Development of Nanoporous Structured Catalysts for Xylenes Production

M. A. Ali1, S. Al-Khattaf, S. A. Ali and K. Al-Nawad
Research Institute, King Fahd University of Petroleum & Minerals
Dhahran, Saudi Arabia

Okamoto and K. Ishikawa
Nippon Oil Research Institute Co
Tokyo, Japan

1Correspondance Author, Email: maali@kfupm.edu.sa, Tel: 966-3-8602659,

ABSTRACT
Five catalysts evaluated in a fixed-bed reaction system were zeolites-based and are as described below: High Molybdenum loaded mordenite based catalyst (HMo-MOR), Low Molybdenum loaded mordenite based catalyst (LMo-MOR), Rhenium loaded mordenite based catalyst (Re-MOR), High Molybdenum-Cerium loaded mordenite based catalyst (5Mo-5Ce-MOR), and Low Molybdenum-Cerium loaded USY based catalyst (3Mo-3Ce-USY).

The feed containing 95% C9 aromatics was used, and the reaction conditions were as follows: reaction temperatures; 340, 360, 380, 400, 420 and 440 ºC, liquid hour space velocity; 1.0, 1.5 and 3.3, hydrogen to feed ratio; 2.0 and hydrogen carrier gas pressure; 3 Mpa. The reaction products were separated into gas and liquid portions and were analyzed using gas chromatography based Analyzers.

All five catalysts exhibited increase in C9 conversion with increase in temperature and decrease in space velocity. Re-MOR catalysts produced more gaseous products as compared to Mo-MOR catalyst. Mordenite-based catalysts offered a number of advantages over the USY-based catalysts which include higher C9 conversion, higher xylenes selectivity, and reduced C10+ and ethylbenzene production, whereas the disadvantages are higher yield of benzene and toluene. The results revealed that high loading of metals decreased C9 conversion. It was determined that for the conversion of C9 aromatics to xylenes, mordenite zeolite are better than USY.

Keywords: Transalkylation, Nanoporous, Mordenite, USY, Xylenes, Heavy aromatics.

1.0 INTRODUCTION
A joint research program has been started between the Nippon Oil Research Institute Co., Japan and King Fahd University of Petroleum & Minerals (KFUPM), Dhahran, Saudi Arabia. The main objective of this program is to develop novel catalytic systems for efficient conversion of heavy aromatics, improved xylene selectivity, and reduced higher aromatics (C10+) formation and lower gas formation.

Transalkylation is the process that converts low-value toluene and heavy aromatics into value-added mixed xylenes. Transalkylation processes use silica-alumina and zeolites such as dealumminated mordenite, ultra stable Y-zeolite (USY) and ZSM-12 [1]. Nippon Oil Corporation has demonstrated a new technology for the production of mixed xylenes via the transalkylation of benzene and C9 aromatics [2]. A high-active catalyst based on nickel supported high silica mordenite was used in the production of toluene and mixed xylenes.
The catalyst showed higher C<sub>9</sub> aromatics conversion activity with less deactivation and higher selectivity to mixed xylenes.

Transalkylation technologies have been developed by a number of companies including UOP, ExxonMobil, Toray, and SK Corporation. The Advanced Transalkylation (ATA) process was developed by SK Corporation to produce high xylenes from the transalkylation of C<sub>9+</sub> aromatics and utilizing a catalyst based on platinum-promoted mordenite. Platinum was used for its hydrogenation function along with tin or lead to control the hydrogenating activity [3]. The catalyst exhibited strong dealkylation activity, the ethyl and propyl groups were easily dealkylated to provide high BTX yield and a low concentration of ethylbenzene and propylbenzene in the product. Toluene disproportionation also occurred as evidenced by the high conversion of toluene. As the concentration of C<sub>9+</sub> aromatics increased in the feed, the TDP reaction was suppressed and hence the toluene conversion and benzene yield decreased while mixed xylenes yield increased. Other processes also utilized zeolite based catalysts mainly mordenite loaded with metals such as molybdenum, rhenium and nickel.

