Catalysis Today 164 (2011) 288–292

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Conversion of methanol over H-ZSM-22: The reaction mechanism and deactivation☆

Jinzhe Li, Yingxu Wei, Yue Qi, Peng Tian, Bing Li, Yanli He, Fuxiang Chang, Xinde Sun, Zhongmin Liu*

National Engineering Laboratory for Methanol to Olefins, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, PR China

ARTICLE INFO

Article history:
Received 1 July 2010
Received in revised form 21 October 2010
Accepted 21 October 2010
Available online 4 December 2010

Keywords:
ZSM-22
Methanol
Methylation
Propene
Ethene
MTO

ABSTRACT

Conversion of methanol to olefins (MTO) over H-ZSM-22 was carried out in the pulse and the continuous-flow reaction systems. ^{13}C labeling technique was used to reveal the reaction mechanism. The materials retained in the deactivated catalyst were detected by GC–MS after dissolving the catalyst framework and then extracting the organic species. The adsorption of these materials in ZSM-22 channels was computationally modeled. The results showed that the olefin methylation-cracking mechanism is the main route for the conversion of methanol over H-ZSM-22. It was suggested that the blockage of the zeolite pore openings by the coke species might be the reason of the relatively rapid deactivation of H-ZSM-22, instead of the prohibition of the formation of large transition-state intermediates involved in hydrocarbon pool mechanism.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Methanol is an important platform product of coal chemistry. Light olefins can be obtained by conversion of methanol over acidic zeolite catalysts through the process known as MTO (methanol-to-olefins). Considerable effort has been devoted to the optimization of the catalyst performance and process conditions [1–3]. In parallel with that, numerous research works have been done to elucidate the reaction mechanism of MTO conversion [4–7] and more than 20 mechanisms have been proposed by different researchers [1]. Among the proposed mechanisms, the hydrocarbon pool mechanism attracted much more attention, which is an indirect mechanism and first proposed by Kolboe and co-workers based on the experiments of the MTO conversion over SAPO-34 [8–10]. According to the hydrocarbon pool mechanism, the reaction cycle involved the methylation of "hydrocarbon pool intermediates" confined in the cages of SAPO-34 by methanol and subsequent elimination of ethylene, propene, and butenes from the intermediates. Later, detailed studies revealed that the polymethylbenzenes composed largest part of the materials retained in the catalyst and that hexamethylbenzene was the most active species for methanol to olefin conversion [11–13]. Haw et al. proposed that the conversion of methanol over ZSM-5 also follows the hydrocarbon pool mechanism [14,15], which was supported by Hunger and co-workers [16,17]. Furthermore, Cui et al. [18] reported that the MTO conversion could only take place on zeolites that allow the hydrocarbon pool mechanism to work, and that due to the transition-state shape selectivity, MTO conversion over ZSM-22 (a zeolite which has one-dimensional channel with 10-member ring opening) could only produce dimethylether as the product. They also found that ZSM-22 displayed a low but appreciable production of olefins at the beginning of methanol conversion, but they believed that it was the result of the impurity phase (ZSM-11) and/or the external acid sites [18].

However, Svelle and Bjorgen [19,20] pointed out that over ZSM-5, ethene and propene maybe produced through dual-cyclic reaction route. Ethene was formed through the hydrocarbon pool mechanism with lower methylated benzene as reactive intermediates, and apart from that, the olefin methylation-cracking cycle was also an effective route for the formation of propene, butenes and higher olefins. This suggests that if the reactions following the hydrocarbon pool mechanism were suppressed, methanol might be converted into olefins through the methylation-cracking route. In fact, our previous work presents a positive result of methylation-cracking route in methanol conversion over ZSM-22. Nearly complete conversion of methanol could be obtained over ZSM-22 at 450 °C (WHSV = 10 h^{-1}) [21]. In a very recent report from the group of Olsbye [22], they also found that under suitable conditions ZSM-22 has a conversion capacity comparable to that of SAPO-34. These results have been somewhat contradictive with the report of Cui et al. [18].

☆ Student Award Paper.

* Corresponding author. Tel.: +86 411 84685510; fax: +86 411 84691570.
E-mail address: liuzm@dicp.ac.cn (Z. Liu).

