Improved Performance of W/HZSM-5 Catalysts for Dehydroaromatization of Methane

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Abstract: The dehydroaromatization of methane over W-supported ZSM-5 with varying degrees of Li$^+$ ion-exchanged catalysts was studied with and without oxygen at 1073 K and atmospheric pressure. Catalyst activity and stability were found to be influenced by the catalyst acidity related to Brønsted acid sites and by the presence of oxygen in the feed. The NH$_3$-TPD and FTIR-pyridine results demonstrated that partially exchanged of H$^+$ ions by Li$^+$ into the W/HZSM-5 catalysts could be used to control the amount of strong acid sites on the catalyst surface. Without oxygen, the 3WHLi-Z (5:1) catalyst that has strong acid sites equal to nearly 74% of the original strong acid sites in the parent HZSM-5 exhibited the highest methane conversion and selectivity towards aromatics. However, the catalyst deactivated in a five hour period. In the presence of oxygen, the catalyst activity and stability could be improved further. The results of this study revealed that a suitable amount of strong Brønsted acid sites as well as oxygen addition in the feed increased the catalyst activity and stability. The 3WHLi-Z(5:1) catalyst exhibited improved performance in the dehydroaromatization of methane.

Key words: dehydroaromatization, methane, W-supported ZSM-5, partial ion exchange, H$^+$ ion, Li ion, catalyst activity, catalyst stability, catalyst acidity, oxygen presence, improved performance

1. Introduction

Natural gas has been used as a source for higher value hydrocarbons and fuels productions. However, the conversion of natural gas to higher hydrocarbons has been limited so far, as natural gas mostly consists of a stable molecule, methane. Currently, the commercialized technology to convert methane to the desirable chemical products and liquid fuels proceeds by an indirect route. In the indirect route, methane is converted to syngas (CO+H$_2$), an important raw material for petrochemical products, which is then converted to the desired chemical products either by Fischer-Tropsch or methanol synthesis (MTG) processes. The indirect route has high capital cost as the formation of syngas is by steam reforming which operates at elevated temperature and pressure [1].

Extensive studies have been conducted on the direct conversion of methane to higher hydrocarbons thus, bypassing the syngas route. The catalytic conversion of methane to higher hydrocarbons such as aromatics has received much attention [1-18,20-25]. It is generally accepted that methane can be converted to aromatics in the absence of oxygen over bifunctional catalysts comprised of specific metal and zeolite in proton H$^+$ form. Earlier studies reported that metals such as Mo, W, and Re supported on zeolites (HZSM-5, HZSM-11, and MCM-22, whose pore diameters are equivalent to the dynamic diameter of a benzene molecule), were found to be active catalysts for the conversion of methane to aromatics [3,4].
However, the methane conversion to aromatics in the absence of oxygen was low. Chen et al. [5] reported a 6.6% methane conversion with 76.5% selectivity to benzene over 3%MoO$_3$/HZSM-5 catalyst under reaction temperature of 973 K and methane space velocity of 1400 ml/(g.h). Zhang et al. [6], obtained a methane conversion of 8% and selectivity to benzene of 90.9% over 3%MoO$_3$/HZSM-11 at 973 K and methanee feed space velocity of 1600 ml/(g.h). The methane conversions achieved at those temperatures were low due to the thermodynamic limitation of the following reaction: methane to aromatics in the absence of oxygen, $6\text{CH}_4 \leftrightarrow \text{C}_6\text{H}_6 + 9\text{H}_2$. Temperatures as high as 1073 K are required in order to obtain higher methane conversion ($\approx 20\%$) [6,7]. However, deactivation of the catalysts occurred due to coke being deposited on the catalysts in such a high temperature [8-17].

Previously, some researchers reported that oxidants such as oxygen [8,9], carbon monoxide and carbon dioxide [3,10,11,15,16] could improve the catalyst stability when added with methane in the gas feed. The studies revealed that the addition of a suitable amount of oxidant into the reactants caused a depression of coke formation in the catalysts. The oxidants had been also encouraging for the formation of metal active phase in the form of $\text{MO}_x\text{C}_y$ (M=Metal) [9]. As a result, the activity and the stability of the catalyst was improved.

The W/HZSM-5 based catalyst was found to be a highly active catalyst for methane dehydroaromatization in the absence of oxygen [6,17]. The catalyst showed a high activity and a high heat resistivity under reaction temperature as high as 1073 K. It was also reported that the addition of a second metal component into the catalyst by sequence impregnation method such as Zn on Mo/HZSM-5 [7], Zn (or Mn, La, Mg, Li) on W/HZSM-5 [17], and Ru on Mo/HZSM-5 [18] enhanced the catalytic performance. The work reported by Xiong et al. [17] demonstrated that the catalyst with medium strength acidity could improve the dehydroaromatization of methane. Additionally, previous studies also demonstrated that the acid-reflux dealumination led to a reduced Brønsted acid sites on HZSM-5 and MCM-22 zeolites and promoted the suppression of carbonaceous deposition that ultimately improved the catalyst stability [3]. These results showed that acidity of a catalyst is extremely important in enhancing the activity and stability of the catalyst in the dehydroaromatization reaction.

