Catalysis Today 171 (2011) 221–228

Contents lists available at ScienceDirect

Catalysis Today

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

Comparative study of MTO conversion over SAPO-34, H-ZSM-5 and H-ZSM-22: Correlating catalytic performance and reaction mechanism to zeolite topology

Jinzhe Li, Yingxu Wei, Guangyu Liu, Yue Qi, Peng Tian, Bing Li, Yanli He, 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 30 October 2010
Received in revised form 20 February 2011
Accepted 23 February 2011
Available online 30 March 2011

Keywords:
ZSM-22
Methanol
Ethene
Propene
MTO

ABSTRACT

Conversion of methanol to olefins (MTO) was comparatively studied over three zeolites with different topologies, *i.e.* SAPO-34, H-ZSM-5 and H-ZSM-22. The correlation between reaction mechanism and the zeolite topology was also investigated. SAPO-34 presented the highest selectivity for light olefins such as ethene and propene, and no aromatics were detected. H-ZSM-5 showed relatively high selectivity for ethene and propene, and large amount of aromatics were detected. Over H-ZSM-22, the selectivity for ethene is very low and a large amount of non-aromatic $C_6{}^+$ olefins generated. With the aid of ^{12}C-methanol/^{13}C-methanol switch technique, the reaction routes followed by methanol conversion over the three catalysts could be distinguished. The reaction mechanisms, which varied with the zeolite topologies, caused the differences in catalytic performances. The co-reaction of ^{13}C-methanol with ^{12}C-olefin or ^{12}C-aromatic, were carried out for further clarification of the operation of the different catalytic cycles in methanol conversion.

1. Introduction

Methanol-to-olefins (MTO) conversion is a very important process for the production of light olefins, such as ethene and propene, from alternative and abundant resources of natural gas or coal. Considerable effort has been devoted to the improvement of the catalyst performances and the process development [1–3]. Recently, the world's first commercial MTO unit, with a production capacity of 600,000 tons of lower olefins per year, was proved to be completely successful in its first commissioning operation [4]. In parallel with the process development, numerous research works have been done to elucidate the reaction mechanism of MTO conversion [5–8] and more than 20 mechanisms have been proposed by different researchers [1]. Among the proposed mechanisms, an indirect mechanism, hydrocarbon pool mechanism, which was firstly proposed by Kolboe and co-workers based on the experiments of the MTO conversion over SAPO-34 (CHA type: containing large cages and narrow 8-member ring openings [9]), attracted much more attention [10–12]. 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 ethene, 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 [13–15]. Haw and co-workers proposed that the conversion of methanol over ZSM-5 (MFI type: containing crossed 10-member ring channels and channel intersections [9]) also follows the hydrocarbon pool mechanism [16,17], which was supported by Hunger and co-workers [18,19].

Furthermore, a work by Cui and co-workers [20] 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 (TON type: one-dimensional channels with 10-member ring openings [9]) 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 the initial conversion resulted from the impurity phase (ZSM-11) and/or the external acid sites [20].

However, hydrocarbon pool mechanism might not be the only one that MTO reactions follow. Because the olefins were the main products of this reaction and the olefins methylation or cracking reactions over zeolite catalysts have been suggested and proved by several research groups [21–23], methanol might be converted to olefins through the mechanism other than aromatic based hydrocarbon pool mechanism, *i.e.* the olefin methylation-cracking reaction cycle. In fact, over H-ZSM-5, Svelle and Bjorgen [24,25] have found that the reaction proceeded through dual-cyclic reaction cycle. Ethene was formed through the reaction route following hydrocarbon pool mechanism with lower methylated benzene as reactive intermediates, and apart from that, the olefin methylation-cracking cycle was responsible for the formation of

---

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

0920-5861/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2011.02.027

propene, butenes and higher olefins. This suggests that if the hydrocarbon pool mechanism were suppressed, methanol conversion over H-ZSM-22 might proceed through the methylation-cracking route. Our previous work on the methanol conversion over H-ZSM-22 showed that nearly complete conversion of methanol could be obtained over H-ZSM-22 at 450 °C (WHSV = 10 h^{-1}) [26]. In a report from the group of Olsbye [27], they also found that under suitable conditions H-ZSM-22 has the conversion capacity comparable to that of SAPO-34. These results have been somewhat contradictive with the report of Cui et al. [20]. Further study on the MTO reaction over H-ZSM-22 is necessary, especially on the reaction mechanism. Just before the submission of our manuscript, a paper focused on the reaction mechanism over H-ZSM-22 has been published by Olsbye and co-workers [28].

In the present study, methanol conversion over H-ZSM-22 was studied with ^{13}C labeling technique with the comparison of that over H-ZSM-5 and SAPO-34 under the identical reaction conditions. To clarify the role of the two catalytic cycles (mentioned by Svelle and Bjorgen [24,25]) in methanol conversion over these three zeolites with different topology, the co-reaction of ^{13}C-methanol and unlabeled olefin/aromatic were also studied.

