EFFECTS OF POST-TREATMENT STEAMING ON CATALYTIC PERFORMANCE OF MODIFIED HZSM-5 CATALYSTS FOR THE CONVERSION OF n-PENTANE TO AROMATICS

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ABSTRACT

This work studied the effects of hydrothermal pretreatment parameters, i.e., steam concentration, steam temperature, and steaming time on modified HZSM-5 on their catalytic performance in aromatization of n-pentane. The steaming was achieved by different conditions. The physical and chemical properties of catalysts were characterized by N\textsubscript{2} physisorption, XRD, XRF, NH\textsubscript{3}-TPD, IPA-TPD, TPO and TPR techniques. Catalytic activity was tested in a continuous flow fixed-bed reactor at 500 °C, atmospheric pressure, and WHSV of 5 h\textsuperscript{-1}. After the modifications, the XRD pattern indicated the highly dispersed gallium and the unchanged crystalinity can be seen without any change after silylation and steaming. The steaming step dislodged fraction of aluminum from the framework to extra framework (EFAI) and generated the mesopores. The acidity of the catalyst exhibited a decrease in the number of Brønsted acid sites and an increase in Lewis sites corresponding to the generated EFAI species resulted in increasing of aromatics selectivity. The modified catalysts showed the higher performances in n-pentane conversion, aromatics selectivity, and p-xylene selectivity than the parent HZSM-5.

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INTRODUCTION

The primary economic aim of petrochemical manufacturers is to maximize the value added of products. Therefore, one of the reasonable routes being recently interesting is to convert the excess low-valued C\textsubscript{5} fraction into high-valued aromatic products. Nowadays, many researchers attempt to produce aromatics especially p-xylene from light naphtha by using ZSM-5 zeolites (MFI) Due to the shape selective properties of ZSM-5 zeolite, BTX are predominantly presented in the aromatic fractions. Aromatization of light naphtha highly effective seems to be the catalysts based on modified gallium ZSM-5 (Ga/ZSM-5) zeolite (J. Kanai, 1988). However, Ga/ZSM-5 showed the moderate to low p-xylene selectivity (D.H. Olson \textit{et al.}, 1984) that can normally be enhanced by chemical liquid deposition (CLD) of silica on HZSM-5 which external acid sites were eliminated resulting in higher p-xylene selectivity (Y.H.Yue \textit{et al.}, 1996). From previous studies, it was shown that the modifications of ZSM-5 zeolite catalysts by gallium ion-exchange, silylation, and strong electrostatic adsorption (SEA), respectively, can reached 100% p-xylene selectivity and moderate
\[ n \]-pentane conversion and aromatic yield. Moreover, the zeolitic acid sites, especially Lewis’s acid site, affect significantly the aromatics yield. Since the \( n \)-pentane aromatization activity of ZSM-5 is directed from the extra-framework Al species in associate with the sites of zeolitic acid where it required to examine on the hydrothermal pretreatment effect on this zeolite. In this work, the effects of different hydrothermal treatment parameters, steam concentration, hydrothermal temperature and time of hydrothermal pretreatment, will be investigated on the acidity and the activity of hydrothermal pretreatment, silylated, Ga ion-exchanged ZSM-5 zeolite for the \( n \)-pentane aromatization reaction to find the optimal condition of the activity of \( n \)-pentane conversion, aromatics and \( p \)-xylene selectivity.

EXPERIMENTAL

A. Catalyst Preparation

The parent HZSM-5 was modified by Ga ion-exchange, silylation, and steaming respectively. The steaming was carried out in various parameters which are steam concentration (5\%, 10\%, 25\%, and 50\% \( \text{H}_2\text{O} \) in \( \text{N}_2 \) by mol), steam temperature (300, 400, and 500 °C) and steaming time (2, 4, and 6 h).

B. Catalytic Activity Testing

The modified HZSM-5 catalyst was reduced with \( \text{H}_2 \) before tested its aromatization activity in a continuous flow fixed-bed reactor. \( n \)-Pentane was injected to the reactor via a syringe pump with 22 \( \text{mL/min} \) helium carrier gas. The products were analyzed by a SHIMADZU 17A gas chromatograph equipped with an HP-PLOT/\( \text{Al}_2\text{O}_3 \) “S” deactivated capillary column and an FID detector. The fraction of xylene isomers was independently analyzed by an Agilent Model 6890N gas chromatograph equipped with a capillary Stabilwax column and FID detector.

C. Catalyst Characterization

The modified catalysts were characterized by various methods. The surface area, micropore volume, mesopore volume, and total pore volume of the catalysts were measured by an Autosorb-1MP surface area analyzer. Crystalline structures and diffraction patterns were confirmed by X-ray diffraction (Rigaku SmartLab RINT 2000) XRD diffractometer. The acidity of prepared catalysts was tested by the isopropylamine and ammonia TPD techniques. The bulk Si/Al ratio was measured by the X-ray florescence spectroscopy. Amount of the coke deposited on the catalysts was determined by TPO technique.

