Microwave catalytic reactor for upgrading stranded shale gas to aromatics

Xinwei Bai, Brandon Robinson, Casey Killmer, Yuxin Wang, Lili Li*, Jianli Hu*,

Chemical & Biomedical Engineering Department, West Virginia University, Morgantown, WV, USA

College of Life Science and Agronomy, Zhoukou Normal University, Zhoukou, Henan, China

Graphical Abstract

Abstract

Microwave (MW) catalytic processing has been applied to science discovery in a number of research fields. The potential of MW assisted catalysis in direct ethane dehydroaromatization was explored in this study. Under MW irradiation, significant enhancement in ethane conversion to aromatics was achieved at 400 °C which otherwise would take up to 600 °C in a thermally heated fixed-bed reactor. The role of MW irradiation in activating ethane over the catalyst and the reaction mechanism were elucidated. The results showed that MW could possibly induce the formation of dipoles on catalyst surface, facilitating electron shifting and sharing between catalyst and reaction intermediates. This activation process has significantly lowered activation energy, allowing the reaction to proceed under lower bulk temperature with enhanced aromatic yield.

1. Introduction

ZSM-5 zeolite has been widely investigated on direct and indirect conversion of natural gas to chemicals [1–12]. During shale gas treating processing, ethane is separated from shale gas to minimize condensation in natural gas pipeline. Transportation and storage of ethane become a challenge. As a result, ethane is either burned in local power plant or flared at wellhead. As an effective way to utilize ethane, direct non-oxidative ethane dehydroaromatization (DHA) on metal doped zeolite catalysts has been studied for decades [13–21], however commercially viable technology has not been available. Traditionally, aromatics are produced from coal or petroleum. Direct natural gas conversion to aromatics has huge potential to revolutionize the aromatic production process due to relatively low price of natural gas in the United States and some regions in the world [22–28]. However, the challenge in direct ethane DHA is the requirement of high temperature to activate stable ethane molecules to achieve a reasonable single-pass conversion [20]. The downside of high temperature operation is the coking reaction that deactivates the catalysts. In conventional thermally heated reactor, lowering reaction temperature yields very low productivity because DHA is endothermic reaction which is not thermodynamically favored at low temperature. There are few literatures...
reporting lower temperature ethane DHA conversion, especially under 400 °C. Therefore, unconventional approaches of activating ethane are sought and microwave (MW) assisted heterogeneous catalysis can be one of the solutions.

The beginning of MW assisted natural gas conversion can be traced back to 1991 when the attempt was made in using microwave irradiation in non-oxidative methane coupling [29]. Some publications show the potential of MW assisted catalysis in natural gas conversion by generating MW plasma [30–35]. Only few articles were focused on elucidating MW irradiation effects on catalytic reaction, especially aromatization reaction [36]. Despite many interesting discoveries about MW catalysis were reported, the research about assisted ethane DHA is lacking.

Recently, our group has reported the DHA performance comparison among different metal-promoted ZSM-5 catalysts including molybdenum and gallium-platinum, which are widely used in DHA reactions. In these studies, we discovered that gallium-platinum loaded ZSM-5 catalyst exhibited good ethane conversion and stability [20,37,38]. Nevertheless, molybdenum is more cost-effective while being able to achieve a reasonable conversion. Meanwhile, molybdenum based ZSM-5 catalysts exhibit an excellent stability by applying promoters based on our previous study [38]. Therefore, this paper presents exploratory research on ethane DHA using molybdenum-based catalysts, under MW irradiation operated at low temperature of 400 °C and ambient pressure. In addition, the reaction mechanism of MW assisted ethane DHA process was elucidated.

2. Experimental

2.1. Catalyst preparation

All the molybdenum-based catalysts were prepared by incipient wetness technique. The H-ZSM5 zeolite support was made by calcining the NH4-ZSM5 purchased from Zeolyst International, Inc. The detailed catalyst composition and preparation method were described in our previous publication [38].

2.2. Reactor configuration and experimental procedure

All DHA reactions were carried out in 10.5 mm inner-diameter (ID) quartz tube reactors. The feedstock contained 36 vol% of ethane, balanced by nitrogen; and the total inlet flow rate was set as 50 mL/min. For the reactions involving MW irradiation, a variable frequency microwave controller (Lambda MC1330-200) was applied under atmospheric pressure. The frequency was set at 6650 MHz. Typically, 0.8 g of catalyst was loaded in each experiment. The catalyst was solely heated by microwave (no thermal heating source was introduced in microwave reactor). Bulk catalyst temperature was measured by two IR sensors that were controlled by software. In every experiment, the catalyst was pre-heated to 400 °C in nitrogen before the feed gas was initiated. The MW irradiation was applied throughout the reaction period. The control experiment was conducted in a thermally-heated fixed-bed reactor using the same quartz reactor operated under the same gas hourly space velocity. The outlet gas was monitored by a 4-channel Inficon Fusion micro gas chromatography (Micro-GC). The temperature of outlet from the reactor was maintained at temperature higher than 150 °C to prevent condensation of benzene and toluene products. The production rates of all products were evaluated by moles of products obtained per minute (mol/min). By integrating the production curves, total production can be calculated. The mole number was obtained by ideal gas law. Nitrogen, as an internal standard was used for calculating conversion and outlet gaseous product flow rate.

