TRANSALKYLATION OF HEAVY AROMATICS FOR ENHANCED XYLENE PRODUCTION

EFFECT OF METAL TYPE AND CONCENTRATION ON THE C9 CONVERSION AND XYLENE SELECTIVITY

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ABSTRACT
These catalysts designated as catalyst-A, catalyst-B, and catalyst-C prepared and supplied by the Nippon Oil Research Institute Co., Ltd. Tokyo, Japan were used in this study. The overall C9 aromatics conversion activity and xylene selectivity for catalysts A was observed higher than catalysts B and C. The overall results show that the C9 aromatics conversion and xylene selectivity was found increasing with increase in reaction temperature and was further increased by optimizing the Mo contents. As the space velocity was increased keeping the reaction temperature constant, the percent concentration of C6 to C8 aromatics was decreased, and C9 aromatics conversion was decreased while the xylene selectivity showed an increasing trend for both Mo-loaded and Re-loaded catalysts. Ethylbenzene was found slightly increased with increase in space velocity, but decreased with increase in reaction temperature. At higher space velocity of 3.3 and reaction temperature of 440 ºC, the C9 aromatics conversion was 70% while the xylene selectivity was 54%. The data analysis showed that at LHSV of 1.5 and reaction temperature of 420 ºC, Catalyst-A showed 71% C9 aromatics conversion and 56% xylene selectivity. The results also indicated that at reaction temperature of 400 ºC and LHSV of 1.0, catalyst-A exhibited 70% C9 aromatics conversion and 57% xylene selectivity. Re-loaded catalyst showed higher amount of gas formation compared to Mo-loaded catalyst showing significant demethylation activity. Mo-loaded catalysts performed better in terms of higher C9 Aromatics conversion and low hydrogen consumption as compared to Re-loaded catalyst. The formation of higher aromatics was also reduced due to the specific pore size and pore structure of mordenite.

INTRODUCTION
Transalkylation is the process that converts low-value toluene and heavy aromatics into value-added mixed xylenes. Transalkylation technologies have been developed by a number of companies including UOP, ExxonMobil, Toray, and SK Corporation. A joint research effort has been started to develop catalyst systems for transalkylation of heavy aromatics for enhanced xylene production. This is a joint program between Nippon Oil Research Institute Co., Japan and King Fahd University of Petroleum & Minerals (KFUPM), Saudi Arabia. The objective of this program is to develop novel catalytic systems for efficient conversion of heavy aromatics, improved xylene selectivity, reduced higher aromatics (C10-C12) formation and lower gas formation.
Transalkylation processes use silica-alumina and zeolites such as dealumined mordenite, ultra stable Y-zeolite (USY) and ZSM-12 [Tsai et al. 2002]. Nippon Oil Corporation has demonstrated a new technology for the production of mixed xylenes via the transalkylation of benzene and C₉ aromatics [Stachelczyk 2000; Boon et al. 2002]. 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 C₉ aromatics conversion activity with less deactivation and higher selectivity to mixed xylenes.

The Advanced Transalkylation (ATA) process uses a catalyst developed by SK Corporation to produce high xylenes from the transalkylation of C₉+ aromatics. The catalyst is based on platinum-promoted mordenite manufactured by Zeolyst International. Platinum was used for its hydrogenation function along with tin or lead to control the hydrogenating activity [Boon, et al. 2002]. 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 C₉+ aromatics increased in the feed, the TDP reaction was suppressed and hence the toluene conversion and benzene yield decreased while mixed xylenes yield increased.

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 (C₉A+) into mixed xylenes and specifically para-xylene.

During the process of xylene production, a number of reactions such as disproportionation, transalkylation, and dealkylation take place (Figure 2). The methyl groups are shifted from one benzene ring to the other via disproportionation and transalkylation 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_{10+}) are involved in the transalkylation reaction; only large-pore zeolites are able to catalyze this reaction. 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, nickel, bismuth, chromium, cobalt, copper, iron, 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 not suitable for disproportionation and transalkylation of C9 or higher aromatic hydrocarbons because of its pore size limitation. ZSM-5 has demonstrated its use in the isomerization of mixed xylenes to increase para-xylene contents.

Catalyst stability is one of the main issues in the transalkylation catalyst development because coking occurs rapidly as a consequence of the high content of aromatics in the feed. Some of the licensed transalkylation technologies cannot process heavy aromatics alone primarily due to the adverse impact on catalyst life. In most industrial processes, the cost of catalyst deactivation is very high and mastering catalyst stability has become as important task.