0920-5861/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2010.10.095

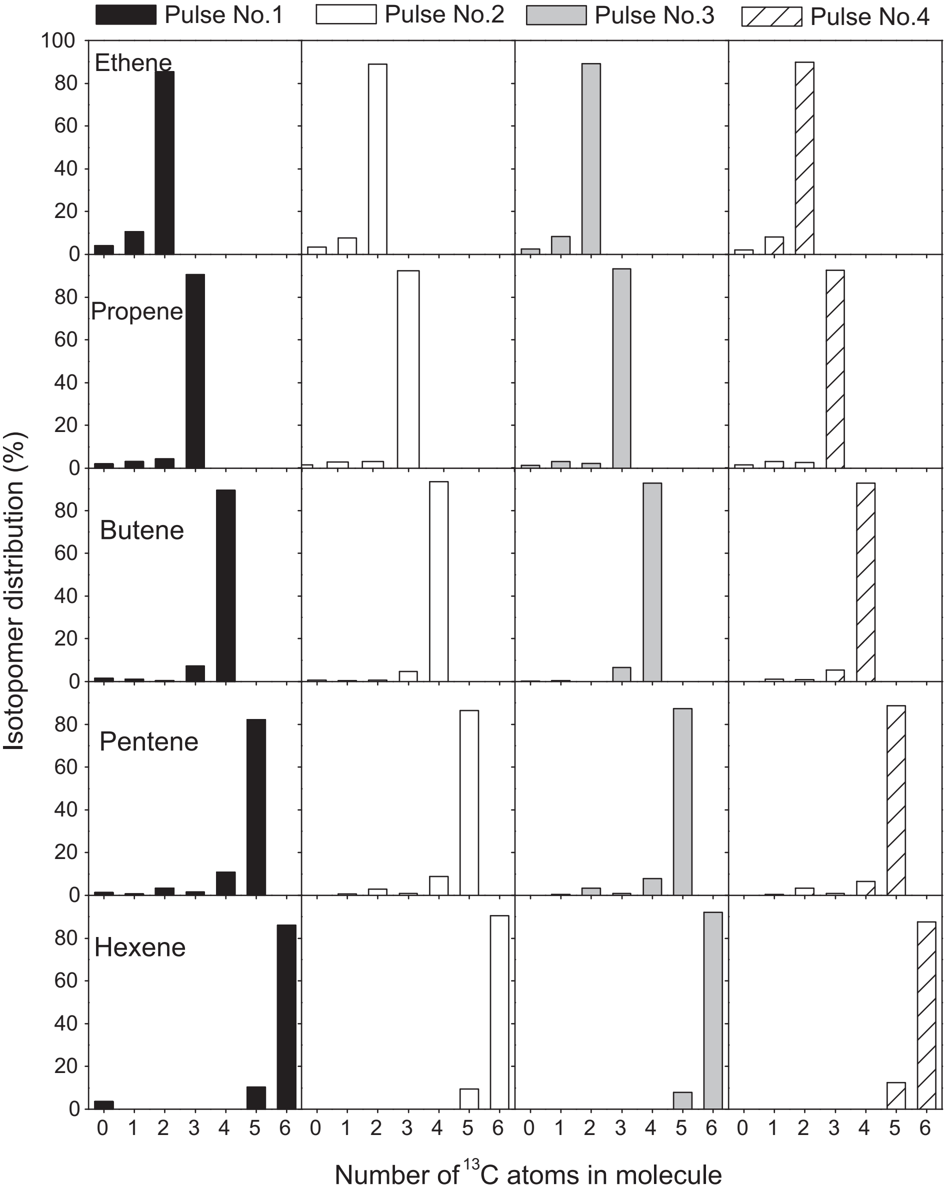

Fig. 1. Isotopic distribution in the effluent products of successive ^{13}C-methanol pulse reaction over ZSM-22 at 450 °C after the pre-reaction of 15 pulses of ^{12}C-methanol, CT = 0.08 s.

In the present study, methanol conversion over ZSM-22 was carried out in the pulse and continuous-flow reaction systems. The reaction mechanism over ZSM-22 was elucidated by the aid of ^{13}C labeling technique. It was demonstrated that the methanol could be converted into olefins over ZSM-22 through olefin methylation and cracking route. The blockage of the channel openings by coke species was proved to be the main reason for the low efficiency of methanol conversion over ZSM-22, instead of the prohibition of hydrocarbon pool species formation associated with the transition-state shape selectivity.

2. Experimental

2.1. Catalyst preparation and characterization

The sample of ZSM-22 (SiO_2/Al_2O_3 = 69) was kindly provided by another research group of Dalian Institute of Chemical Physics. The NH_4-ZSM-22 was obtained by ion-exchanging the calcined solid with the solution of ammonium nitrate. After the ion-exchange, the sample was washed with deionized water, dried at 110 °C and finally calcined at 550 °C for 4 h to achieve H-ZSM-22.

The crystallinity and phase purity of the samples was characterized by powder X-ray diffraction (RIGAKU D/max-rb powder diffractometer) with Cu K_α radiation.

The acidity of the catalysts was determined by temperature programmed desorption of ammonia (NH_3-TPD). A catalyst sample of 0.14 g was loaded into a U-shaped micro-reactor and pre-treated at 650 °C for 30 min in a flow of helium. After the pre-treatment, the sample was cooled to 100 °C and saturated with ammonia. The temperature was increased from 100 to 600 °C at a constant heating rate of 10 °C/min under a He flow of 40 ml/min. The concentration of ammonia in the exit gas was monitored continuously with a TCD detector.

2.2. Methanol conversion

Methanol conversion was performed in a fixed-bed quartz tubular reactor at atmospheric pressure. In the pulse reactions, a catalyst

Download English Version:

https://daneshyari.com/en/article/56338

Download Persian Version:

https://daneshyari.com/article/56338

Daneshyari.com