Research Article

Deoxygenation of Methanol over ZSM-5 in a High-Pressure Catalytic Pyroprobe

Deoxygenation is a critical step in making hydrocarbon-rich biofuels from biomass constituents. Although the thermal effects of oxygenate aromatization have been widely reported, the effect of pressure on this critical reaction has not yet been closely investigated, one primary reason being the unavailability of a reactor that can pyrolyze oxygenates, especially those in solid form, under pressurized conditions. Here, the first of a series of studies on how oxygenates behave when catalytically pyrolyzed under elevated pressure and temperature conditions is reported. Methanol, the simplest alcohol, was selected as the candidate to study the chemical phenomena that occur under pressurized catalytic pyrolysis. The reactions were carried out over the shape-selective catalyst ZSM-5 (SiO$_2$/Al$_2$O$_3$ = 30) under varying pressure (0 to 2.0684 MPa (300 psi) in 0.3447 MPa (50 psi) increments) and temperature (500 to 800 °C in 50 °C increments) conditions. Benzene, toluene, ethyl benzene, and xylenes (BTEX) were analyzed as the deoxygenated products of the reaction. The results indicate that the reactor pressure significantly affects deoxygenated product composition.

Keywords: Catalysis, Gasoline, High-pressure catalytic pyroprobe, Methanol, ZSM-5

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1 Introduction

The interest on methanol to aromatic conversion has steadily grown since its accidental discovery in 1977 by Silvestry and Chang in Mobil Oil Company [1]. They reported that a shape-selective zeolite can catalyze the conversion of oxygenates to hydrocarbons. Since then, there has been a significant interest in studying the associated chemistry to optimize hydrocarbon yields [2].

Methanol can be considered as an economical feedstock for hydrocarbon production as it can be produced from natural gas in two easy steps. In the first step, methane is converted to CO and H$_2$ (syngas) and then in the second, the syngas is sent over a catalyst such as Cu/ZnO/Al$_2$O$_3$ to form methanol. When methane is obtained via biogenic means, methanol and methanol-based products are considered biorenewable.

There are two key processes that convert methanol to hydrocarbons: (a) the methanol-to-olefins (MTO) process and (b) the methanol-to-gasoline (MTG) process [3]. Olefins such as ethylene and propylene are polymer precursors with high industrial significance. For the MTO process, different catalysts such as ZSM-5, SAPO-34, and mordenite have been successfully used [4–7]. With the increasing demand for higher-quality motor fuels via cheaper and more environmentally friendly pathways, the MTG process has proven to be a potential alternative to produce synthetic gasoline [2]. Although most of the industrial-scale production of motor fuel is yet petroleum-based, the use of methanol as a feedstock for fuel production would lessen the impact on environment. However, due to unfavorable process economics, the MTG process is not yet widely adopted for industrial-scale gasoline production. There exist only a few operational plants worldwide (e.g., in New Zealand).

The reaction mechanism of the methanol-to-hydrocarbon process has not yet been completely resolved. In an earlier simplified version of the reaction mechanism as given in Fig. 1, methanol is dehydrated to form dimethyl ether (DME) and water [8]. From this intermediate mixture of oxygenates, alkenes are said to be produced. This explanation has led to a long-standing disagreement as to how the first C–C bond is formed from the intermediates [9]. According to the early work done by Chang and Silvestri, a carbine-like intermediate is produced by the α-elimination process that involves Brønsted acid sites and base sites [1, 10]. A more recent widely accepted idea is the hydrocarbon pool mechanism which was formulated in the early 1990s. The hydrocarbon pool is...
described as a catalytic scaffold with organic molecules adsorbed onto the zeolite structure acting as cocatalysts inside the zeolite pores [11]. When methanol is added to the system, alkenes and water are produced in a closed cycle where high-energy intermediates are avoided.