RESULTS AND DISCUSSION

A. Surface area analysis

The surface area and pore volume of the parent HZSM-5 and modified HZSM-5 were summarized in Table 1. The results showed that loading of gallium on HZSM-5 zeolite by ion-exchange leads to the slight decrease of surface area, micropore volume due to deposition of gallium in HZSM-5 zeolite pore. Silylation by tetraethyl orthosilicate (TEOS) on Ga/HZSM-5 decreased the total pore volume, micropore volume, and mesopores
because of the deposition of silica inert layer on the external surface of zeolites. However, the surface area after steaming on CLD/Ga/HZSM-5 were lessen since the common forming of extra-framework aluminum species that can be removed off the framework, but it mainly located in the zeolites’ internal pore. On the other hand, there was the significant increasing of mesopores because the releasing of aluminum from the lattice secondary mesoporosity forming. (Mihalyi et al., 2011). Moreover, higher steam concentration led to higher mesopore generated in the zeolites catalyst pore.

**Table 1** BET surface area, total pore volume, micropore and mesopore volume of the parent and modified HZSM-5 zeolite catalyst.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface area (m²/g)</th>
<th>Total pore volume (cc/g)</th>
<th>Micropore Volume (cc/g)</th>
<th>Mesopore Volume (cc/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parent HZSM-5</td>
<td>348</td>
<td>0.282</td>
<td>0.227</td>
<td>0.055</td>
</tr>
<tr>
<td>Ga/HZSM-5</td>
<td>322</td>
<td>0.248</td>
<td>0.193</td>
<td>0.056</td>
</tr>
<tr>
<td>CLD/Ga/HZSM-5</td>
<td>307</td>
<td>0.203</td>
<td>0.151</td>
<td>0.051</td>
</tr>
<tr>
<td>Stc5/CLD/Ga/HZSM-5</td>
<td>300</td>
<td>0.216</td>
<td>0.149</td>
<td>0.067</td>
</tr>
<tr>
<td>Stc10/CLD/Ga/HZSM-5</td>
<td>296</td>
<td>0.216</td>
<td>0.145</td>
<td>0.071</td>
</tr>
<tr>
<td>Stc25/CLD/Ga/HZSM-5</td>
<td>294</td>
<td>0.210</td>
<td>0.135</td>
<td>0.075</td>
</tr>
<tr>
<td>Stc50/CLD/Ga/HZSM-5</td>
<td>289</td>
<td>0.210</td>
<td>0.133</td>
<td>0.077</td>
</tr>
<tr>
<td>Sttc300/CLD/Ga/HZSM-5</td>
<td>303</td>
<td>0.207</td>
<td>0.148</td>
<td>0.059</td>
</tr>
<tr>
<td>Sttc500/CLD/Ga/HZSM-5</td>
<td>306</td>
<td>0.214</td>
<td>0.137</td>
<td>0.077</td>
</tr>
<tr>
<td>Stti2/CLD/Ga/HZSM5</td>
<td>303</td>
<td>0.209</td>
<td>0.146</td>
<td>0.063</td>
</tr>
<tr>
<td>Stti6/CLD/Ga/HZSM-5</td>
<td>282</td>
<td>0.212</td>
<td>0.135</td>
<td>0.077</td>
</tr>
</tbody>
</table>

**B. X-ray diffraction**

The MFI structures of parent and modified HZSM-5 catalysts were confirmed by XRD. The scanning region of the diffraction angle 2θ was 5-50°. The X-ray diffraction patterns reflect the remained unchanged of the catalysts’ crystal structure according to the methods of Ga ion-exchange, silylation, and steaming, as can be seen in Figure 1. The peak XRD represents for the HZSM-5 crystalline MFI structure. The XRD patterns’ high intensity of peaks indicated for the highly crystalline of zeolite catalysts. From Figure 1, the absence of diffraction peak of Ga₂O₃ of 2θ = 31.7 and 35.2° on the Ga ion-exchanged catalysts (Ga/HZSM-5) was observed in comparison with the parent HZSM-5. This indicates the highly dispersed gallium in the catalyst. Furthermore, structure and the relative catalysts crystallinity can be seen without any change after silylation. The peak intensities at diffractive angles of 2θ = 24° in steaming has slightly decreased related to the aluminum removed from lattice. (Ding, Liang et al. 2007)
C. Ammonia-TPD