In this work, we intend to improve the dehydroaromatization of methane over a series of W-supported ZSM-5 with varying degrees of Li$^+$ ion exchanged catalysts with and without the presence of oxygen. The combined effects of reduced catalyst acidity and added oxygen will be correlated to catalyst activity and stability. The acidic properties of W/HLi-ZSM-5 catalysts which contain different degrees of Li content are characterized by means of NH$_3$-TPD and FTIR-pyridine techniques. The coke deposition on the used catalysts was observed by using temperature programmed oxidation (TPO), while Nitrogen Adsorption (NA) method was used to determine the effect of coke formation on the surface area and pore size of the catalysts.

2. Experimental

2.1. Catalyst preparation

NH$_4$-ZSM-5 (Si/Al=30) was obtained commercially (Zeolyst international Co., Ltd.). It was converted to H-ZSM-5 by calcinations at 823 K for 4 h. Partially Li-exchanged HZSM-5 was prepared by the repeated ion exchange of H-ZSM-5 using mixtures of 1 mol/L LiNO$_3$ and 1 mol/L NH$_4$NO$_3$ solution for three times (6 h per exchange) at 353 K. The degree of H$^+$ exchange on the HLi-ZSM-5 catalyst was varied using different concentrations of NH$_4$$^+$/Li$^+$ ratios i.e. 5:1, 4:1, and 1:1, respectively. The materials were then dried at 373 K overnight and calcined at 873 K for 4 h.

Similar procedure was applied for the preparation of fully Li-exchanged HZSM-5 using 1 mol/L LiNO$_3$ solution. The resulting materials were then impregnated with a calculated amount of ammonium meta tungsten solution ((NH$_4$)$_6$W$_{12}$O$_{40}$H$_2$O) to obtain 3% W supported on HZSM-5 (or HLi-ZSM-5 and Li-ZSM-5) catalyst. The impregnated catalysts were dried overnight and calcined at 823 K for 4 h. All the catalysts were crushed and sieved to between 35–60 mesh. Finally, the catalysts are known as H-Z for HZSM-5, 3WH-Z for impregnated HZSM-5, 3WHLi-Z(x) for partially Li-exchanged catalyst where $x$ is the ratio of H$^+$ to Li$^+$, and 3WLi-Z for fully Li-exchanged ZSM-5 catalyst with the number 3 indicating the 3% of W supported on the ZSM-5 catalysts. The amount of Li$^+$ exchanged into HZSM-5 was determined by ICP technique. The ICP results revealed that for 3WHLi-Z(5:1), 3WHLi-Z(4:1), and 3WHLi-Z(1:1) samples, the degrees of Li$^+$ exchange on HZSM-5 were 10%, 12%, and 46%, respectively.
2.2. Catalytic testing

The catalyst test was conducted in a fixed bed micro quartz reactor with internal diameter of 9 mm and length of 300 mm under atmospheric condition and 1073 K. In each run, the catalyst charge was in the range of 0.5–1 g. Prior to the catalytic testing, the catalysts were pretreated in nitrogen stream for 1 h at 823 K. For non-oxidative reaction, feed gas containing \( \text{CH}_4 + 10\% \text{N}_2 \) was passed through over the catalyst bed at WHSV of 1800 ml/(g·h) whereas a WHSV of 20868 ml/(g·h) was applied for oxidative methane dehydroaromatization reaction. The feed stream comprised of gaseous methane, oxygen, and nitrogen. The mole percent of the oxygen in the feed was 7.6%. Nitrogen was used as an internal standard for calculating methane conversion and selectivity of the reaction products. The reaction products were analyzed by an on-line GC equipped with TCD, using Porapak N and molecular sieve 5A columns. The condensable products such as benzene, toluene, xylene, benzaldehyde were collected using ice traps and identified by an off-line GC-MS (Perkin Elmer, Clarus 500).

2.3. Catalyst characterization

X-ray diffraction (XRD) was recorded using a Broker X-ray diffractometer with Cu \( K_\alpha \) radiation (\( \lambda = 0.15406 \) nm). The patterns were obtained with the X-ray gun operated at 50 kV and 30 mA using a scan rate of 0.2°/min (29).

\( \text{NH}_3 \)-TPD was performed by a TPDRO 1100 Thermoquest CE Instrument. The catalyst charge was 0.2 g for each experiment. Initially, the catalyst sample was pretreated with nitrogen flow while heating at 773 K for 30 min, followed by cooling down to 373 K. Next, the sample was saturated in ammonia gas flow for 30 min, and subsequently flushed by nitrogen stream at a flow rate of 20 ml/min for 30 min, and finally cooled down to room temperature. The ammonia was desorbed by flushing the sample with helium at a flow rate of 25 ml/min while heating at 15 K/min in the temperature range of 298–873 K. The \( \text{NH}_3 \)-TPD results showed the amount and acid strength distribution of the catalyst.