With the renewed interest on the MTG process, more attention has been given to improving the performance of the catalyst. Catalyst performance can be affected by a number of parameters such as the acid strength, acid site density, catalyst topology, crystallite size, etc. [12–14]. According to some studies, the product selectivity and yield can be improved by the presence of a metal/metal-oxide on the catalyst [13, 15]. A number of studies are related to the effect of metal loading (primarily transition metals) on ZSM-5. The common consensus is that the metals help in bond cleavage while aromatization takes place in the Brønsted acid sites of the zeolite [10]. It has been clearly demonstrated that lower Si/Al ratios tend to favor aromatization while 30–40 % are described as optimum. Also more than 10 % metal loading is highly discouraging since higher metal loadings consume the acid sites available for aromatization.

In addition to the catalyst modification, reaction parameters such as temperature and pressure can be used to investigate changes in the aromatic product distribution. For example, it is well known that the increase in pressure enhances the surface adsorption of gas molecules. Yet, the effect of pressure has not been reported with respect to the MTG process, most likely due to technical challenges associated with the high-pressure systems. The MTG reaction has been conducted at elevated pressures with a uniquely configured high-pressure pyroporbe reactor. In this study, we specifically explored the effect of pressure on the selectivity of aromatic products of the MTG process that include benzene, toluene, ethylbenzene, and xylenes (BTEX).

### 2 Experiments

The experiment was performed using the high-pressure CDS Pyroprobe 5200 (CDS analytical, Oxford, PA, USA). A sample of 0.5 μL methanol (Sigma Aldridge, St. Louis, MO, USA) was injected into a one-inch long micro quartz tube filled with quartz wool. The exit end of the tube was filled with 5 mg of the catalyst ZSM-5 (SiO₂/Al₂O₃ = 30) (Zeolyst International, Conshohocken, PA, USA). The micro quartz tube was tightly packed with quartz wool to prevent methanol vapor escaping from the inlet end.

The catalyst used was ground and sieved using a 400-μm sieve. The quartz tube with the sample was placed in the probe’s filament where the sample was heated at different temperatures ranging from 500 to 800 °C in 50 °C increments. The probe’s filament was fired for 20 s and then the products generated were purged through a Tenax adsorbent gas trap for 1 min. The reactor pressure was controlled by a backpressure regulator from 0 to 2.0684 MPa (300 psi) in 0.3 MPa (50 psi) increments. A steady helium flow rate of 30 mL min⁻¹ was maintained in the reactor.

Following the adsorption run, the products were desorbed by purging the trap with gas chromatography (GC) carrier gas (helium) at 300 °C into the GC inlet. The desorption of the trap and starting of the GC-mass spectrometer (MS) were automatically synchronized. The GC-MS analysis was performed using an Agilent 7890 GC coupled with an Agilent 5890 MS detector (Agilent Technologies, Santa Clara, CA, USA). The column used for MS analysis was HP-5ms (30 m, 0.25 mm OD, 0.25 μm ID). For quantitative analysis a flame ionization detector (FID) was used with a DBWAX (30 m, 0.25 mm OD, 0.25 μm ID) column.

\[
2 \text{CH}_3\text{OH} \rightarrow \text{C}_6\text{H}_4 + \text{C}_7\text{H}_8 + \text{C}_8\text{H}_{10} + 11 \text{H}_2 \quad (1)
\]

The products that were detected in the reaction can be put into a stoichiometric form as represented in Eq. (1). Methanol conversion was calculated according to Eq. (2) where \(N_0\) is the total number of methanol moles fed into the sample tube and \(N_i\) is the number of unreached methanol moles which was measured from the chromatogram. Selectivity of the catalytic reaction toward BTEX was calculated considering the carbon balance. The selectivity was calculated according to Eq. (3) given below where \(N_i\) is the number of moles of the \(i\)th product and \(n_i\) is the number of carbon atoms in that respective compound.

\[
\text{Methanol conversion } (X_{\text{MetOH}}) = \frac{(N_0 - N_i)}{N_0} \quad (2)
\]

\[
\text{Selectivity of products } = n_iN_i/(\sum n_iN_i) \quad (3)
\]