2. Experimental

2.1. Catalyst preparation

SAPO-34 was synthesized hydrothermally using triethylamine as the template [29–32]. Pseudoboehmite, orthophosphoric acid and colloidal silica were used as the sources of aluminum, phosphorus and silicon, respectively. The chemical compositions of starting gels were 1.0 Al_2O_3: 1.0 P_2O_5: 0.6 SiO_2: 3 NEt_3: 50 H_2O, which were prepared as follows. Pseudoboehmite was added to vigorously stirred water in a glass beaker and then phosphoric acid was added. After stirring for a determined time, colloidal silica was added to this mixture, which was then stirred for a further half hour before triethylamine was added. The resulting gel was then transferred to a Teflon-lined stainless steel autoclave. The crystallization was carried out at 200 °C under autogenously pressure. The H-SAPO-34 was obtained by the calcination of the crystallized products at 550 °C for 4 h.

ZSM-5 (SiO_2/Al_2O_3 = 95) was purchased from Nanda Catalyst Co., Ltd. The protonic form ZSM-5 was obtained by calcination of the ammonium form sample at 550 °C for 4 h. The sample of ZSM-22 (SiO_2/Al_2O_3 = 69) was kindly provided by another 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.

2.2. Characterization

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.

2.3. Methanol conversion

Methanol conversion was performed in a fixed-bed quartz tubular reactor at atmospheric pressure. For pulse reactions, a catalyst sample of 45 mg (60–80 mesh) was loaded into the reactor. The reactor was heated to reaction temperature and maintained for 1 h before reaction. Then an injection of methanol of 1 μL was conducted onto the catalyst, and the effluent was kept warm and analyzed by online gas chromatography (Varian GC3800) equipped with a PoraPLOT Q-HT capillary column and a FID detector. In the ^{13}C labeling experiments, pre-reaction of 15 pulses of ^{12}C-methanol was performed and that was followed by successive pulses of ^{13}C-methanol. The effluent products of each ^{13}C-methanol pulse reaction were collected and analyzed by Agilent 6890/5973N MSD GC–MS. For the co-reaction of ^{13}C-methanol and unlabeled olefin/aromatic, only one pulse of reactants mixture was injected onto the catalyst bed at 450 °C and then the effluent was analyzed by GC-MS. The molar ratio of ^{13}C-methanol to unlabeled reactant was 20. In the co-reaction of ^{13}C-methanol and butene, 1-butanol was used as the reactant which was easily converted into butene in situ.

3. Results and discussion

MTO conversions over different type of zeolites were performed on the pulse reaction system using ^{13}C labeling technique and the results were displayed in Tables 1–3 and Figs. 1–4. For comparison, all the reactions were carried out at 450 °C with reactant-catalyst contact time of 0.08 s. The conversion in the context was referred to the percent of methanol which were converted into hydrocarbons, that is to say, dimethylether was also considered as reactant in the following discussion.

In Table 1, when the first methanol injection was conducted onto SAPO-34 catalyst, the methanol conversion was 40.4%. After 15 injections of methanol, the conversion increased to 91.6%. This presented the performance difference in the induction period and steady-state period of MTO over SAPO-34. It is interesting to

Table 1
Methanol conversion and product selectivity of MTO over SAPO-34.

Pulse number	Conversion (%)	Selectivity (C%)							
	CH_3OH	C_1^0	$C_2^=$	C_2^0	$C_3^=$	C_3^0	C_4	C_5	C_6^+
1	40.4	3.5	6.6	0.0	60.8	1.3	15.6	7.6	4.7
15	91.6	0.8	26.8	0.2	42.4	6.8	16.0	5.8	1.2
19	96.0	0.8	27.3	0.2	44.1	4.0	16.0	6.3	1.4

Table 2
Methanol conversion and product selectivity of MTO over ZSM-5.

Pulse number	Conversion (%)	Selectivity (C%)							
	CH_3OH	C_1^0	$C_2^=$	C_2^0	$C_3^=$	C_3^0	C_4	C_5	C_6^+
1	76.0	1.8	8.4	0.0	37.3	1.4	15.4	11.1	24.6
15	82.5	2.2	10.8	0.1	36.2	1.2	14.9	8.6	26.0
19	78.5	2.0	9.1	0.1	37.1	1.1	14.5	10.6	25.5

Table 3
Methanol conversion and product selectivity of MTO over ZSM-22.

Pulse number	Conversion (%)	Selectivity (C%)							
	CH_3OH	C_1^0	$C_2^=$	C_2^0	$C_3^=$	C_3^0	C_4	C_5	C_6^+
1	76.5	2.3	3.7	0.4	22.3	3.4	17.2	28.6	22.1
2	66.8	1.8	3.0	0.3	20.2	3.9	16.9	28.4	25.5
5	63.7	2.1	3.0	0.3	19.6	3.4	16.3	28.7	26.6
15	53.7	2.5	3.0	0.3	19.3	3.2	15.8	27.8	28.1
19	40.4	3.3	3.0	0.2	20.0	2.7	15.7	27.8	27.3