Mixed xylenes fraction consists of three isomers namely: para-xylene, ortho-xylene, and meta-xylene (Figure 1). The ortho-xylene and meta-xylene are processed further by isomerization reaction to produce para-xylene, which is used for the production of polyester fibers, resins, and films. Because of the growth in demand for para-xylene, new technologies are needed to convert low value aromatics (C<sub>9</sub>A+) into mixed xylenes and specifically para-xylene.

![Figure 1. Isomers in mixed xylenes fraction][2]

During the process of xylene production, a number of reactions such as transalkylation, disproportionation, and dealkylation take place. The methyl groups are shifted from one benzene ring to the other via transalkylation and disproportionation to produce mixed xylenes. During dealkylation, the ethyl, propyl, and butyl groups attached to benzene and methylbenzenes are removed to produce benzene and methylbenzene. Undesirable reactions that may occur include ring saturation (lead to substituted cyclohexanes), hydrocracking (lead to ring opening) and coking and condensation (many benzene rings condensed to produce polynuclear aromatics).

Since large aromatic molecules such as trimethylbenzenes, methylethylbenzenes and heavier alkylsubstituted aromatics (C<sub>10+</sub>) are involved in the transalkylation reaction; relatively large-pore zeolites are able to catalyze this reaction towards maximum xylenes formation. The literature reported a variety of supports and metals used to prepare the catalysts for these reactions. The supports utilized include zeolites including mordenite, Y, beta, L, omega, and MCM and SAPO while the metals that have been used include molybdenum, bismuth,
chromium, cobalt, copper, iron, nickel, lead, lanthanum, palladium, platinum, silver and zirconium. Catalysts having strong acid sites are less selective for producing mixed xylenes and are easily deactivated by coke. Zeolites with small and medium pores such as ZSM-5 act only by the external active sites. However, ZSM-5 alone can be applied for toluene disproportionation reaction, but is not suitable for disproportionation and transalkylation of C_9 or higher aromatic hydrocarbons because of its pore size limitation. Mordenite and zeolite Y have better performance in the conversion of C_9+ aromatics to BTX.

1.1 Literature Review

Transalkylation and disproportionation are the two main processes for the conversion of aromatics by alkyl group transfer reactions, especially for the production of dialkylbenzenes. Transalkylation process provides conversion of toluene and heavy aromatics, for example C_9 alkylbenzenes, to xylenes, while disproportionation reaction yields benzene and xylenes using toluene as a feed. The mixed xylene yields produced by conventional transalkylation and disproportionation processes are strictly controlled by thermodynamic equilibrium isomer distribution. Since the thermodynamic equilibrium xylene yield is known to increase with increasing feed methyl-to-ring ratio, transalkylation reaction is more favorable than toluene disproportionation especially in terms of the demand of xylenes over benzene and the availability of excessive heavy aromatics [4]. Developments of cost effective transalkylation process tend to aim at the utilization of heavy aromatics which possess high methyl-to-ring ratio. This in turn, promotes the thermodynamic equilibrium xylene yields and also the feed cost is lowered.

Zeolites that possess 12 membered ring pore aperture, including beta [5,6], mordenite [7] and USY [8] are the potential solid acid catalysts for conversion of alkylbenzenes. The major problem associated with heavy aromatics feed is that it contains catalyst poisoning components, which deactivate the catalyst due to coke formation and hence its efficiency and cycle length are reduced. It has been reported that the coke formed during toluene disproportionation over USY is mostly polyaromatic in nature, and its structures depend on the reaction temperature; the higher the temperature the more condense rings are formed during coking [9]. A probable solution to resolve the aging problem during heavy aromatics processing is to incorporate metals into the zeolite catalyst to hydrogenate polyaromatics coke precursors. Different zeolites incorporated with various metals (Cu, Ni, Pt, etc.) have been studied for transalkylation [6,7,10-12].

