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Methane formation route in the conversion of methanol to hydrocarbons

Wenping Zhao, Baozhu Zhang, Guiru Wang, Hongchen Guo*

Department of Catalytic Chemistry and Engineering, State Key Laboratory of Fine Chemicals,
Dalian University of Technology, Dalian 116024, Liaoning, China

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Abstract

The influence factors and paths of methane formation during methanol to hydrocarbons (MTH) reaction were studied experimentally and thermodynamically. The fixed-bed reaction results show that the formation of methane was favored by not only high temperature, but also high feed velocity, low pressure, as well as weak acid sites dominated on deactivated catalyst. The thermodynamic analysis results indicate that methane would be formed via the decomposition reactions of methanol and DME, and the hydrogenolysis reactions of methanol and DME. The decomposition reactions are thermal chemistry processes and easily occurred at high temperature. However, they are influenced by catalyst and reaction conditions through DME intermediate. By contrast, the hydrogenolysis reactions belong to catalytic processes. Parallel experiments suggest that, in real MTH reactions, the hydrogenolysis reactions should be mainly enabled by surface active H atom which might come from hydrogen transfer reactions such as aromatization. But H_2 will be involved if the catalyst has active components like NiO.

Key words
methane; methanol to hydrocarbons; decomposition; hydrogenolysis; thermodynamic analysis

1. Introduction

Methanol has played a significant role for a long time in converting carbon source into useful chemicals and liquid fuels [1]. Recently, the conversions of methanol to hydrocarbons (MTH) have attracted increasing industrial and academic attentions because that methanol can be easily produced from coal, natural gas and biomass, and that MTH process developing is one of the good ways to protect environment and energy security [2].

So far, several MTH processes have been known, including methanol to gasoline (MTG), olefins (MTO), propylene (MTP) and aromatics (MTA). MTG reaction over high silica ZSM-5 zeolite was discovered by Mobil Research Laboratories in 1970s, which was first commercialized in New Zealand in 1985 [3,4], and a new 100 kt/y demonstration plant was brought on stream in Shanxi province, China in 2009 [5]. Most recently, Topsøe integrated gasoline synthesis process based on biomass gasification has been announced for demonstration in USA [6]. A semi-commercial MTO demonstration unit was brought on-stream in Feluy, Belgium in 2009 [7]. The first MTO commercial unit based on DMTO process (600 kt/y) was started in Baotou, China in 2010 [8]. More commercial MTO units have been announced since then. MTP technology was developed by Lurgi and the first MTP plant with an annual capacity of 500 kt/y (propylene) was established in China in 2010 [9,10].

A great deal of academic work has been done on these MTH processes. The primary emphases of these work have been given to reaction mechanism, the stability of catalyst, as well as the selectivities to main products [11−17]. It is well-known that the reaction conditions and zeolitic catalysts (e.g., crystal structure, acidity and crystal size) have remarkable influence on MTH conversion [18−20]. So far, SAPO-34 molecular sieve catalyst and fluid bed technology have been developed for MTO process, while ZSM-5 zeolite catalyst and fixed bed technology have been developed for MTP and MTG processes [2,11,13]. Besides MTA processes based on both fluid bed and fixed bed technologies, ZSM-5 zeolite catalyst were also announced [21−23].

In spite of these efforts, there are still some questions need to be clarified, such as the paths and influence factors of methane formation. Methane was once suggested as the reaction product of surface methoxy species abstracting a hydride from methanol [24]. Later, it was inferred that the surface methoxy species might abstract a hydride from hydrocarbon products to form methane [25,26]. These reports have similarity in that the hydride donors are gaseous molecules while

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* Corresponding author. Tel: +86-411-84986120; Fax: +86-411-84986120; E-mail: hongchenguo@163.com

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the hydride acceptor is surface methoxy species. On the other hand, Schulz recently reported that methane was formed by the hydride transfer of unsaturated compounds such as ionic olefins or coke with methanol [27]. In this case, the hydride donors are surface species while the hydride acceptor is gaseous molecule. That is, the formation of methane would be related to catalyst coking deactivation. Beside, methane was also considered as the product of the dealkylation of methy benzenes [28], and the product of the joint decomposition reaction of methanol and DME [29]. It is obvious that the formation path of methane in MTH processes has not been well understood so far. In addition, the influence factors of methane formation during MTH reactions were seldom reported. Therefore, the present work was focused on investigating the influence factors and the routes of methane formation in MTH conversion by means of experimental and thermodynamic analysis.

