FREQUENCY EFFECTS IN THE CATALYTIC OLGOMERIZATION OF METHANE VIA MICROWAVE HEATING

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Introduction

Many efforts have been focused on the activation of methane to more valuable products in the last two decades. Many studies have been done in order to produce more valuable products from natural gas, of which methane is the major constituent. Natural gas is an inexpensive and abundant energy resource. Therefore, effective and economic processes to obtain higher hydrocarbons, methanol and/or synthesis gas would be valuable.

Thermal,1,3 homogeneous,4,6 and heterogeneous5,10 catalytic conversions of methane to higher hydrocarbons have been studied by many authors. Due to the high thermodynamic stability of methane compared with that of higher hydrocarbons, methane can only be thermally converted to C₂, hydrocarbons at temperatures higher than 1400 K. The products are unreacted and unstable hydrocarbons such as acetylene. Therefore, appropriate temperature, residence time, and rapid reaction quenching are necessary to achieve selectivity to desired products. Otherwise, carbon and hydrogen will be the only products.

The use of microwave heating to induce chemical reactions has been studied for several years. Over the past decade microwave heating has been employed extensively in organic17-41 and inorganic synthesis.41-55 Microwave-induced catalytic reactions have been studied extensively by Wan and coworkers.25,35,27,29,38-41 We have studied the oligomerization of methane to higher hydrocarbons using Ni powder, Fe powder, and activated carbon.65 Oligomers ranging from C₂ to C₆ hydrocarbons have been produced in a relatively high selectivity depending on the nature of the catalyst, power level, and the presence of He as a diluent gas.

Nickel catalysts have been shown to be highly selective and effective catalysts to lower the activation energy of breaking the carbon-hydrogen bond. Although microwave heating has been studied very systematically for the oligomerization of methane it is not clear yet what other factors might affect the activity and product distribution of this reaction. In this work, we studied the systematic effects of frequency and magnitude of the applied microwave radiation on the conversion and product distribution of methane oligomerization using nickel catalysts in the presence and absence of He as a diluent gas.

Experimental Section

Microwave Apparatus and Gas System. Oligomerization of methane was carried out in a flow reactor system. A Lambda Technologies variable frequency unit, Vari-Wave model VW-2750 was used for these experiments. The reactor, a straight 3/8 in-quartz tube, was mounted horizontally inside the cavity. Methane gas as well as He diluent gas was mixed in a panel when necessary and flowed into the quartz reactor. High Purity (HP) grade methane obtained from Matheson and Ultra High Purity (UHP) helium purchased from Airgas were used.

Various frequencies and modes were produced in the microwave cavity. This cavity allows TM₀ₙₐ modes (n = 2 to 9) over a frequency range of 2.400 to 5.056 GHz. The cavity was designed by Lambda Technologies to have different modes for each frequency. Our experiments were done with and without diluent at 2.40 GHz at TMₙ₀ and also at 4.60 GHz at TM₉₀, for comparison. Thermal paper was inserted into the microwave cavity and used to map the heating patterns of the various modes.

The length of the aluminum cavity was 29.5 cm and the radius was 5.15 cm. In order to ensure microwave absorption for a specific frequency value and power level, the reflected power had to be minimized first by means of a tuning knob and the frequency tuning control on the main panel. Therefore, the working frequency is a result of the tuning process. Reflected power higher than 60 W makes the safety feature of the unit shut off. Thus, not all frequencies are possible for a particular system.

Catalyst. Nickel powder catalyst with morphology of branched filaments was used for these experiments. The diameters of the filaments were 2.5 µm as measured in a Scanning Electron Microscopy (SEM) photograph. Clusters of nickel metal particles were aggregated to form the filaments. The catalyst (100 mg) was placed inside the reactor with high purity quartz wool on either side of the catalyst bed. The reactor was placed in the center of the aluminum cavity. Helium was flushed for 30 min through the reactor to purge the atmosphere.

The experiments were run at two different flow rates: 3 mL/min of pure methane; and 12 mL/min of a 3:1 mixture of helium and pure methane respectively at atmospheric pressure. Samples for analyses were taken after 3 min of irradiation time for each power level (100, 130, 170, 210, 300, and 370 W).

