, 36, (2003), 317-326.