**EXPERIMENTAL**

**Catalyst Configuration and Catalytic Evaluation**

Three catalysts were used in this study which are designated as catalyst-A (Medium Mo-content mordenite catalyst), catalyst-B (low Mo-content mordenite catalyst) and catalyst-C (Re-loaded mordenite catalyst). These catalysts were prepared and supplied by the researchers at the Nippon Oil Research Institute Co., Japan. These catalysts were characterized for surface and porosity characteristics. The 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 °C and LHSV in the range 1.0 to 3.3 using the aromatic feedstock containing 95% C_{9} aromatics. The reaction products were analyzed using a gas chromatographic based PIONA Analyzer.

**RESULTS AND DISCUSSION**

The data analysis revealed that at LHSV of 1.5 and reaction temperature of 420 °C, Catalyst A showed 71% C_{9} aromatics conversion and 56% xylene selectivity. The results also indicated that at reaction temperature of 400 °C and LHSV of 1.0, catalyst A exhibited 70% C_{9} aromatics conversion and 57% xylene selectivity. For catalysts A, the overall C_{9} aromatics conversion activity and xylene selectivity was observed higher than catalysts B and C. The overall results show that the C_{9} aromatics conversion and xylene selectivity was found increasing with increase in reaction temperature and was further increased by optimizing the Mo contents. However, too
high metal contents on the catalysts were found to have adverse effect on the conversion and xylene selectivity. As the space velocity was increased keeping the reaction temperature constant, the percent concentration of C$_6$ to C$_8$ aromatics was decreased, and C$_9$ aromatics conversion was decreased while the xylene selectivity showed an increasing trend for both Mo-loaded and Re-loaded catalysts. This is evident from the plot of LHSV vs liquid product composition at 400 °C reaction temperature for catalyst-A and catalyst-B given in Figures 3 and 4. Ethylbenzene was found slightly increased with increase in space velocity (Figure 5). At higher space velocity of 3.3 and reaction temperature of 440 °C, the C$_9$ aromatics conversion was 70% while the xylene selectivity was 54%. Re-loaded catalyst showed higher amount of gas formation compared to Mo-loaded catalyst showing greater demethylation activity. Mo-loaded catalysts performed better in terms of higher C$_9$ Aromatics conversion and low hydrogen consumption as compared to Re-loaded catalyst. The formation of higher aromatics was also lowered due to the specific pore size and structure of mordenite.

![Figure 3. Effect of space velocity on the product composition (Mo-loaded catalyst)](image-url)
CONCLUSIONS  
The gas components in the gas products of all three catalysts show the following trends of concentration: C2 > C3 > C4 > C1. The liquid components has xylene concentration in the following trend: metaxylene > paraxylene > orthoxylene. Total C10 and C11 were found decreasing with increase in reaction temperature.

The data analysis revealed that catalyst-A possesses the best activity in terms of higher C9 aromatics conversion, higher xylene selectivity and lower gaseous components formation. Lowering the metal contents on the catalyst (catalyst-B) decreased the C9 aromatics conversion.
Comparatively for catalysts-A, the overall C9 aromatics conversion activity and xylene selectivity was observed higher than catalyst C.

Re loaded catalyst-C showed higher amount of gas formation and methane was observed to be a component of the gas product showing relatively higher undesirable demethylation activity.

The gaseous components include methane, C2 and C3 components which are break apart from ethylbenzene, propylbenzene and methyl substituted ethylbenzene and propylbenzene. Methane was a minor component detected and thus all the catalysts do not showed undesirable demethylation activity.

With increase in reaction temperature, the C9 aromatics conversion and the toluene contents were found increasing, while the xylene selectivity was remains almost constant for all three catalysts. The ethylbenzene was found decreased with increase in reaction temperature.

The liquid space velocity was found to have inverse relation with the conversion as expected. At high space velocity, the C9 aromatics conversion was decreased while the xylene selectivity remained same at all space velocities. The ethylbenzene concentration was found slightly increased with increase in space velocity but decreased with increasing reaction temperature.

Mo loaded catalysts performed better in terms of higher C9A conversion and low hydrogen consumption as compared to Re loaded catalyst.

The overall results shows that the C9 aromatics conversion and xylene selectivity was observed higher with increasing Mo contents. However, too high metal contents on the catalysts were found to have adverse effect on the conversion and xylene selectivity.

ACKNOWLEDGEMENT
The authors appreciate and acknowledge the support of the Japan Cooperation Center, Petroleum (JCCP), with the subsidy of the Ministry of International Trade and Industry, Japan, and King Fahd University of Petroleum & Minerals, Dhahran, Saudi Arabia, for this work under the Joint Saudi-Japanese Joint Research Program.

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