The effect of pressure on coke formation was studied using a thermogravimetric analyzer (TGA; TA Instruments, New Castle, DE, USA). Samples from 0, 0.6894 (100), and 1.3789 MPa (200 psi) runs were used for this study. Each sample was heated in an air stream at a rate of 10 °C min⁻¹ up to 1000 °C. Samples were run in random order in a full factorial design. Results were analyzed at \(a = 0.05\) significance level using the Design-Expert software (Stat-Ease, Inc., Minneapolis, MN, USA). The response surface method was used to best describe the behavior of the data points. The surfaces were generated approximating the response (e.g., conversion, selectivity) to a quadratic polynomial of temperature (T) and pressure (P). The coefficients for the respective surfaces are given in Tab. 1.
The polynomial for the respective surfaces can be represented as a function of temperature (Table 1).

### Table 1. Coefficients of the polynomials representing the response surfaces.

<table>
<thead>
<tr>
<th>Coefficients</th>
<th>Methanol</th>
<th>Benzene</th>
<th>Toluene</th>
<th>Ethylbenzene</th>
<th>Xylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_0$</td>
<td>$+69.62413 \pm 1.61$</td>
<td>$+20.73756 \pm 0.72$</td>
<td>$-22.64308 \pm 0.43$</td>
<td>$+21.76454 \pm 0.36$</td>
<td>$+48.60725 \pm 1.74$</td>
</tr>
<tr>
<td>$C_1$</td>
<td>$+0.035630 \pm 1.26$</td>
<td>$-0.064909 \pm 0.56$</td>
<td>$+0.097496 \pm 0.34$</td>
<td>$-0.047865 \pm 0.28$</td>
<td>$+0.13801 \pm 1.36$</td>
</tr>
<tr>
<td>$C_2$</td>
<td>$-19.68451 \pm 1.26$</td>
<td>$-3.75414 \pm 0.56$</td>
<td>$+2.30741 \pm 0.34$</td>
<td>$-4.91295 \pm 0.28$</td>
<td>$-18.18425 \pm 1.36$</td>
</tr>
<tr>
<td>$C_3$</td>
<td>$-0.016617 \pm 1.90$</td>
<td>$+0.018556 \pm 0.84$</td>
<td>$+0.014503 \pm 0.50$</td>
<td>$+1.48641 \cdot 10^{-5} \pm 0.43$</td>
<td>$+0.012322 \pm 2.05$</td>
</tr>
<tr>
<td>$C_4$</td>
<td>$-1.45730 \cdot 10^{-3} \pm 2.19$</td>
<td>$+6.46774 \cdot 10^{-3} \pm 0.97$</td>
<td>$-7.00721 \cdot 10^{-5} \pm 0.58$</td>
<td>$+3.22819 \cdot 10^{-5} \pm 0.49$</td>
<td>$-1.40266 \cdot 10^{-4} \pm 2.36$</td>
</tr>
<tr>
<td>$C_5$</td>
<td>$+14.98558 \pm 2.19$</td>
<td>$-3.85812 \pm 0.97$</td>
<td>$-4.79596 \pm 0.58$</td>
<td>$+1.30255 \pm 0.49$</td>
<td>$+2.58133 \pm 2.36$</td>
</tr>
</tbody>
</table>

The polynomial for the respective surfaces can be represented as a function of temperature ($T$) and pressure ($P$) as follows:

$$Y = C_0 + C_1 T + C_2 P + C_3 TP + C_4 T^2 + C_5 P^2$$

## 3 Results and Discussion

The overall reaction of methanol to aromatics can be considered as a highly exothermic dehydration reaction [7]. The heat of reaction estimated using Eq. (1) is $-868.27 \text{ kJ mol}^{-1}$. The active sites of ZSM-5 are the acid sites which exist in two forms as shown in Fig. 2i) [16, 17]. For the dehydration reaction to occur, the coexistence of a Brønsted acid site and a base site is a must. According to literature [1], methanol is chemisorbed onto a Brønsted acid site and a base site as shown in Fig. 2ii). Upon dehydration, the Brønsted acid site will be converted to a Lewis acid site. The acidity of the catalyst depends on the SiO₂/Al₂O₃ ratio: the higher the ratio, the lower is the number of acid sites, as acidity builds up around the aluminum atom. Methanol conversion to aromatics happens in multiple steps (Fig. 3). In the first step, methanol reaches an equilibrium with DME and water followed by a kinetic induction period. At the end of the induction period, the DME forms the first C–C bond [13, 15]. The primary product DME is short-lived and the secondary products such as olefins mask the primary products. In the final product mixture, methane, water, CO, CO₂, and H₂ are significantly present. Quantifying these products was not a focal point of this study. More information on this subject could be found elsewhere [10, 18]. The aforementioned products indicate that a number of parallel reactions are likely to occur simultaneously with the methanol dehydration. Eqs. (4)–(6) show possible reactions that could occur in parallel, including methane reforming, water gas shift, and methanol synthesis.

$$\text{CH}_4 + \text{H}_2 \text{O} \leftrightarrow \text{CO} + 3 \text{H}_2 \quad \Delta H = +206 \text{ kJ mol}^{-1} \quad (4)$$  
$$\text{CO} + \text{H}_2 \text{O} \leftrightarrow \text{CO}_2 + \text{H}_2 \quad \Delta H = +206 \text{ kJ mol}^{-1} \quad (5)$$  
$$2 \text{H}_2 + \text{CO} \leftrightarrow \text{CH}_3\text{OH} \quad \Delta H = -92 \text{ kJ mol}^{-1} \quad (6)$$

### 3.1 Methanol Conversion

The variation of methanol conversion with respect to temperature and pressure is depicted by a response surface plot in Fig. 4. The statistical analysis shows that the pressure and temperature interaction significantly affects methanol conversion. The highest conversion obtained in the experiment was 94.65 ± 0.18% at 700°C and 0 MPa (0 psi). On the other hand, with 63.72 ± 0.18% the lowest conversion occurred at 600°C and 0.689 MPa (100 psi). The studies show that methanol conversion passes through a minimum around 1.034 MPa (150 psi). When the methanol synthesis reaction given in Eq. (6) and methanol conversion reaction given in Eq. (1) are taken into consideration, we can possibly explain the behavior seen in Fig. 4: at low pressure the conversion of methanol is high. Low pressure likely facilitates the conversion by providing more dual sites (an acidic site and a basic site) available for adsorption of methanol molecules. When the pressure is increased, more methanol molecules get adsorbed onto the catalyst surface. This would significantly reduce the availability of dual sites.
(consisting of both an acidic and a basic site) for a single methanol molecule to bind. As explained in Fig. 2ii), the presence of this dual site for a methanol molecule is important for the conversion reaction. Therefore, it can be expected that the increase in pressure would result in decreasing the methanol conversion. But the reduction in conversion can be seen only up to 1.034 MPa (150 psi). The rapid increase of conversion after 1.034 MPa (150 psi) implies that methanol diffusion into the catalyst pores increases, favoring the conversion.

### 3.2 Benzene Selectivity

From the products considered in this study, benzene shows an interesting behavior as demonstrated in Fig. 5. According to the statistical analysis on benzene selectivity, the interactive effects of temperature and pressure are significant. The shape of the surface plot shows that at a given temperature the selectivity passes through a maximum around 1.0342 MPa (150 psi) and with increasing temperature the selectivity further increases. The highest benzene selectivity for this experiment was observed at 800 °C and 1.0342 MPa (150 psi) which is 18.11 ± 0.89 %. Benzene, presented in Fig. 3, can be considered as an intermediate for the formation of many other aromatics including toluene, ethylbenzene, and xylene.

### 3.3 Toluene Selectivity

Like for benzene, the selectivity of toluene in Fig. 6 passes through a maximum for each temperature at 1.3789 MPa (200 psi). The highest selectivity was reported at 800 °C and 1.3789 MPa (200 psi) with a value of 19.63 ± 2.61 %. According to the statistical analysis, the temperature and pressure interaction significantly affected the toluene selectivity. Formation of toluene can be attributed to the alkylation of benzene in the presence of methanol or methane [19, 20]. As shown in Fig. 3, benzene, which is a major component of the product spectrum, may have contributed to the formation of a series of aromatics via alkylation in the presence of methanol. The trend of increase in selectivity with increase in temperature is due to the increase in reaction rate as explained by the Arrhenius principle.