Roger et al. [13,14] studied the conversion of 1,2,4-trimethylbenzene over amorphous silica-alumina and HZSM-5 in gas phase. It was concluded that paring reaction played a decisive role during the conversion over H-ZSM-5 at elevated temperature (450 °C) and in the reaction sequence; xylenes and TeMBs were produced as intermediates. Over both silica-alumina and H-ZSM-5, isomerization of 1,2,4-TMB to 1,2,3-TMB and 1,3,5-TMB were found to be the fastest reaction having 90% selectivity. This reaction was believed to occur on the external surface of the zeolite crystals. They also reported that over silica-alumina, the reaction almost terminated at the disproportionation step, whereas over H-ZSM-5, the disproportionation of 1,2,4-TMB was followed by rapid paring dealkylation of the TeMBs. Cejka and others [15] used beta, Y, L and mordenite type zeolites which exhibited significant difference in conversion. They found higher conversions of TMBs and high selectivity to xylenes and TMBs at 400 °C with Y and beta compared to other large pore zeolites (mordenite and zeolites L). Collins and co-workers [16] have reported transformation of trimethylbenzenes over Y zeolite-based catalysts. They have concluded that disproportionation reaction seems to be directly proportional to the total conversion over
most of the conversion range studied for both 1,2,4- and 1,3,5-trimethylbenzene (TMB), whereas for 1,2,3-TMB, isomerization was much more favored than disproportionation (Figure 2). In the disproportionation reaction, the transfer of one methyl group from TMB led to the formation of equal amount of xylene and tetramethylbenzene (TeMB) isomers. It has been concluded by Matsuda and coworkers [17] that isomerization reaction of TMB were found to occur only over Bronsted acid sites, whereas both Bronsted and Lewis sites are responsible for disproportionation reaction.

![Figure 2. Reactions scheme for conversion of trimethylbenzene [15].](image)

This paper presents the results of five catalysts utilized for the conversion of heavy aromatics into xylenes. Effect of zeolite type, metal type and their concentrations on the catalytic activity is discussed and highlighted.

2.0 EXPERIMENTAL

2.1 Catalysts Preparation

Five catalysts were used in this study and are described as follows: High Molybdenum loaded mordenite based catalyst (HMo-MOR), Low Molybdenum loaded mordenite based catalyst (LMo-MOR), Rhenium loaded mordenite based catalyst (Re-MOR), 3%Molybdenum-3%Cerium loaded USY based catalyst (3Mo-3Ce-USY), and 5%Molybdenum-5%Cerium loaded USY based catalyst (5Mo-5Ce-USY). The zeolite mordenite and USY were acquired from Tosoh Chemicals, Japan. Alumina binder AP# was obtained from Chemicals and Catalysts Industries Company, Japan. All catalysts were prepared in extrudate form and the metal loading was performed by impregnation method.

Mo-MOR was prepared by the following method: Alumina binder was dispersed in deionized water and added with Mordenite zeolite (HSZ-690HOA), mixed and kneaded well. The kneaded material was converted into 1.5 mm extrudates. The ratio of mordenite zeolite to AP3 was 2:1. The extrudates were dried and calcined. The extrudates were impregnated with Mo to achieve 3 wt% loading. The extrudates were again dried and calcined. In case of LMo-MOR, the procedure was similar to HMo-MOR catalyst except molybdenum loading was 1%. Re-MOR was prepared in the similar way using the same type of materials as Mo-MOR catalysts except the metal loaded was 0.5 wt% rhenium. 3Mo-3Ce-USY was prepared by the following method. The alumina binder was dispersed in deionized water, added with USY (HSZ-370HUA), mixed, kneaded well, converted into 1.5 mm extrudates, dried at 120 ºC and calcined at 500 ºC for 2 hours. The extrudates were impregnated sequentially with 3 wt% Mo.
and 3 wt% Ce using hexaammonium heptamolybdate tetrahydrate and cerium nitrate hexahydrate salts. The resulting catalyst was dried and calcined. 5Mo-5Ce-USY was prepared in the similar way using the same type of materials as 3Mo-3Ce-USY catalysts except the Mo and Ce metal loading was 5 wt% each.