The NH$_3$-TPD profiles of the catalysts showed three types of desorption peaks as listed in Table 2. The quantities of strong, medium and weak acid site are measured by the amount of ammonium desorbed at 100-200, 200-300 and 300-550 °C, respectively. Parent HZSM-5 exhibited the highest acidity. After loading of gallium, the weak and strong acidity were decreased which could be the result from the exchangeable Ga$^{3+}$ or GaO$^+$ with the strong acid site, however the presence of Ga in Ga/HZSM-5 could generate the medium acid site (200-300 °C). The significant decrease in total acidity was detected due to the elimination of external acid sites after the deposition of inert silica layer by silylation. After post-treatment by steaming, the weak and medium acidity were slightly increased because steaming could extract the Al framework leading to a decrease of the concentration of strongly acidic OH groups of the bridged type as well as to the appearance of new types of OH groups with weaker acidic properties.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Total Acidity (µmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Weak</td>
</tr>
<tr>
<td>Parent HZSM-5</td>
<td>376</td>
</tr>
<tr>
<td>Ga/HZSM-5</td>
<td>155</td>
</tr>
<tr>
<td>CLD/Ga/HZSM-5</td>
<td>129</td>
</tr>
<tr>
<td>Stc5/CLD/Ga/HZSM-5</td>
<td>157</td>
</tr>
<tr>
<td>Stc10/CLD/Ga/HZSM-5</td>
<td>135</td>
</tr>
<tr>
<td>Stc25/CLD/Ga/HZSM-5</td>
<td>145</td>
</tr>
<tr>
<td>Stc50/CLD/Ga/HZSM-5</td>
<td>145</td>
</tr>
<tr>
<td>Stte300/CLD/Ga/HZSM-5</td>
<td>166</td>
</tr>
<tr>
<td>Stte500/CLD/Ga/HZSM-5</td>
<td>157</td>
</tr>
</tbody>
</table>
Figure 2 illustrates the effect of steam concentration on aromatization activity, the result showed that mild steaming (5% H₂O in N₂) exhibited highest aromatics and p-xylene selectivity among all conditions. It was known that steaming led to dealumination of the zeolite structure. During this treatment extra-framework aluminum species (EFAI) were generally formed, mainly stays in the internal pore systems that aluminium removed from the framework occupied cationic positions with an octahedral coordination and exhibited Lewis acid properties. The positive charge sited on the extra framework AlO⁺ species will be partially neutralized by electron donation from the hydroxyls oxygens and from oxygens of water molecules; a decrease in the number of Bronsted acid sites and an increase in Lewis sites corresponding to Al species resulted in increasing of aromatics selectivity. Moreover, steaming led to an increase in the stability of the zeolite catalysts, this fact is explained since a mesopore structure can be produced as a consequence of aluminum extraction in dealuminated zeolites (Bauer, Bilz, & Freyer, 2004) as confirmed by BET in Table 1. The formation of this new structure could act positively in catalysts deactivation behavior, as it can reduce diffusional limitations in the zeolitic channel resulting in higher conversion of steamed modified zeolites than CLD/Ga/HZSM-5. Among the steaming temperature tested, the catalyst steamed at 500°C exhibited the highest aromatic selectivity because high temperature was suitable condition to generate Al species. Finally, steaming time at 2 and 4 hours, the activities of catalysts were not significantly different which that time could conclude as mild steaming. (Niwa et al., 2012) However, steaming at 6 hours decreased the n-pentane conversion significantly indicating that the extra-lattice aluminum atoms begin to form larger clusters and blocked pore of zeolite catalyst as also shown by BET results. (Ong et al., 2012)
Figure 2  Effect of steam concentration of CLD/Ga/HZSM-5 zeolite on aromatization activity (Reaction condition: 500 °C, 1 atm, WHSV = 5 h⁻¹, and TOS = 140 min).

CONCLUSIONS

In order to study the effect of hydrothermal post-treatment parameters, i.e. steam concentration, steam temperature, and steaming time on modified HZMS-5 of n-pentane to aromatics. The results indicated that the addition of Ga greatly improve the conversion and aromatics selectivity due to the presence of GaO⁺ species which is favorable for dehydrogenation of cyclic hydrocarbon to aromatics. Silylation on Ga/HZSM-5 exhibited the lower conversion and aromatics selectivity because silylation eliminated protonic acid sites resulting in a decrease of acidity. While the p-xylene selectivity was greatly increased to 100%. Steaming could extract Al framework located in zeolites’ lattice to aluminum extra-framework leaving mesopore in HZMS-5 catalysts. Steaming resulted in a decrease in the number of Brønsted acid sites and an increase in Lewis acid sites corresponding to Al species. The catalytic performance of n-pentane including, n-pentane conversion, aromatics selectivity, and p-xylene selectivity was able to enhance under carefully controlled conditions depending on several variables. EFAl, acted as one electron acceptors, could extract an electron from n-pentane molecule resulting in the formation of a pentane carbenium ions, which are important precursor to produce aromatics.

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REFERENCES


