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## Investigating zeolite catalysts toward isomerization of Xylenes

Armin Mirchi<sup>1</sup>, Mohammad Kazemeini<sup>\*2</sup>, Saeed Soltanali<sup>3</sup>, S. Reza Seif Mohaddecy<sup>4</sup>

<sup>1</sup> PhD. Student, Department of Chemical and Petroleum Engineering, Sharif University of Technology, Tehran, Iran

<sup>2</sup> PhD. Professor, Department of Chemical and Petroleum Engineering, Sharif University of Technology, Tehran, Iran

<sup>3</sup> PhD. Associate Professor, Catalyst Technology Development Division, Research Institute of Petroleum Industry, Tehran, Iran

<sup>4</sup> MSc. Instructor, Catalyst Technology Development Division, Research Institute of Petroleum Industry, Tehran, Iran

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### 1. ABSTRACT

Given the importance and high demand for para-, meta-, and ortho-xylenes, they are isomerized to produce para-xylene in xylene isomerization units. Amongst different catalysts used in this process, zeolites with medium pore size show high efficiency due to their unique shape-selective properties, which further are significantly important in reducing xylene loss as well. Moreover; numerous methodologies have been investigated to enhance catalyst efficiency in the xylene isomerization reaction, increase para-xylene yield, and reduce xylene loss. In this context, several surface modification methods, such as chemical liquid deposition of silica, dealumination, and pre-coking through passivating non-selective acidic sites on the external surfaces of catalysts, lead to reduced xylene loss and increased para-selectivity, rather effectively. On the other hand, using different structures of zeolites and metallic components, as well as hierarchical structures has proved effective in improving the performance of the xylene isomerization process. This article examines the most significant studies conducted to develop optimal catalysts for the xylene isomerization process, aiming to increase paraxylene productivity and minimize xylene loss.

**Keywords:** Xylene Isomerization, MFI Zeolite, Shape-Selectivity, Surface Modification Methods, Hierarchical Structures.

### 2. INTRODUCTION

Global demand for benzene, toluene, and xylenes (BTX) is ever-increasing with the rise of population and their developed needs for textiles and packaging materials. The global market for xylene mixtures is estimated at 67.3 million tons in 2023 and is expected to reach 89.9 million tons by 2030. In this context, Fig. 1 displays a global supply-demand as well as operating rates for BTX aromatics production. Amongst them, paraxylene is known as the most important isomer in xylene mixtures due to its multiple applications, accounting for more than 90% of the global xylene demand in 2023 [1]. To meet the high demand for paraxylene, Meta- and ortho-isomers are further isomerized into paraxylene through the xylene isomerization process due to a relatively lower demand for them. On the other hand, during xylene isomerization, several side reactions can reduce the yield of paraxylene and lead to xylene loss. Therefore, in general, paraxylene yield, xylene loss, and ethylbenzene conversion are key parameters for evaluating the performance of the xylene isomerization unit [2].

On the other hand, zeolites, due to their high specific surface area, large pore volume, uniform micropore channels, and high thermal stability, are widely used as catalysts in industrial processes such as petroleum refining and the production of valuable chemicals. In the past decades, several zeolite catalysts have been developed for the isomerization of C<sub>8</sub> aromatics, including ZSM-5, Beta, MOR, ZSM-12, EU-1, SSZ-33, and TNU-9 [3].

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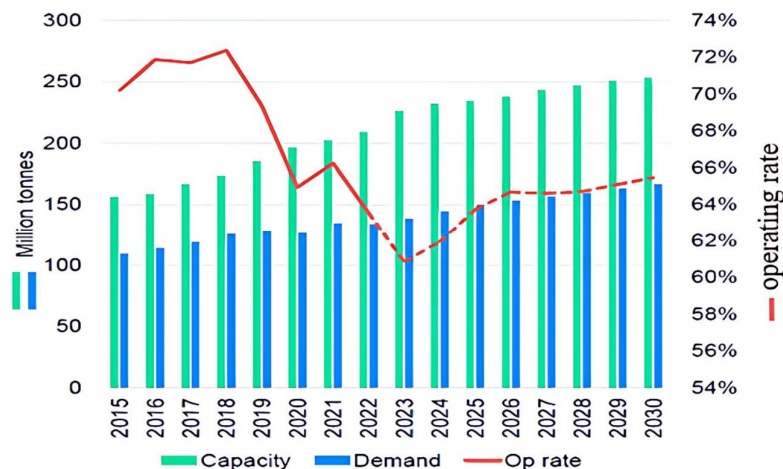


Figure 1. Global supply, demand, and operating rate for BTX aromatics [1].

### 3. MATERIALS AND METHODS

In the current study, these researchers aimed at achieving the optimal catalyst for the xylene isomerization process to maximize para-xylene yield and minimize xylene loss as well as; tried to show the effect of operating conditions, considering different supports and metals utilized for such a process. Surface modification methods and hierarchical structures have also been investigated to improve the process performance.

### 4. RESULTS AND DISCUSSION

#### 4.1. Operating conditions

It is reiterated that increasing the temperature, pressure, and hydrogen-to-hydrocarbon ratio, as well as decreasing the WHSV shall lead to enhanced para-xylene production. In this venue however; the xylene loss will also be raised as well [4].

#### 4.2. Surface modification methods

It is well accepted that various surface modification methods, including silanization, dealumination, pre-coking, and selective poisoning, increase para-selectivity and reduce xylene loss by selectively deactivating acidic sites on the external surface which are indeed responsible for side reactions. Therefore, using two or more surface modification methods together may lead to improved efficiency of the xylene isomerization process.

#### 4.3. Different supports and metals

To achieve the optimal catalytic composition in the xylene isomerization process, various zeolite supports, metals, and promoters have been understudied. The zeolite structures undertaken included ZSM-5, ZSM-12, Beta, MOR, and ZSM-50, while the metals examined comprised platinum, palladium, nickel, molybdenum, rhodium, and rhenium.

#### 4.4. Zeolites with hierarchical structure

The incorporation of mesopores alongside micropores in the structure of zeolites—known as hierarchically structured zeolites—enhances mass transfer. However, the introduced mesopores reduce para-selectivity by creating additional acidic sites on the external surface, due to the lack of shape-selectivity. To increase para-selectivity while preserving the mesoporous structure and high catalytic activity, a promising approach is the selective deactivation of acidic sites on the external surface [5].

### 5. CONCLUSION

Achieving optimal performance in the xylene isomerization process with the aim of maximizing para-xylene production to meet its high demand, as well as, preventing xylene loss remains a significant challenge. In this study, various strategies for optimizing the catalyst have been investigated, including the effects of operating conditions, surface modification methods, different supports, and metals, as well as hierarchical zeolite structures. Amongst the studied materials, ZSM-5 zeolite has demonstrated superior performance due to its unique shape-selectivity, high activity, and thermal stability, which collectively contribute to minimized xylene loss and effective separation of para-xylene from other bulkier isomers. Furthermore, the application of surface modification techniques such as silanization, dealumination, and pre-coking, either individually or in combination, along with the incorporation of hierarchical structures, has proven to be an effective approach toward enhancing para-selectivity and reducing xylene loss.

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