In order to confirm the number of Brønsted and Lewis acid sites in the catalysts, the IR-spectra of pyridine adsorption was performed. In each test, 10 mg of the sample was pressed and placed into self-supporting wafers. The wafer was introduced in a quartz IR-cell equipped with CaF\(_2\) window. The cell was heated at 673 K for 4 h which was connected with vacuum system (\( p = 0.1 \) Pa) before exposing the sample to pyridine vapor at room temperature for 15 min followed by out gassing at 423 K for 30 min. The IR spectra were recorded in a region of 1300–1700 cm\(^{-1}\) at a resolution of 2 cm\(^{-1}\) using an Infrared Spectrophotometer (model: Shimadzu-8000).

The temperature-programmed oxidation (TPO) was conducted using TPDRO 1100 Thermoquest CE Instrument equipped with a TCD. Prior to TPO measurement, the samples were heated to 393 K in He flowing at 30 ml/min and held at this temperature for 30 min before subsequently cooled down to room temperature. In each TPO analysis, a \( \text{O}_2 \)/He ratio of 7% at 15 ml/min was passed through the catalyst samples with temperature increase from ambient to 1073 K at a heating rate of 15 K/min.

The presence of coke on the used catalysts was also examined by TGA characterization. TG profiles were recorded on a Perkin-Elmer TG Pyris 6 instrument. The used catalyst was first heated in the \( \text{N}_2 \) flow from room temperature to 393 K in order to eliminate adsorbed water from the sample. Then, the sample was heated from 303 to 1023 K in \( \text{O}_2 \) flow of 20 ml/min. The profile that is attributed to the weight loss of the catalyst sample was recorded.

Nitrogen adsorption was used to determine the surface areas and pore volumes of the fresh and used catalysts using NOVA 1000 Quantachrome. A known amount of the sample was placed in the cell and outgassed at 573 K under vacuum for three hours. The results of surface areas and pore dimensions were obtained by applying methods of BET and Dubinin Radushkevich equations.

3. Results and discussion

3.1. Characterization of fresh catalysts

The XRD patterns of all the catalysts used in this study are shown in Figure 1. The peaks corresponding to \( \text{WO}_3 \) crystalline do not appear on the 3WHZ-5, 3WLi-Z and a series of the 3WHLi-Z catalysts. The results are attributed to the relatively small tungsten loaded onto the HZSM-5 catalysts that eventually lead to a well distributed tungsten on the ZSM-5 supports. Based on the previous studies on tungsten and molybdenum supported catalysts characterized by XRD, the presence of metals that can be detected in the catalyst depended on the amount of metal loaded and calcination temperature. The
XRD study by Lucas et al. [19] on the structures of WHZSM-5 catalysts containing various W loadings calcined at 948 K found that WO$_3$ crystallites began to be visible for tungsten loading higher than 4.0%. In another XRD characterization reported by Chen et al. [5] and Xu et al. [13], Mo crystallites of tri-oxide and polymolybdenum oxide could be observed by XRD measurement for Mo/HZSM-5 with Mo loading larger than 10%. As can be seen in Figure 1, the patterns in Figure 1(2)–(6) do not exhibit WO$_3$ crystals with 3% of W loading possibly due to highly dispersed WO$_3$ species on the surface and partly in the channels of the HZSM-5 zeolite. The same effect was also observed on 2%Mo/HZSM-5 catalyst calcined at 773 K [20]. Based on the XRD pattern, there is no indication the zeolite crystallinity is reduced for all the catalysts. The peak intensity corresponding to HZSM-5 diffraction patterns is also observed for all samples indicating the modification of HZSM-5 has not destroyed the catalyst structures.

The NH$_3$-TPD results of the HZSM-5, 3WH-Z, 3WHLi-Z(5:1), 3WHLi-Z(4:1), 3WHLi-Z(1:1), and 3WLi-Z catalysts are exhibited in Figure 2 and Table 1. Except for the 3WLi-Z catalysts, one can observe two peaks for all the catalysts denoted as L and H peaks (Figure 2). The L peak, assigned to NH$_3$ weak adsorption on Bronsted acid sites as well as NH$_3$ associated with extraframework Al or Si—OH sites [18], appears at around 423–673 K. Meanwhile, the H peak attributed to strong NH$_3$ adsorbed at Bronsted acid sites in the Si—OH—Al groups [8,17,18,21,22] is seen at around 723 K.
Table 1. NH₃-TPD data of fresh catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>NH₃-desorption peak temperature (K)</th>
<th>Amount of NH₃-desorbed (mmol/g)</th>
<th>Total number of acid sites (mmol/g)</th>
<th>Relative amount of strong acid sites (Peak)**</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Peak L</td>
<td>Peak H/M</td>
<td>Peak L</td>
<td>Peak H/M</td>
</tr>
<tr>
<td>HZSM-5</td>
<td>451.53</td>
<td>723.02</td>
<td>1.289</td>
<td>0.499</td>
</tr>
<tr>
<td>3WH-Z</td>
<td>459.47</td>
<td>730.34</td>
<td>1.120</td>
<td>0.468</td>
</tr>
<tr>
<td>3WHLi-Z(5:1)</td>
<td>420.71</td>
<td>685.12</td>
<td>0.877</td>
<td>0.369</td>
</tr>
<tr>
<td>3WHLi-Z(4:1)</td>
<td>425.33</td>
<td>683.51</td>
<td>0.838</td>
<td>0.347</td>
</tr>
<tr>
<td>3WHLi-Z(1:1)</td>
<td>471.30</td>
<td>680.43</td>
<td>0.809</td>
<td>0.313</td>
</tr>
<tr>
<td>3WLi-Z</td>
<td>460.62</td>
<td>623.79*</td>
<td>0.549</td>
<td>0.507*</td>
</tr>
</tbody>
</table>