2.2 Characterization
These catalysts were characterized for surface area and porosity characteristics using NOVA 1100 system. The degassing temperature for each catalyst was 250 ºC maintained for 10 min under helium atmosphere. After cooling, nitrogen gas was adsorbed and then desorption process was started. At the end of the run, the system performed the necessary calculations and results were obtained.

2.3 Catalytic Evaluation
All five catalysts were evaluated for transalkylation reactions. These catalysts were reduced under hydrogen gas flow prior to catalytic reaction. The catalysts were evaluated in fixed-bed reaction system in the temperature range 340 to 440 ºC at 1.0, 1.5 and 3.3 LHSV using the aromatic feedstock containing 95% C\textsubscript{9} aromatics. The liquid reaction products were analyzed using a gas chromatography based PIONA Analyzer.

3.0 RESULTS AND DISCUSSION
3.1 Characterization
The surface area and porosity characteristics values for all five catalysts are given in Table 1. The results indicated higher surface area for USY-based catalysts as compared to mordenite-based catalysts. This is because the USY zeolite obtained from Tosoh Chemicals in powder form has a surface area of 640 m\textsuperscript{2}/g while modenite has 420 m\textsuperscript{2}/g. Following the similar trend, USY-based catalysts have higher total pore volumes and average pore radii.

3.2 Catalytic Evaluation
The catalytic results obtained for converting C\textsubscript{9}+ into C\textsubscript{6}, C\textsubscript{7} and C\textsubscript{8} were evaluated. Figure 3 shows C\textsubscript{9} conversion obtained as a function of temperature at 1.5 LHSV. C\textsubscript{9} conversion was observed increasing with increase in reaction temperature. Mordenite-based catalysts exhibited higher C\textsubscript{9} conversion as compared to USY-based catalysts. The plot revealed that at 1.5 LHSV and 30 bar hydrogen pressure and reaction temperature of 400 ºC, Mo-MOR exhibited 69% C\textsubscript{9} conversion and 58% xylene selectivity.

Table 1. Surface area and Porosity of Catalysts.

<table>
<thead>
<tr>
<th>Catalyst Designation</th>
<th>Surface Area (m\textsuperscript{2}/g)</th>
<th>Total Pore Volume (cc/g)</th>
<th>Average Pore Radius (Angstrom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HMo-MOR</td>
<td>389</td>
<td>0.36</td>
<td>16.6</td>
</tr>
<tr>
<td>LMo-MOR</td>
<td>381</td>
<td>0.31</td>
<td>16.5</td>
</tr>
<tr>
<td>Re-MOR</td>
<td>384</td>
<td>0.31</td>
<td>16.4</td>
</tr>
<tr>
<td>3Mo-3Ce-USY</td>
<td>503</td>
<td>0.59</td>
<td>23.4</td>
</tr>
<tr>
<td>5Mo-5Ce-USY</td>
<td>437</td>
<td>0.49</td>
<td>22.5</td>
</tr>
</tbody>
</table>

Figure 4 shows C\textsubscript{9} conversion plots obtained using five catalysts as a function of reaction temperature in the range 340 to 440 ºC at 3.3 and 1.0 LHSV. C\textsubscript{9} conversion was observed increasing with reaction temperature and decreasing space velocity. Both plots indicated that Mo-MOR exhibited higher C\textsubscript{9} conversion as compared to Re-MOR catalyst at 3.3 and 1.0 LHSV. The plot exhibited that Mo-MOR exhibited 70% C\textsubscript{9} conversion at 3.3 LHSV and 440
°C, which is similar to C9 conversion at 1.0 LHSV and 400 °C.

Figure 3. C9 conversion as a function of reaction temperature at 30 bar hydrogen pressure and 1.5 LHSV.

