Surface Modified Acidity of Zeolites for Selective Production of para-Xylene in Toluene Methylation: A Brief Review

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KEYWORDS
- Zeolites
- Toluene methylation
- P-xylene
- Shape selective
- Surface modified

ABSTRACT
This paper provides an insight into the enhancement of para-xylene selectivity in the toluene methylation process by tailoring the acidity on the surface of zeolites. Based on the previous works, the external acid sites were confirmed contributing to the reduction of p-xylene selectivity. The modification method by deposition of inert silica on the surface has been proved to alter the external acidity and narrowing the pore, hence, improve the selectivity. Therefore, this paper aims to gather an overview of the surface acidity modification of zeolites and the results of the p-xylene selectivity.

1. Introduction
p-Xylene is a highly desirable product among xylene as it is the starting material for the production of various polymers [1,2]. High purity of p-xylene is demanded for oxidation to terephthalic acid and easier separation from C8 fraction by distillation [2, 3]. Taking advantage of excess toluene produced from petrochemical industry, toluene methylation is a promising alternative to balance the deficiency of p-xylene production [4,5]. The process was extensively studied as zeolite acid-catalysed reaction due to the zeolites that posses tunable acidity and pore size, and environmental friendly [6,7]. The product distribution of toluene methylation reactions varies greatly depending on the acid-base properties of the zeolite. Since alkylation and isomerization reaction occur simultaneously on acidic sites, a mixture of three xylene isomers is obtained. Thus, the modification of acidity and structure of zeolites has been intensely investigated to reduce by-products and improve the selectivity of methylation of toluene to p-xylene [8, 9]. In many cases of reaction, it is difficult to achieve high conversion meanwhile retaining high selectivity of desired product i.e. p-xylene. The conversion and selectivity usually change inversely. It was found that selectivity to para-isomer and external surface acidity are inversely related [4]. Hence, in order to achieve better p-selectivity, it is essential to reduce external surface acidity. The last few decades have brought many studies concerning acidity adjustment of zeolites to enhance para-selectivity by metal impregnation and deposition of inert silica on the pore mouth of zeolite. Thus, a brief review was prepared to provide an insight into the enhancement of para-xylene selectivity in the toluene methylation process by tailoring the acidity on the surface of zeolites.

2. Surface Acidity Modification
Zeolite has been generally known to possess strong Bronsted acid sites on its external and internal surface sites [10]. The external active sites of the zeolites have been known to be not shape selective. The catalytic reactions that occur on the sites proceed similarly to those on an unrestricted surface, and their contribution to the overall catalytic reaction might not be negligible. Thus, it is necessary to minimize the external active sites in order to obtain the high shape selectivity of the desiring product in certain catalytic reaction. This can be achieved by deposition of tetrathyl-orthosilicate (TEOS) on the zeolite surface [1,4,10,12,13].
The method exhibits a significant influence on the distribution of acid sites across their acid strength, where the method has been proved to minimize the Bronsted acid site concentration on the zeolite surface. The polymeric silica (SiO₂) layer has been observed lead to a narrowing of the pore entrance of zeolite which can impose diffusional hindrances that could be exploited for achieving higher para-selectivity [5,10,13]. Quantitatively, the amount of external acid sites can be determined by the adsorption of diterbutyl pyridine (DTBPpy), a large molecule that cannot enter the pores of the catalyst. Technically, the surface modification by TEOS decreased the fraction of Bronsted acid sites accessible by the probe molecules due to its larger kinetic diameter (0.96 nm) than the size of zeolite pores. Consequently, only Bronsted acid sites at the pore mouth region were affected by the probe molecules [10,11].

3. Applications in Toluene Methylation

In the methylation of toluene process, the reaction is induced by the strong Bronsted acid sites of the catalyst. Table 1 shows the comparison of surface modified catalysts in toluene methylation.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Acid_{ext} (%)</th>
<th>X_{tot} (%)</th>
<th>S_{PX} (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>HZSM-5</td>
<td>21.9</td>
<td></td>
<td>23</td>
<td>[12]</td>
</tr>
<tr>
<td>Zn/P/ZSM-5</td>
<td>12.8</td>
<td>1.9</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>Zn/P/Si/ZSM-5</td>
<td>8.0</td>
<td>-</td>
<td>89</td>
<td></td>
</tr>
<tr>
<td>HZSM-5</td>
<td>24</td>
<td>26</td>
<td>&gt;99</td>
<td>[1]</td>
</tr>
<tr>
<td>0.81% Zn/ZSM-5</td>
<td>26</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>0.35% Zn/ZSM-5/Si</td>
<td>24</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>HZSM-5</td>
<td>64</td>
<td>85</td>
<td></td>
<td>[13]</td>
</tr>
<tr>
<td>Si/ZSM-5</td>
<td>90</td>
<td>62</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HZSM-5</td>
<td>39</td>
<td>65</td>
<td></td>
<td>[4]</td>
</tr>
<tr>
<td>13% SiOz/ZSM-5</td>
<td>65</td>
<td>20</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The introduction of metal species on protonated ZSM-5 (HZSM-5) showed that the percentage of external acid sites (Acid_{ext}) of the metal-containing HZSM-5 zeolites is slightly reduced by introducing the zinc and phosphorous species [1,12]. Meanwhile, the surface modification by TEOS has been proved to greatly diminish the Bronsted acid site concentration on the zeolite surface [12,13] indicating that the density of surface reactive silanol (SiOH) group has been reduced. Hence, minimize the isomerization at the outer surface. In [12], it can be observed that p-xylene selectivity was in the same range over HZSM-5 and Zn/P/ZSM-5. In contrast, the selectivity was increased sharply to 89.6 % when ZSM-5 firstly silylated before doped with Zn and P. Similar trend was observed in [1]. These results clearly shown surface modified by TEOS or silylation is an effective procedure to selectively produce para-xylene.

4. Conclusion and Future Prospects

To summarize, the surface modification by deposition of inert silica reduced the external acid sites, hence, improved the para-xylene selectivity. The additional diffusional hindrances imposed possibly aid in improving the selectivity. However, there is lack of concern in coking and catalytic lifetime study which are crucial for commercialization of catalyst in industry application. Hence, need more attention from researchers.

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References


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