* Peak M (Medium)
**Relative amount of strong acid sites = amount of strong acid sites of modified catalysts/amount of strong acid sites of HZSM-5

The appearance of both the L and H peaks for the 3WH-Z sample supports similar results previously reported [17]. The total number of acid sites (strong+weak acid sites) decreased by 11.2% for the 3WH-Z sample compared to the parent HZSM-5 as shown in Table 1. However, the reduction in the strong acid sites was insignificant on the strong H peak suggesting that the decrease of the H peaks might be due to the deposition of tungsten species in the channels and also on the external surface of the zeolite. As a result, the pore size in the zeolite and, consequently the area of NH₃ adsorbed are reduced. According to Weckhuysen et al. [23], the transition metal ions prefer to deposit at the outer surface of the catalyst as small clusters or a thin film of the oxide. The transition metal ions only partly diffused into the zeolite channel which interacts with the Brønsted acid sites and the metal species preferentially react with the silanol groups at the outer surface of the zeolite. Eventually, considerable amount of the Brønsted acid sites are still available in the catalyst.

The amount of NH₃ desorbed for each catalyst is listed in Table 1. As expected, considerable effect on the strong acid sites occurs on the samples with Li ions: 3WHLi-Z(5:1), 3WHLi-Z(4:1), 3WHLi-Z(1:1), and 3WLi-Z. The intensity of the strong acid sites decrease significantly with the introduction of Li component by ion exchange in the zeolite catalysts. The decrease in the intensity of the H peak becomes significant with increasing Li content in the ratio order of H:Li=1:1>4:1>5:1 (Li contents in the zeolites are 46%, 12%, and 10%, respectively). The amount of strong acid sites in the 3WHLi-Z(5:1), 3WHLi-Z(4:1), 3WHLi-Z(1:1) catalysts are 0.369, 0.347 and 0.313 mmol/g, respectively. The decreasing trend is due to Li ions replacing the H⁺ positions in the Si—OH—Al group of Brønsted acid sites. The total number of acid site for the fully exchanged 3WLi-Z catalyst is 1.055 mmol/g. However, only medium temperature peak and no high temperature peak was observed for the 3WLi-Z catalyst implying that all H⁺ positions in the Si—OH—Al groups have been replaced leaving behind only weak and medium acid sites at about 623 K.

Figure 3 exhibits the IR spectra of pyridine adsorption for all the fresh catalysts while Table 2

![Figure 3](image-url)
presents the integrated areas and the number of Brønsted and Lewis acid sites in each catalyst. The spectra were recorded at room temperature after outgassing the adsorbed pyridine sample at 423 K. Except for the 3WLi-Z catalyst, all the other catalysts produce three different bands located at wavenumbers 1545, 1490, and 1454 cm$^{-1}$, respectively. According to literature [12,24,25], the pyridine band at around 1547 cm$^{-1}$ is assignable to pyridine ions on the Brønsted acid sites, the band at 1454 cm$^{-1}$ is pyridine adsorbed on weak Lewis acid sites, and the band at 1490 cm$^{-1}$ is assigned to both the Brønsted and Lewis acid sites. The strongest of these three pyridine adsorbed bands appears on the HZSM-5 sample.

A decrease in the relative intensity of the different hydroxyl groups by impregnating 3% of W species on HZSM-5 is observed. The relative intensity further decreased with the loading of Li species on the 3WHLi-Z(x) samples. Obviously, the intensity of the band at 1545 and 1490 cm$^{-1}$ decreased sharply with the increase in Li content on the 3WHLi-Z(x) samples most probably owing to the Li ion species occupying the OH group associated with tetrahedral framework. For the fully ion exchanged sample (3WLi-Z), no spectra is observed at 1545 cm$^{-1}$ indicating that all of the H$^+$ protons on the OH group located on the framework have been replaced by the basic Li ions. On the other hand, the distribution of the Lewis acid strength assigned to the 1454 cm$^{-1}$ band does not change significantly except for the fully exchanged sample. The results suggest that the introduction of Li ions by the ion exchange method does not affect the number of the Lewis acid sites. However, an increase in the number of Lewis acid sites is found in the 3WLi-Z sample.