2.3. Characterizations

X-ray Diffraction (XRD) analysis was performed on a PANalytical X'Pert Pro (PW3040) and the analytical conditions were 45 kV and 40 mA. Cu Kα radiation was used. A JEOL TEM-2100 transmission electron microscope (TEM) was applied to observe metal particles and carbon structures of spent catalyst samples under 200,000–400,000 times magnification.

3. Result and discussion

3.1. Catalyst performance comparison

Catalytic performance tests were carried out to compare the effect of MW irradiation with traditional thermal effect in ethane DHA. The comparison results are shown in Table 1 and Fig. S1.

As shown in Table 1, at bulk catalyst temperature of 400 °C, a maximum ethane conversion of 80.80% is reached while applying MW irradiation onto molybdenum-iron-zeolite catalyst system. As a comparison, in the control experiment carried out in traditional thermally-heated fixed-bed at 400 °C, ethane conversion is almost not initiated. This is largely because at low reaction temperature, ethane molecule cannot be fully activated in order to catalyze dehydrogenation of ethane to form ethylene intermediate [17,20]. Most of literature reports about ethane DHA were operated at 550 °C or higher. Compared with our previously published results using thermally-heated fixed-bed reactor for DHA conversion at 615 °C [38], the conversion in MW reactor is more than doubled. By comparing maximum ethane conversion obtained at 6 min time-on-stream with the conversion after 45 min, a trend of catalyst deactivation is observed which is apparently caused by coking. The results indicate that, under MW irradiation, the intrinsic nature of the reaction is catalytic but not merely the MW-only effect, otherwise catalyst deactivation would not have had any impact on the ethane conversion. MW irradiation combined with heterogeneous catalysis can synergistically increase the reaction rate. XRD patterns of spent catalysts obtained from MW reactor are presented in Fig. S2. The high intensity peaks between 8 and 10° and 22–25° represent featured crystalline structure of ZSM-5 zeolite. This is a strong evidence that applying MW irradiation to the catalysts at 400 °C would not cause crystallinity change of ZSM-5 material. Therefore, the catalyst deactivation in MW reactor is attributed to the formation of agglomerated metal particle and carbon deposit. In our previous study, Mo/ZSM-5 catalyst was found to exhibit a better ethane conversion (Table 1).

Table 1

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Conversion at 6 min Time-On-Stream in MW Reactor, 400 °C, 6650 MHz</th>
<th>Conversion at 45 min Time-On-Stream in MW Reactor, 400 °C, 6650 MHz</th>
<th>Conversion at 6 min Time-On-Stream in Fixed Bed, 400 °C</th>
<th>Conversion at 7 min Time-On-Stream in Fixed Bed, 615 °C [38]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo/ZSM5</td>
<td>64.70%</td>
<td>22.40%</td>
<td>1.98%</td>
<td>29.91%</td>
</tr>
<tr>
<td>Mo-Zn/ZSM5</td>
<td>69.60%</td>
<td>13.80%</td>
<td>1.23%</td>
<td>26.63%</td>
</tr>
<tr>
<td>Mo-Fe/ZSM5</td>
<td>80.80%</td>
<td>15.30%</td>
<td>2.31%</td>
<td>27.72%</td>
</tr>
<tr>
<td>Mo-Fe-Zn/ZSM5</td>
<td>78.60%</td>
<td>17.00%</td>
<td>3.11%</td>
<td>27.33%</td>
</tr>
</tbody>
</table>
However, when applying MW irradiation under 400 °C, the conversion of ethane on plain Mo-ZSM5 catalyst appeared to be the lowest among those four catalysts at 6 min time-on-stream, but to be the highest after 45 min reaction. In microwave catalysis, the sensitivity of active sites (metal clusters) on the support plays key role in the reaction. At the beginning of the reaction, the bimetallic or trimetallic catalysts may be more sensitive to MW in absorbing electromagnetic energy, leading to higher conversion than mono metallic catalyst. As reaction proceeds, coking and metal agglomeration interfered with MW irradiation, reducing the sensitivity to electromagnetic energy.