Product Analysis. Products were trapped using a 4 way-gas sampling valve and analyzed by using an HP5890 Series II Chromatograph equipped with a mass detector. Details about the Gas Chromatographer/Mass Spectrometer (GC/MS) were published elsewhere.

Results

Microwave-induced oligomerization (MIO) of methane was performed at two different frequency levels (2.40 and 4.60 GHz). It was not possible to set the unit to operate under other frequencies. The effect of power and the presence of helium as diluent gas on conversion and product distribution were also studied at these two different frequency values. A summary of the results can be seen in Table 1.

<table>
<thead>
<tr>
<th>Feed</th>
<th>Flow rate (mL/min)</th>
<th>Time (min)</th>
<th>Power (W)</th>
<th>Astex Unit</th>
<th>Var. Freq. Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>3</td>
<td>3</td>
<td>130</td>
<td>NR</td>
<td>2.45 GHz</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>370</td>
<td>Y</td>
<td>2.40 GHz</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Y</td>
<td>4.60 GHz</td>
</tr>
<tr>
<td>CH₄:He</td>
<td>39</td>
<td>3</td>
<td>130</td>
<td>NR</td>
<td>2.45 GHz</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>370</td>
<td>Y</td>
<td>2.40 GHz</td>
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<td></td>
<td></td>
<td></td>
<td>Y</td>
<td>4.60 GHz</td>
</tr>
</tbody>
</table>

Table 1. Summary Results. N.R. = no reaction; Y = see Fig. 4 - 7 for product distribution. 100, 130, 170, 210, 300, 370 Watts of power level were used. Those not shown in the table were neither relevant nor reaction detected at any frequency. It was not possible to set other frequency values with successful microwave absorption.

No visible arc formation was detected during these runs and the catalyst bed remained the same after reaction (checked by SEM photographs). Ethylene, acetylene and ethane were the major C₂ products observed for the oligomerization of methane via microwave
heating using Ni powder as a catalyst. Benzene was also formed with selectivities that ranged from 10 to 29%. In the case of 25% diluted methane as a feed and low frequencies (2.45 GHz), low selectivities of benzene were detected (2 to 5%).

Figure 1. Effect of applied power on product distribution at 4.60 GHz using pure methane as a feed and nickel powder catalyst

Pure Methane as Reactant. When using pure methane as reactant, as power increased from 130 to 370 W at 4.60 GHz, conversion increased from 8 to 24%. Selectivities towards \( \text{C}_2 \) decreased from 60 to 45% and selectivities to \( \text{C}_4 \) increased from 6 to 29% (Figure 1). Acetylene was not detected at low power (130 W). At 370 W, the relative proportions of \( \text{C}_2 \) products were ethylene > acetylene > ethane. At a low frequency (2.45GHz), when using pure methane as reactant, oligomerization was not achievable using the variable frequency unit. Therefore, for pure methane, the effect of frequency was compared using an ASTEX unit at the same conditions except at a fixed 2.45 GHz frequency (for more detail see previous publication). The selectivities towards \( \text{C}_2 \), decreased from 71 to 45% and the selectivities towards benzene (\( \text{C}_6 \)) increased from 20 to 29% when the frequency was increased from 2.45 to 4.60 GHz at 370 W. The selectivities towards ethylene, acetylene, and ethane decreased as frequency increased, maintaining their relative proportions (Figure 2).

Figure 2. Frequency effect on product distribution at 370 W using pure methane as a feed and nickel powder catalyst

Methane Diluted in He (25%). When the feed was changed to 25% methane in helium, as power was increased from 130 to 370 W at 4.60 GHz, conversion increased from 6 to 8%, selectivities towards \( \text{C}_2 \) decreased from 83 to 72%, and selectivity towards benzene increased from 1 to 10%. Conversion levels were lower than those in the case of using pure methane as a feed (6 and 8% compared to 8 and 24%). Also, while increasing power, less drastic changes in selectivity towards \( \text{C}_2 \) and \( \text{C}_4 \) were observed than those when using pure methane (See Figures 1 and 3).