### Table 2. Integrated band area of Brønsted and Lewis acid sites and the number of Brønsted and Lewis acid sites in the fresh catalysts

<table>
<thead>
<tr>
<th>Sample</th>
<th>I.B.A.B (A/cm$^{-1}$)</th>
<th>I.B.A.L (A/cm$^{-1}$)</th>
<th>No.B.S (mmol/g)</th>
<th>No.L.S (mmol/g)</th>
<th>IB/IL</th>
</tr>
</thead>
<tbody>
<tr>
<td>HZSM-5</td>
<td>19.35</td>
<td>15.24</td>
<td>0.643</td>
<td>0.403</td>
<td>1.596</td>
</tr>
<tr>
<td>3WH-Z</td>
<td>18.09</td>
<td>15.81</td>
<td>0.598</td>
<td>0.416</td>
<td>1.437</td>
</tr>
<tr>
<td>3WHLi-Z(5:1)</td>
<td>15.19</td>
<td>15.13</td>
<td>0.501</td>
<td>0.398</td>
<td>1.259</td>
</tr>
<tr>
<td>3WHLi-Z(4:1)</td>
<td>14.67</td>
<td>15.36</td>
<td>0.484</td>
<td>0.404</td>
<td>1.197</td>
</tr>
<tr>
<td>3WHLi-Z(1:1)</td>
<td>11.36</td>
<td>14.48</td>
<td>0.375</td>
<td>0.381</td>
<td>0.983</td>
</tr>
<tr>
<td>3WLi-Z</td>
<td>0</td>
<td>14.62</td>
<td>0</td>
<td>0.352</td>
<td>0</td>
</tr>
</tbody>
</table>

| I.B.A.B=Integrated Band area of Brønsted acid sites |
| I.B.A.L=Integrated Band area of Lewis acid sites |
| No.B.S.=Number of Brønsted acid sites |
| No.L.S.=Number of Lewis acid sites |
| IB/IL=Ratio of Number of Brønsted acid sites per Lewis acid site |

The results in Table 2 show the integrated areas of the pyridine adsorbed on Brønsted acid sites decrease for the impregnated W supported HZSM-5 and also for the Li exchanged 3WHLi-Z(x) catalysts. The integrated area increases in the order of decreasing number of Brønsted acid sites as the Li content on the zeolite support catalyst increases: 3WHLi-Z(5:1)>3WHLi-Z(4:1)>3WHLi-Z(1:1).

The results of FTIR Pyridine also showed the ratio of Brønsted and Lewis acid sites (IB/IL) decreases in the order of: HZSM-5>3WH-Z>3WHLi-Z(5:1)>3WHLi-Z(4:1)>3WHLi-Z(1:1).

There is no pyridine adsorbed at around 1547 cm$^{-1}$ on the fully Li ion exchanged sample (3WLi-Z) indicating Brønsted acid sites no longer exist on the catalyst surface.

### 3.2. Results of catalytic testing

#### 3.2.1. Methane dehydroaromatization under non-oxidative condition

The catalytic performances of 3WH-Z, 3WHLi-Z(5:1), 3WHLi-Z(4:1), and 3WHLi-Z(1:1) catalysts are presented in Figure 4. Dehydroaromatization of methane was conducted in the absence of oxygen with the following reaction conditions: methane gas feed flow rate of 1800 ml/(g.h), temperature of 1073 K under atmospheric pressure. Initially, a maximum methane conversion of $\approx$16% with corresponding aromatic selectivity of $\approx$93% are obtained over the 3WH-Z catalyst, but the conversion and selectivity decrease considerably to $\approx$8% and $\approx$56%, respectively at 320 min of time on stream. The ethylene selectivity however, increases significantly from $\approx$2% to $\approx$10% at 320 min of time on stream.
Figures 4(a)–(c) depict the activity of the 3WH-Z catalyst decreases significantly with an increase of time on stream owing to the coke deposited on the catalyst. It has been reported that coke formation was the main reason for catalyst deactivation leading to the decrease in the catalyst activity [8–17]. The coke formation on the 3WH-Z catalyst could be observed by the darkening catalyst after reaction for 320 min.

Figure 4. Results of catalytic testing for the conversion of methane to aromatics hydrocarbons in the absence of oxygen over the catalysts.

(1) 3WH-Z, (2) 3WHLi-Z(5:1), (3) 3WHLi-Z(4:1), (4) 3WHLi-Z(1:1)

(a) Methane conversion vs time on stream, (b) C2 selectivity vs time on stream, (c) aromatics selectivity vs time on stream

(Reaction conditions used were 1 atm, T=1073 K, WHSV: 1800 ml/(g·h))

Xu et al. [14] reported that the Brønsted acid sites on the catalyst were responsible for the formation of aromatics but an excess of the Brønsted acid sites led to severe coke formation. From the NH3-TPD results, the 3WH-Z catalyst had considerable amount of strong acid sites. The result of the pyridine adsorption by FT-IR also showed about 0.598 mmol/g or 93% of the strong Brønsted acid sites in the parent HZSM-5 still exist on the 3WH-Z catalyst. The deposition of coke on the 3WH-Z catalyst showed notable influence on the formation of higher hydrocarbons products. The selectivity of aromatic products decreased markedly by increasing time on stream while the selectivity of ethylene increased rapidly. The reduced amount of aromatics may be attributed to coke deposited in the catalyst pores and in the channels of the zeolite thus, reducing the pore size. As a result, the selectivity of aromatics decreased since the deactivated catalyst is accessible to the production of lower molecule hydrocarbons. Tan et al. [8] discussed the reduced benzene formation and increased C2-hydrocarbon yield in the methane dehydroaromatization over Mo/HZSM-5 catalysts. The deactivation of the catalyst resulted in the decreased amount of Brønsted acid sites and reduced pore volume and led to the suppression of C2-hydrocarbon oligomerization to form benzene.