### 3.4 Ethylbenzene Selectivity

As shown in the reaction scheme in Fig. 3, ethyl benzene is formed by ethylene combining with benzene. Ethylene has been reported to be present in the primary product mix in similar studies [21]. However, it has been shown that highly reactive ethylene has a short life in analogous reaction mixtures. Consequently, it is likely that ethylene combined with other moieties to form more stable products – in this case ethylbenzene. According to Fig. 7, it is noteworthy that the effect of pressure and temperature is not significant for ethylbenzene selectivity. The response surface plot shows a minimum selectivity for ethylbenzene around 1.3789 MPa (200 psi) and 650 °C. In this reaction, the highest selectivity for ethylbenzene was 8.08 % ± 0.18 % at 0 MPa (0 psi) and 500 °C.

### 3.5 Xylene Selectivity

According to the reaction scheme in Fig. 3, the formation of xylene is a result of further alkylation of benzene. The highest selectivity for xylenes was 82.43 ± 6.23 % at 500 °C and 0 MPa (0 psi) as shown in Fig. 8. The results indicate that methanol dehydration over ZSM-5 is highly selective toward xylene formation. According to statistical analysis, the pressure and temperature interaction effects on xylene selectivity are significant.
3.6 Catalyst Deactivation

Methanol aromatization over ZSM-5 can deactivate the catalyst by two methods. Deposition of carbonaceous products at the active sites, which is commonly known as coke, is quite significant [22, 23]. Due to the 5.4×5.6 Å straight channel pore structure of ZSM-5, there is a greater possibility of blocking the pores with high-molecular-weight carbonaceous products [24]. Usually, benzene has a kinetic diameter of 5.8 Å, thus providing an order of magnitude higher mobility in the pore structure than o- or p-xylens [25]. The second method of deactivation is by dealumination that can occur as a result of alumina reaction with steam [9, 26]. Water is a major by-product in a deoxygenation reaction and at the temperature range at which the reactions are carried out, water will exist as steam. As it is shown in Tab. 2, the coke formation in the experiment was very mild. The highest average coke formation was recorded at 0 MPa (0 psi), being 2.42%. This low amount of
Table 2. Average coke formation at different pressures.

<table>
<thead>
<tr>
<th>Pressure [psi]</th>
<th>Average coke [w/wcat %]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.42 ± 0.63</td>
</tr>
<tr>
<td>100</td>
<td>2.16 ± 0.33</td>
</tr>
<tr>
<td>200</td>
<td>1.81 ± 0.36</td>
</tr>
</tbody>
</table>

coke formation can be considered as a result of short duration of the reaction in the reactor.

4 Conclusions

In this study, the effect of pressure on methanol aromatization over a ZSM-5 catalyst was elucidated. The highest conversion of methanol was observed at 700 °C at 0 MPa (0 psi). The lowest conversion occurred at 600 °C and 0.689 MPa (100 psi) which is 63.72 ± 0.18%. However, the pressure and temperature combination was significant for products including benzene, toluene, and xylene whereas it was not significant for ethylbenzene. The reaction had a remarkably high selectivity of 17.8 ± 0.5% for ethylbenzene. The reaction had a remarkably high selectivity of 18.11 ± 0.89% at 1.0342 MPa (150 psi) and 800 °C. The overall selectivity of the reaction to ethylbenzene was low. The highest selectivity of ethylbenzene was 8.08 ± 0.18% at 0 MPa (0 psi) and 500 °C. It was noted that the change of temperature or pressure did not significantly affect ethylbenzene selectivity. The reaction was fairly resistant to coking. The highest average coke percentage with 2.42 % w/wcat was recorded when the pressure did not significantly affect ethylbenzene selectivity.

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References