2. Experimental

Nano-ZSM-5 zeolite powder (commercial product, $SiO_2/Al_2O_3 = 29$, 20~50 nm) was synthesized with N-butylamine as structure directing agent [30] and was extruded with alumina binder before being subjected to the conventional ammonium ion-exchange to obtain nano-HZSM-5 catalyst. Nano-HZSM-5 was further modified by incipient wetness impregnation of $NaNO_3$ solution, and the modified nano-HZSM-5 catalysts were donated as x%Na-HZSM-5 (x% means weight percentage of Na in catalyst). In addition, γ-Al_2O_3 and Ni modified γ-Al_2O_3 (0.5 wt% Ni) were used as reference catalysts. γ-Al_2O_3 catalyst was prepared according to literature [31]. Ni modified γ-Al_2O_3 catalyst (denoted as 0.5% Ni-γ-Al_2O_3) was prepared by impregnation with $Ni(NO_3)_2$ solution, which was in situ reduced with H_2 (flow rate of 30 mL/min) at 723 K for 10 h before use.

The acidity of catalysts was evaluated using ammonia temperature-programmed desorption (NH_3-TPD) method on Quantachrome Chembet 3000 chemisorb instrument. The sample (140 mg) was firstly pretreated at 600 °C for 1 h in He flow (20 mL/min), then cooled down to 150 °C, and saturated with NH_3 for 30 min. Subsequently, the sample was purged by He flow for 1 h at 150 °C. Finally, the TPD profile was recorded while the sample was heated from 150 °C to 600 °C with a constant heating rate of 14 °C/min in He flow.

MTH reaction experiment of methanol was carried out in a 10 mm-id small-scale fixed-bed reactor, the catalyst loading was 2.0 g for each run. The reactor effluents were collected into oleic phase, aqueous phase and gaseous phase, which were weighed and analyzed by three offline gas chromatographs for mass balance calculation: a Shimadzu GC-2014C (OV-1 capillary column, 50 m×0.2 mm×0.2 μm, FID detector) for oleic phase, a domestic GC SP-6800A (PEG-20M capillary column, 30 m×0.32 mm×0.5 μm, FID detector) for aqueous phase and a domestic GC-7890F (PLOT Al_2O_3 capillary column 50 m×0.53 mm×25 μm, FID detector and 60~80 mesh-TDX-01 packed column, 1.5 m×2 mm, TCD detector) for gaseous phase, respectively.

The thermodynamic analysis was carried out with the Matlab software program from 300 °C to 500 °C to calculate the Gibbs free energy changes ($G_r(T)$) and the thermodynamic equilibrium constants ($K_p(T)$) of concerned reactions. The standard thermodynamic data of all involved substances at 298.15 K were taken from chemical handbook [32].

3. Results and discussion

3.1. Methane formation over HZSM-5 zeolite catalyst

3.1.1. Effects of reaction conditions

The effects of reaction temperature, reaction pressure and feed space velocity (weight hourly space velocity (WHSV)) on MTH reaction were investigated with nano-HZSM-5. All the data were obtained at TOS (time on stream) = 50 h during continuous fixed bed operation. Figure 1 shows that the formation of methane was favored by high reaction temperature. Figure 2 shows that the formation of methane was favored at low reaction pressure and high feed space velocity. At these conditions, there was always a low hydrocarbons (C_{2+}) selectivity. The dependence of methane formation on reaction pressure and feed velocity revealed that the formation route of methane competes with MTH reactions.

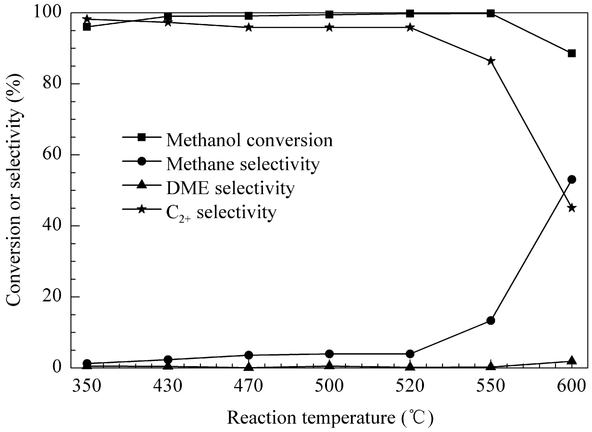

Figure 1. Effect of reaction temperature on methanol conversion and product selectivity (0.1 MPa, WHSV = 1.0 h^{-1}, TOS = 50 h)

3.1.2. Effects of catalyst acidity

The effect of catalyst acidity on methanol conversion and methane selectivity during MTH reaction was studied with Na^+ modified nano-HZSM-5 zeolite (x%Na-HZSM-5) under the conditions of 500 °C, 0.1 MPa, WHSV = 1.0 h^{-1} and TOS = 50 h. Figure 3 shows that, with the increase of Na content (x = 0.5, 1.0, 1.5, 2.0 wt%), the strong acid sites (corresponding to high temperature peak of NH_3-TPD) of catalyst decreased gradually. At the same time, an increase in the intensity of low temperature peak of NH_3-TPD could also be observed. It means that the weak acid sites of catalyst (related to loaded Na^+) increased to some extent.