As can be seen in Figures 4(a)–(c), the introduction of a certain amount of Li into the ZSM-5 catalyst influences the catalytic performance of dehydroaromatization of methane under the nonoxidative condition. Methane conversion and selectivity to aromatics are higher over the 3WHLi-Z(5:1) catalyst compared to the 3WH-Z catalyst at the same operating condition. Over the 3WHLi-Z(5:1) catalyst, with 74% of the strong acid sites of the parent HZSM-5, the selectivity to aromatics decreased slightly from $\approx$91% at methane conversion of $\approx$18% in the initial time on stream to $\approx$85% with methane conversion of $\approx$12% at 320 min of time on stream, while selectivity to C2 hydrocarbon increases slightly from $\approx$4.7% to $\approx$7.8%. However, with more Li content, the activity of the catalyst decreased as can be seen for 3WLi-Z(4:1) and 3WLi-Z(1:1) samples. These results may be attributed to the change in the acidic properties of the catalysts. According to the TPD results, the strong acid sites were markedly reduced and the relative amount of strong acidity decreased by $\approx$31% over the 3WHLi-Z(4:1) catalyst and by $\approx$37% over the 3WHLi-Z(1:1) catalyst as compared to the parent H-ZSM-5 catalyst. By using FT-IR of pyri-
dine adsorption measurement, the decreases in the Brønsted acid sites of 3WHLi-Z(5:1), 3WHLi-Z(4:1), and 3WHLi-Z(1:1) catalysts are by 22%, 25%, and 42%, respectively. The results imply that the catalyst performance could be improved by reducing a suitable amount of the strong acid sites, but too large of a reduction in the amount of acidity particularly the Brønsted acid sites is unfavorable for the nonoxidative methane dehydroaromatization. This observation is in accordance with the results reported in [24] as the suitable amount of strong acid sites plays an important role in methane conversion to form aromatics hydrocarbons. The 3WHLi-Z(5:1) catalyst is found to be the suitable catalyst as it has the optimum Brønsted acid sites and consequently, give the maximum methane conversion and selectivity to aromatics.

The decrease in the catalyst acidity by introducing Li influences not only the catalyst activity but also the catalyst stability. Previously, Xiong et al. [17] demonstrated that the catalytic performance of W/HZSM-5 could be improved by the addition of a second metal with subsequent impregnation method. Their results showed that introducing a second metal such as Mg$^{2+}$, Zn$^{2+}$ or Li$^+$ as promoters resulted in the elimination of a large portion of the strong acid sites and generation of a new medium strength acid sites thus simultaneously prolonging the lifetime of the catalyst. However, a very weak catalyst is not good for gaining decent methane conversion and aromatics selectivity. Interestingly, the results of our catalyst activity tests during 320 min time on stream over the 3WHLi-Z(x) catalysts with different H$^+$: Li$^+$ ratio evidently indicate that the catalyst stability could be improved by reducing a suitable amount of Brønsted acid sites on the catalyst. The selectivity to C$_2$ hydrocarbons is also influenced by the Li content, as shown in Figure 4(b). The selectivity to C$_2$ products increased over the 3WHLi-Z(5:1) sample compared to the 3WHLi-Z(1:1) sample whose Li content increase from 10% to 46%. Apparently, the Li ions also assist in stabilizing the catalyst. The selectivity to C$_2$ hydrocarbons remained nearly constant during the 320 min time on stream. Based on this result, it is suggested that Li ion exchanged catalyst promotes the C$_2$ selectivity and catalyst stability. In contrast, the sample without lithium, 3WH-Z, shows a low C$_2$ selectivity at first, but steadily increases with time on stream. Tan et al. [8] reported that coke formed on the acidic sites of the catalyst led to a reduced amount of Brønsted acid sites and a decrease in the volume of the zeolite pores. As a consequence, the C$_2$-hydrocarbon oligomerization and cyclization reactions are suppressed, but the C$_2$-hydrocarbons yield is increased.

Figure 4(c) shows the effect of Li content on the selectivity to aromatics. As can be seen, the selectivity to aromatics over the 3WH-Z sample is high at the initial reaction time, but decrease quickly with the increase in time on stream. By introducing Li ion into the HZSM-5 framework, the aromatics products are relatively constant with time on stream. However, excessive Li content in the 3WHLi-Z(4:1) and 3WHLi-Z(1:1) catalysts leads to a large reduction in the relative amount of strong acid sites and the number of Brønsted acid sites. Likewise, the selectivity to aromatics also decreases. The result is in accordance with the work reported by Weckhuysen et al. [23] where a decreasing number of Brønsted acid sites on the catalyst surface resulted in a gradual decreased in the benzene formation.