Fig. 1 compares the aromatic (benzene and toluene) production rate between the experiments carried out in MW reactor and thermally-heated fixed-bed reactor. Overall, the aromatics production rate in MW reactor shows two orders of magnitude higher than that obtained in the thermally-heated fixed-bed reactor under the same temperature of 400 °C. In MW reactor, Mo/ZSM-5 catalyst shows a stable aromatic production rate after 15 min time-on-stream, whereas Mo-Fe/ZSM-5 catalyst exhibits the highest maximum aromatics production rate among all tested catalysts. In thermally-heated fixed-bed reactor, the aromatics production rate appears to be consistent but at a very low level, which shows the same trend as shown in the ethane conversion. The numerical data are summarized in Supporting Information where...
the maximum aromatics production rate in MW reactor at 400°C is shown even higher than what achieved in thermally-heated fixed-bed reactor under 615°C (Table S1). This result demonstrates the advantages of using MW irradiation in assisting a catalytic reaction.

3.2. Gaseous hydrocarbon product composition

In ethane DHA reaction, the major gaseous hydrocarbon products are methane, ethylene, benzene and toluene. Selectivity curves versus time-on-stream are plotted for comparison (Figs. 2 and 3). As shown in Fig. 2, adding Zn promoter (Fig. 2b and d) can improve aromatics selectivity at early stage, which is consistent with our observation in previous study using thermally-heated fixed-bed reactor [38]. However, the absolute selectivity is not as high as the reaction carried out under 615°C (Fig. 4). As illustrated in Fig. 2, an interesting discovery is, methane selectivity in MW reactor is significantly higher at the beginning, while the ethylene selectivity is lower. Throughout the reaction period, the selectivity of methane has been dropping while the selectivity of ethylene is increasing. In contrast, in thermally-heated fixed bed reactor under low or high reaction temperature (Figs. 3 and 4), the selectivity of methane is consistently lower than the selectivity of ethylene, and the selectivity do not show similar increasing or decreasing trend as observed in MW reactor. These discoveries indicate that ethane DHA may undergo different reaction pathways by applying MW irradiation, which will be discussed in later sections.

3.3. Reaction mechanism

Microwave irradiation influences catalytic reaction through different mechanisms: first, MW can activate active sites on the catalyst. MW energy penetrates SiO2 material effectively, hence SiO2 which is the major component of ZSM-5 zeolite (Si/Al = 23, in our case), cannot be efficiently heated up by MW. However, MW energy can be effectively absorbed by metal particles, specifically nano-scale metal particles, due to eddy current induced by strong electromagnetic field inside the reactor chamber [39]. Therefore, hot spots are generated on active metal sites and aluminum component over zeolite, which are known as the Brønsted and Lewis acid sites [20]. Furthermore, during our previous study, the main reasons of catalyst deactivation are metal agglomeration as well as the formation of carbon deposit [37]. The change of metal particle sizes was observed and measured by TEM analysis. As shown in Fig. S, at 400°C, agglomerated metal particles are presented on the catalyst under MW irradiation only, while the metal particles cannot be observed in fixed-bed spent catalyst samples.

Fig. 3. Hydrocarbon selectivity of reactions carried out in thermally heated fixed-bed reactor for different catalysts: (a): Mo/ZSM-5; (b): MoZn/ZSM-5; (c): MoFe/ZSM-5; and (d): MoFeZn/ZSM-5, T = 400°C; 400°C; 1 atm; feedstock flowrate = 50 mL/min with 36 vol% of ethane, balanced by nitrogen.
According to our previous discovery, metal agglomeration is caused by high reaction temperature. Therefore, under MW irradiation, local hot spots might likely exist, which favors DHA reaction thermodynamically. As shown in Fig. 7, carbon nanotubes are observed on the spent catalyst with iron promoter under MW irradiation. This result is consistent with what we observed at high temperature (615°C) fixed bed experiment using iron-promoted catalyst [38]. The results indicate that MW irradiation does not change the function of metal promoters. Carbon nanotubes were not observed on the spent catalyst obtained from 400°C fixed-bed experiment due to very limited ethane conversion at such a low temperature.