Acetylene was not detected at 130 W and 4.60 GHz frequency. The relative proportion of \( \text{C}_2 \) changed from ethylene > ethane to ethane > ethylene > acetylene as power was increased from 130 to 370 W (Figure 3), which was different from the proportion of \( \text{C}_2 \), in the case of pure methane as a feed (ethylene > acetylene > ethane). The systematic effect of frequency was studied using the Lambda variable frequency unit and comparisons were also made when using the fixed frequency ASTEX unit in order to check for reproducibility of results at low frequency (2.45 GHz).

Figure 3. Effect of applied power on product distribution at 4.60 GHz using methane diluted in helium (25%) and nickel powder catalyst.

The data here show that both the ASTEX fixed frequency and the Lambda variable frequency systems behave almost the same when comparing data at low frequency (2.45 GHz) with respect to conversion levels (about 7%) and product distributions (Figure 7) at 370 W. As frequency was increased from 2.45 to 4.60 GHz, selectivities towards \( \text{C}_2 \), decreased from 81 to 72% and selectivity towards benzene increased from 5 to 10% (Figure 4). When using H\( \text{e} \) as diluent at 370 W, the only \( \text{C}_2 \) detected was ethane at a low frequency value (2.45 GHz). As frequency was increased from 2.45 to 4.60 GHz, the proportion of \( \text{C}_2 \) products changed from ethane to ethylene > acetylene (Figure 4). The effect of frequency on product distribution among \( \text{C}_2 \) was different with respect to the case of pure methane in the feed as seen in Figures 5 and 7. The proportion of \( \text{C}_2 \), changed from ethylene > acetylene > ethane to ethane > ethylene > acetylene at 4.60 GHz. At 4.60 GHz and pure methane, selectivity of benzene was higher than that at 4.60 GHz and diluted methane (29 vs. 10% respectively).

Figure 4. Frequency effect on product distribution at 370 W using methane diluted in helium (25%) and nickel powder catalyst

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The formation of acetylene as power increased. Equations 1-7 summarize some of the proposed reactions:

\[
\begin{align*}
\text{CH}_4 & \rightarrow \text{CH}_2 + \text{H}_2 \quad \text{(1)} \\
2 \text{CH}_4 & \rightarrow \text{C}_2\text{H}_2 + 2 \text{H}_2 \quad \text{(2)} \\
2 \text{CH}_4 & \rightarrow \text{C}_2\text{H}_2 + 3 \text{H}_2 \quad \text{(3)} \\
\text{C}_2\text{H}_4 + \text{H}_2 & \rightarrow \text{C}_2\text{H}_6 \quad \text{(4)} \\
3 \text{C}_2\text{H}_2 & \rightarrow \text{C}_6\text{H}_6 \quad \text{(5)}
\end{align*}
\]

The presence of \( \text{H}_2 \) from reaction (1) leads to hydrogenation of olefins and production of ethane as shown in reaction (4). The highly reactive methylene (\( \cdot \text{CH}_2 \)) intermediate can be used to elucidate the formation of ethylene and acetylene as indicated in reactions (2) and (3). The formation of benzene may be explained by the well-known cyclization reaction given in Equation (5). This is in agreement with the fact that selectivity of benzene increases as selectivity of acetylene also increases. Another viable mechanism for ethylene and acetylene formation could involve the dehydrogenation of secondary hydrocarbons:

\[
\begin{align*}
\text{C}_2\text{H}_6 & \rightarrow \text{C}_2\text{H}_4 + \text{H}_2 \quad \text{(6)} \\
\text{C}_2\text{H}_4 & \rightarrow \text{C}_2\text{H}_2 + \text{H}_2 \quad \text{(7)}
\end{align*}
\]