3.2.2. Methane dehydroaromatization under oxidative condition

Figures 5(a)–(c) present the catalytic performance of methane dehydroaromatization in the presence of oxygen in the gas feed. The catalysts tested were 3WH-Z, 3WHLi-Z(5:1), 3WHLi-Z(4:1), 3WHLi-Z(1:1), and 3WLi-Z, with 0, 10%, 12%, 46%, and 100% of Li$^+$ exchanged, respectively. The reaction condition was fixed as follows; atmospheric pressure, reaction temperature of 1073 K, feed flow rate of 20868 ml/(g-h) containing CH$_4$+O$_2$+N$_2$ with 7.6% oxygen (N$_2$ was used as an internal standard). It is obvious the methane conversion is almost stable during time on stream over all the catalysts as revealed in Figure 5(a). The presence of oxygen in the methane feed enhanced the catalyst activity and stability of all the catalysts. For example, without the effect of Li ions, the methane conversion over the 3WH-Z catalyst is higher than that under the non-oxidative condition. This result is apparently shown by comparing the methane conversion with time on stream in the Figures 4(a) and 5(a). The methane conversion decreases from $\approx17.3\%$ to $\approx11.6\%$ for 10 h time on stream with an addition of oxygen in the feed while under the non-oxidative condition the conversion decreases from $\approx16\%$ to $\approx8\%$ within 5.3 h of reaction time only.
It has been reported [8,9] that with the presence of a suitable amount of oxygen in the feed, the reactivity of methane aromatization is raised due to the active sites of the catalyst maintained as MO_xC_y. The stability of the catalyst in the presence of oxygen in the methane feed is due to the partial removal of coke in the catalyst. It seems that methane activation is promoted by adding oxygen in the feed leading to enhanced methane conversion although relatively a higher WHSV is employed. These results are in accordance with the case of adding carbon dioxide in the methane feed as previously reported [11]. The activity and selectivity of the catalyst decreased drastically when methane flow rate was increased at a space velocity as high as 9000 ml/(g*h) over 6%Mo/HZSM-5 catalyst in methane dehydroaromatization reaction, but after addition of 5% carbon dioxide the stability of the catalyst improved significantly [11]. However, the selectivity of aromatics over the 3WH-Z catalyst is lower than that under the non-oxidative condition possibly due to the side reactions where aromatics reacted with oxygen to form CO_x products.

In order to improve the activity and the stability of the catalysts, the effect of strong acid sites is studied by varying the Li contents in the catalysts. The effect of Li content in the catalysts on methane conversion, C_2 selectivity and aromatics selectivity can be seen in Figure 5. With the addition of Li content on the 3WHLi-Z(5:1) catalyst, the methane conversion increased. The average selectivity to aromatic hydrocarbons is found to be higher over the 3WHLi-Z(5:1) catalyst (79.8%) than that over the 3WH-Z catalyst (66.8%).

The improved performance of the 3WHLi-Z(5:1) catalyst compared to the 3WH-Z catalyst as revealed in Figures 5(a)–(c) implies that the acidic properties of the catalyst also exert influence on the methane dehydroaromatization reaction in the presence of oxygen. The maximum methane conversion of ≈19% with selectivity to aromatics of ≈70% is achieved at 80 min of time on stream then decrease slightly to ≈15.4% with corresponding aromatics selectivity of ≈84% at 10 h of time on stream. The result indicates that not only the presence of oxygen in the feed, it is also the amount of strong acid sites of the catalyst that are crucial in suppressing the coke formation even when severe operating conditions are employed; in this case WHSV of 20868 ml/(g*h) and temperature of 1073 K are used.

Additional Li ions introduced onto the catalysts resulted in a reduced methane conversion and aro-
matic hydrocarbons selectivity owing to a weakened acidity strength thus suppressing the catalyst activity, but the catalyst stability could be maintained over a prolonged period of time. As can be seen in Figure 5(c), the selectivity of aromatic products over Li$^+$ exchanged samples are in the following order:

$$3\text{WHLi-Z(5:1)} > 3\text{WHLi-Z(4:1)} > 3\text{WHLi-Z(1:1)}.$$ 

Similar trend is also observed for the NH$_3$-TPD and pyridine FTIR results indicating the important role of acidity in the activity study of methane to aromatics. Liu $et al.$ [24] suggested that a suitable amount of Bronsted acid sites on a bifunctional catalyst was important for promoting not only methane activation ($\text{CH}_4 = \text{CH}_x + n\text{H}_2$), but also oligomerization of ethane to aromatics.

Over the fully ion-exchanged of H$^+$ by Li$^+$ on 3WLi-Z catalyst, negligible amount of aromatics was observed in the products. However, the selectivity to C$_2$ hydrocarbons increase significantly with Li$^+$ content due to the changes in the catalyst acidic properties which are beneficial for the formation of C$_2$ hydrocarbons. Comparison of the C$_2$ selectivity in oxidative and non-oxidative conditions, the results in Figures 4(b) and 5(b) reveal that C$_2$ selectivity is higher without adding oxygen than that with adding oxygen in the methane feed due to the undesirable reactions of C$_2$ hydrocarbons to form CO$_x$ products.