Figure 4. C9 conversion as a function of reaction temperature at 30 bar hydrogen pressure.

Figure 5 shows two plots of xylenes selectivity and p-xylene selectivity as a function of temperature for all five catalysts at 1.5 LHSV. Xylenes selectivity was found increasing with reaction temperature at all space velocity. At 1.5 LHSV, xylenes selectivity and p-xylene selectivity of Re-MOR is slightly better than Mo-MOR catalyst. Xylenes selectivity and p-xylene selectivity of 3Mo-3Ce-USY and found better than 5Mo-5Ce-USY catalysts probably due to less metal loading. This trend is also reflected in Figure 6 that shows higher xylenes selectivity of Mo-MOR compared to Re-MOR at 3.3 LHSV in the temperature range 340 to 440 °C.

Figure 5. Xylenes and p-xylene selectivity as a function of reaction temperature at 30 bar
hydrogen pressure.

**Figure 7** shows that the concentration of $C_{10}$ and $C_{11}^+$ in the reaction products obtained at 1.5 LHSV and were found lower for mordenite-based catalysts compared to USY-based catalysts. This is because mordenite does not facilitate formation of higher aromatics due to its unique pore size and structure as compared to USY.

**Figure 8** shows the benzene and toluene concentration in the reaction products at 1.5 LHSV and 30 bar hydrogen pressure. Benzene and toluene concentrations were observed higher for mordenite-based catalysts as compared to USY-based catalysts. This is because of the higher pore size and three-dimensional pore structure of USY zeolite.

**Figure 8** exhibited ethylbenzene concentration obtained at 30 bar hydrogen pressure and 1.5 LHSV in the temperature range 340 to 400°C. An interesting trend was observed for EB concentration associated with the type of zeolite used in the catalyst preparation. The EB concentration increased with rise in temperature for USY-based catalysts while decreased for mordenite-based catalysts with increase in temperature. EB concentration was observed lower for mordenite-based catalysts compared to USY-based catalysts.

![Figure 6. Xylenes selectivity as a function of reaction temperature for two catalysts at 30 bar hydrogen pressure and at 3.3 LHSV.](image1)

![Figure 7. $C_{10}$ and $C_{11}^+$ concentration obtained at 30 bar hydrogen pressure and 1.5 LHSV in the temperature range 340 to 400°C.](image2)
Figure 8. Benzene and toluene concentration at 30 bar hydrogen pressure and 1.5 LHSV in the temperature range 340 to 400 °C.

Figure 9. Ethylbenzene concentration obtained at 30 bar hydrogen pressure and 1.5 LHSV in the temperature range 340 to 400 °C.

CONCLUSIONS
Following conclusions were drawn from this study:

1. All five catalysts exhibited increase in C9 conversion and xylene selectivity with increase in temperature and decrease in space velocity.
2. High molybdenum loading (HMo-MOR) provided higher C9 conversion as compared to low molybdenum loading (LMo-MOR).
3. Mordenite-based catalysts offered a number of advantages over the USY-based catalysts which include higher C9 conversion, higher xylenes selectivity, and reduced C10+ and ethylbenzene production, whereas the disadvantages are higher yield of benzene and toluene.
4. The results revealed that very high loadings of metals on the catalysts decreased C9 conversion.
5. It was determined that for the conversion of C9 aromatics to xylenes, mordenite zeolite based catalysts performed better than USY.
6. Mo loaded mordenite based catalysts performed better in terms of higher C9 conversion as compared to Re loaded catalyst.
7. The EB concentration increased with rise in temperature for USY-based catalysts while decreased for mordenite-based catalysts with increase in temperature. EB concentration was observed lower for mordenite-based catalysts compared to USY-based catalysts.
8. Benzene and toluene concentrations were observed higher for mordenite-based catalysts as compared to USY-based catalysts.
9. The concentrations of C_{10} and C_{11+} were found lower for mordenite-based catalysts as compared to USY-based catalysts.

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