Other than selective heating, the electron cloud of metal atoms on the catalyst may exhibit displacement which results in the formation of electric dipoles. Notice that this polarization effect does not relevant to MW heating [40]. For ethane dehydroaromatization, it is widely acknowledged that the loaded metal catalyzes formation of ethylene intermediate, which forms aromatics via shape selective catalysis over zeolite [20,41,42]. These dipoles, existed on the metal sites, catalyze the formation of polarized ethylene intermediate which facilitates ethane conversion. It is reported that microwave irradiation can accelerate electron transfer [43]. Therefore, we believe that under microwave irradiation, the formation of dipoles on these active sites facilitates electron transfer between catalyst and reaction intermediates at catalyst-reactant interface. Higher production of ethylene intermediate results in higher aromatics production which is confirmed by our experiment data. As shown in Fig. 2, reactions carried out in MW reactor exhibit high methane selectivity which is not observed in either low or high temperature ethane DHA in fixed-bed reactor (Figs. 3 and 4). This is related to ethylene hydrogenolysis reaction catalyzed by MW irradiation. Flaherty et al. reported C–C bond activation and cleavage in unsaturated C2 intermediates, which further form activated C1 species and produce CH4 [44]. Enlightened by this interesting discovery, we postulate that MW irradiation can potentially activate ethylene intermediate and further break the C–C bond on the activated metal sites. It is observed that under MW irradiation, the selectivity to ethylene increases with time-on-stream while methane selectivity decreases. This is a strong proof that the hydrogenolysis reaction is competing with ethylene oligomerization reactions. The reason that methane selectivity was decreasing could be ascribed to metal agglomeration, which caused the loss of active metal sites. This phenomenon also indicates that the hydrogenolysis reaction is catalyzed by molybdenum. As a result, distracted by MW favored ethylene hydrogenolysis, aromatics selectivity is
suppressed, which can explain the experimental results that the aromatics selectivity in MW reactor was much less than the reaction carried out in fixed-bed under high operating temperature (615 °C). The reaction pathways occurred under MW irradiation are described in following (Eqs. (1)–(6)).

\[
\begin{align*}
\text{C}_2\text{H}_6 \xrightarrow{\text{Metal, microwave}} & \text{C}_2\text{H}_4 \star + \text{H}_2 \\
\text{3C}_2\text{H}_4 \xrightarrow{\text{Microwave, ZSM-5}} & \text{C}_6\text{H}_{12} + \text{H}_2 \\
\frac{7}{2} \text{C}_2\text{H}_4 \xrightarrow{\text{Microwave, ZSM-5}} & \text{C}_7\text{H}_{14} + 3\text{H}_2 \\
\text{C}_2\text{H}_4 \star + (2x - 4)\text{H}_2 & \rightarrow 2\text{CH}_x \star \\
\text{CH}_x \star + \left(\frac{4 - x}{2}\right)\text{H}_2 & \rightarrow \text{CH}_4 \\
\text{C}_2\text{H}_4 \star \xrightarrow{\text{desorption}} & \text{C}_2\text{H}_4
\end{align*}
\]

\(1\)
\(2\)
\(3\)
\(4\)
\(5\)
\(6\)

4. Conclusion

Microwave irradiation showed promising synergistic effect on activating catalytic material as well as forming activated hydrocarbon intermediates. Under MW irradiation, ethane dehydroaromatization can take place over metal doped zeolite catalysts at 400 °C bulk temperature. Ethane conversion of 80% was achieved over iron promoted molybdenum zeolite catalyst. Meanwhile, aromatics production rate reached 32.5 µmol/min as compared to 20 µmol/min obtained from high temperature thermally-heated fixed-bed reactor [38]. Metal agglomeration was observed based on TEM analysis on the spent catalyst obtained at 400 °C MW reactor, indicating the existence of hot spots with temperature higher than 400 °C on metal active sites. The increase of aromatics production can be explained by the formation of MW-induced dipoles on catalyst surface, facilitating the formation of active reaction intermediate. It was noticed that the MW catalyzed C–C bond cleavage on ethylene intermediate, which lowered overall aromatic selectivity by increasing methane selectivity. It was observed that methane selectivity decreased throughout the reaction, probably due to metal agglomeration which further indicated that hydrogenolysis reaction took place on the metal active sites. In addition, in MW reactor, the effect of promoters over Mo-ZSM-5 catalyst exhibited similar behavior as shown in a thermally heated fixed-bed reactor, indicating that MW does not change the catalytic functions of promoters. Future work will be focused on decreasing methane selectivity and increasing aromatics selectivity. Also, the reaction kinetics of DHA reaction under MW irradiation will be investigated.
Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fuel.2019.01.147.

References


Fig. 6. TEM images of spent catalysts from fixed bed reactor; 400 °C; 1 atm; feedstock flowrate = 50 mL/min with 36 vol% of ethane, balanced by nitrogen.

Fig. 7. Image of carbon nanotubes in spent catalysts with iron promoter from MW reactor; 400 °C; 1 atm; feedstock flowrate = 50 mL/min with 36 vol% of ethane, balanced by nitrogen.