The increase in the duration of the pulse in order to achieve a certain average power and therefore an increase in the surface temperature of the catalyst explains the general trend where conversion increases as power increases. Conversion levels were smaller when using He as a diluent in the feed due to the fact that the residence time was about four times smaller than that when using pure methane in the feed (0.08 vs. 0.33 min\(^{-1} \) respectively). Allowing the reactant to spend more time in the reaction zone will permit the methane molecules to find adequate sites for reaction to occur. Since the irradiation time of the catalyst was small (3 min), the bulk temperature was not completely homogeneous. That is, there were hot spots, cold spots, and intermediate temperature spots. Methane will only react on those sites that have reached the proper temperature. Thermodynamic analysis has indicated that a catalyst particle surface temperature on the order of 1400°C – 1600°C is required to yield \( \text{C}_2 \) products from methane.\(^{67} \) The proportion of \( \text{C}_2 \) products changed from ethylene > acetylene > ethane when using pure methane to ethylene > ethane > acetylene when using methane and He in the feed. More benzene was also formed when using pure methane. These observable facts can be explained by both the difference in reagent residence time and the difference in concentration of methane. Wan found that sudden cooling of products would favor the formation of ethylene and ethane.\(^{67} \) For the case of \( \text{CH}_4\text{-He} \) feed, low concentration of active intermediates and products, relatively cold \( \text{He} \) molecules combined with low residence time, would give the molecules more likelihood for rapid quenching. As mentioned previously, benzene very likely comes from the trimORIZATION of acetylene. High concentrations of methane will statistically favor the formation of acetylene and benzene. Including a diluent in the feed will help prevent the coupling of intermediates to these products.\(^{53,66} \)

At present, the issue of microwave effects is very controversial. Unfortunately, many of the expected results from microwave processing such as rapid and uniform heating, more uniform microstructures, inverse temperature profiles, and selective heating are included in the general category of microwave effects. However, only those anomalies that cannot be predicted or easily explained based on our present understanding of differences between thermal and microwave heating should be referred to as microwave effects.\(^{44,68} \) “Microwave specific” activation has been a debated concept which actually refers to a unique interaction, reaction, or activation, specific to the microwave radiation. Two models of the chemical mechanisms in such reactions have emerged from research work done so far on microwave induced reaction chemistry. One model assumes that rate enhancement is simply due to thermal dielectric heating and the other assumes that there is a specific activation due to microwave radiation that occurs in addition to the dielectric heating mentioned earlier.\(^{69} \)

Our work is unique in the sense that systematic frequency effects have been found to markedly influence conversion and selectivity under microwave radiation in the oligomerization of methane. The effect of frequency on product distribution for the oligomerization of methane was studied with and without He as a diluent. It is a fact that when increasing microwave frequency, selectivities towards \( \text{C}_2 \) decreased and selectivity towards \( \text{C}_6 \) increased for both cases (with and without diluent).

All \( \text{C}_2 \) hydrocarbons decreased as frequency increased when using pure methane feed. When using He as a diluent, ethylene and acetylene increased as frequency increased while ethane decreased (see Figures 4 and 7). These effects on product distribution are related to the transverse magnetic modes at different frequencies that would generate diverse transient heating patterns. The two parameters that define the dielectric properties of materials and
As quenching of intermediates has an important role in ethylene formation, different transient heating patterns would affect the environment in which the reaction is taking place, consequently affecting the selectivities of the final products. The dielectric constant, $\varepsilon'$, describes the ability of the molecules to be polarized by the electric field. At low frequencies this value will reach a maximum as the maximum amount of energy that can be stored in the material. As frequency increases $\varepsilon'$ decreases as shown by Mingos et al. The dielectric loss, $\varepsilon''$, measures the efficiency at which microwave energy can be converted into heat and goes through a maximum as frequency increases. The relationship between these two parameters $\varepsilon''/\varepsilon'$ defines the dielectric loss tangent, $\tan \delta$, which measures the ability of a material to convert electromagnetic energy into heat at a given frequency and temperature. The dielectric loss also goes through a maximum as frequency increases. Therefore, higher formation of benzene-acetylene at higher frequency in our experiments can be explained by the increase of the dielectric loss as frequency increases before going through the maximum. Greater dielectric loss is directly related to greater temperatures, consequently related to acetylene formation. Acetylene is later consumed in the trimerization reaction to obtain benzene, which is detected in the final products.

Conclusions

Systematic effects of power level, He as diluent, and microwave frequency were studied for the microwave oligomerization of methane using Ni powder catalyst with branched filament morphology. We are not aware of other heterogeneous catalysis studies where either direct or indirect frequency effects have been observed under microwave radiation. As frequency increased, selectivity towards benzene also increased. When using He as a diluent, as frequency increased, selectivities towards ethylene and acetylene also increased. When pure methane was used, the opposite result was observed. These changes in product distribution are most likely due to different transverse modes that generate different transient heating patterns and changes in dielectric constant and loss of the catalyst.

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