The improved methane conversion, selectivity to aromatic hydrocarbons and stability exhibit by the 3WHLi-Z(5:1) catalyst can be associated with the combined effects of both reducing a suitable amount of the strong acid sites on the HZSM-5 catalyst support and adding oxygen in the feed. As a result, the stability of the catalyst also improves. The suggestion that the combined effects improved the catalyst activity and stability is supported by the improvement in the catalyst stability for up to 10 h over the 3WHLi-Z(5:1) catalyst in the presence of oxygen with a relatively higher WHSV employed. On the contrary, the enhancement of the catalyst stability after modification of the catalyst acidic sites was observed for only 300 min in a non-oxidative condition as reported by Xiong $et al.$ [17]. According to Shu $et al.$ [3] the addition of a few percent of carbon monoxide and carbon dioxide into the methane feed over Mo/HZSM-5 and Re supported on MCM and HZSM-5 catalysts resulted in remarkable enhancement of the catalysts stability. The addition of an oxidant in the methane feed led to coke deposited in the catalyst to be effectively removed by the following reaction: $\text{O}_2 + \text{C}$ (coke deposited on the catalyst surface) $\rightarrow \text{CO, CO}_2$ [3,8,10,17]. The addition of oxygen in the methane feed kept Mo on the Mo/HZSM-5 catalysts in form of MoO$_x$Cy which is the active centre for the methane dehydroaromatization reaction [9].

### 3.3. Characterization of used catalysts

Figure 6 shows the TPO profiles of used 3WH-Z and 3WHLi-Z(5:1) catalysts in the absence of oxygen and in the presence of 7.6% oxygen in the feed for the used 3WH-Z catalyst. The total amount of coke deposited on the 3WH-Z catalyst is markedly reduced by adding oxygen in the feed as shown by an obvious reduction in the areas of the peaks. The TPO peaks also appear to shift downward to a lower temperature of the used catalyst in the presence of oxygen showing the different nature of the coke deposited on the catalyst. The results of the TPO measurements are in accordance with the result of the catalytic testing supporting the fact oxygen added to the methane feed could eliminate the coke formed on the catalyst. Figures 6(1) and (2) indicate the amount of coke deposited on the 3WHLi-Z(5:1) catalyst is lower compared to the 3WH-Z catalyst for the non-oxidative condition. As presented in the previous section, the introduction of a certain amount of Li into the HZSM-5 catalyst support exerts positive influence on the stability of the catalyst due to the suitable reduction in the number of Bronsted acid sites in the catalyst.

![Figure 6](image-url)
The presence of coke on the used catalyst was also examined by TGA characterization. The profile which is attributed to the weight loss of the catalyst sample was recorded. The results showed the weight decreased from 653 to 973 K which is related to the burning off the coke deposited in the catalyst [26]. The results confirmed that the percentage of the weight loss in the catalyst samples increased in the order of: 3WH-Z (with addition of 7.6% oxygen in methane feed)≈3%<3WHLi-Z (non oxidative)≈9%<3WHZ (non oxidative)≈15%.

The effects of controlling the strong acid sites and the presence of oxygen in the feed on the BET surface areas and the pore volumes of the catalysts were determined by NA characterizations. The results of NA of fresh and used 3WH-Z and 3WH-Li(5:1) catalysts in Table 3 show that the BET surface areas and the pore volumes decrease for both catalysts after reaction. Coke deposition was notably lower over the 3WLi-Z(5:1) catalyst compared to the 3WH-Z catalyst in the absence of oxygen. In the presence of oxygen, a further reduction of coking was observed over the used 3WHZ catalyst while the NA results showed that suitable amount of strong acid sites and oxygen presence in the feed did not greatly reduced both the surface areas and the pore volumes of the catalysts. Furthermore, comparison between the BET surface area and the pore volume of the used 3WH-Z and 3WH-Li(5:1) catalysts in the non-oxidative condition indicate that the surface area and pore volume of the 3WH-Li(5:1) catalyst are larger than that of the 3WH-Z catalyst implying the influence of acidity on the catalyst stability.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area (m²/g)</th>
<th>Pore volume (ml/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3WH-Z (fresh)</td>
<td>457</td>
<td>0.176</td>
</tr>
<tr>
<td>3WH-Li(5:1) (fresh)</td>
<td>423</td>
<td>0.151</td>
</tr>
<tr>
<td>3WH-Z (used, without O₂ addition)</td>
<td>149</td>
<td>0.051</td>
</tr>
<tr>
<td>3WH-Z(5:1) (used, without O₂ addition)</td>
<td>142</td>
<td>0.089</td>
</tr>
<tr>
<td>3WH-Z (used, with O₂ addition)</td>
<td>299</td>
<td>0.109</td>
</tr>
<tr>
<td>3WH-Z(5:1) (used, with O₂ addition)</td>
<td>283</td>
<td>0.122</td>
</tr>
</tbody>
</table>

4. Conclusions

The performances of W/HLiZSM-5 catalysts with varying Li⁺ exchanged of HLiZSM-5 were investigated under both the non-oxidative and oxidative conditions. The activity and stability of the catalysts for the conversion of methane to aromatics over W supported HZSM-5 could be improved by replacing H⁺ proton associated with Brønsted acid with a suitable Li content on the ZSM-5 support and be further improved by adding oxygen in the feed. It was found that 3WHLi-Z(5:1) catalyst having 74% of the original HZSM-5 strong acid sites exhibited maximum activity and stability under both conditions: with and without oxygen addition in the feed gas. The enhanced performance by 3WLi-Z(5:1) catalyst is attributed to the suitable amount of Brønsted acid sites in the catalysts and the performance of the catalyst is further improved with the presence of oxygen in the feed.

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