



ISOMERIZATION OF M-XYLENE OVER THE MODIFIED NATURAL MORDENITE

Aytan Zakir Mamedova, Iman Ali Gurbanli

Azerbaijan State Oil and Industry University

E-mail: ayten1551@mail.ru

In the temperature range of 300-400 °C in a fixed bed continuous flow type quartz reactor in the presence of hydrogen, the regularities of the transformation of m-xylene in the presence of H- and cationic forms of natural mordenite modified with transition metals were studied. It is shown that in the presence of H-mordenite, m-xylene undergoes isomerization to p- and o-xylenes in approximately equal amounts. Paraselectivity of the catalyst is 53.3%. Transition metal cations (Gd^{3+} , Ni^{2+} , Mn^{2+}) exerting a promoting effect directs the transformation of m-xylene towards the formation of p-xylene, which leads to an increase in the paraselectivity of the catalyst. The maximum paraselectivity (77.6%) is achieved over the 0.74 Ni-mordenite at 450 °C.

Keywords: natural mordenite, isomerization, Mn, Ni, Gd, xylenes, paraselectivity

INTRODUCTION

Xylenes, especially n-xylene, are valuable semi-products of petrochemistry and can be used for production of the terephthalic acid, polyethylene terephthalate, fibers, plasticizers, and other valuable products [1-4]. The main source of xylenes production is aromatic fraction of hydrocarbons that is generated by catalytic reforming and cracking of petroleum distillates. For an additional resource increase of n-xylene, isomerization of m-xylene on zeolite-containing catalysts at atmospheric pressure and under hydrogen pressure in the temperature range of 425-485 °C is important [5-8]. Halloysite, MCM-41, mordenites, high silica zeolites, such as ZSM-5 act effectively in the isomerization of the xylenes.

Recently, catalysts of natural zeolites are of great importance in the transformation of the alkyl-aromatic hydrocarbons. We have lots of reserves of these minerals, and physiochemical properties allow to replace expensive synthetic zeolites.

Specific and unique properties of natural zeolites, also possibility of modifying them by ion exchange with transition metal cations, stimulates works focused on the development of new effective catalyzers (based on natural zeolites) and transformation of the alkyl-aromatic hydrocarbons.

The purpose of this work is to study patterns of transformation of m-xylene over the natural mordenite modified by transition metal cations.

MATERIAL AND METHODS

The natural zeolite mordenite ($SiO_2 / Al_2O_3 = 8.68$) from the Chananab deposit of the Republic of Azerbaijan was used to prepare the catalysts. Modification of natural mordenite was carried out by ion exchange. Mordenite by ion exchange with a 1 N solution of NH_4Cl was transferred to NH_4 -shape. For conversion to H-form NH_4 -the zeolite form was calcined at 550 °C within 4 hours [6].

Cationic forms of mordenite were obtained by triple ion exchange of the initial zeolite with 2% solutions of gadolinium, manganese and chromium nitrates at pH = 4.5-6.7 and a temperature of 80 °C. One stage lasted 2 hours. After completion of the ion exchange, the zeolite was washed with distilled water until the absence of NO_3^- ions, dried in air (14 h), in an oven at 110 °C (4 h), and calcined in a muffle furnace at 350 °C and 550 °C respectively 2 hours. The degree of ion exchange in the zeolite for cations was, % (eq.) Gd - 78; Mn - 70, Ni - 74.

The experiments were carried out in a fixed bed reactor (4 cm^3) in the temperature range $300\text{--}450^\circ \text{C}$, m-xylene transfer volume rate equal to 1.0 h^{-1} , pressure 1.0 atm . The molar ratio of hydrogen: xylene = 3:1. The reaction products were analyzed by chromatographic method.

RESULT AND DISCUSSION

Isomerization of m-xylene enhanced by the presence of H and cation forms of natural mordenite shows different outcomes based on the temperature dependence of reaction. H form was preferably experienced the selectivity between $300\text{--}350^\circ \text{C}$. Respective total conversion of m-xylene to p- and o- xylene fluctuates between 16.7 - 24.6 wt. %. Temperature growth up to 452°C enhances total conversion to 36 %. Temperature grows from 300 to 450°C conversion percentage of p-xylene increases from 8.2 to 19.2 wt. % and from 7.9-16.8% for o-xylene (Fig.1).

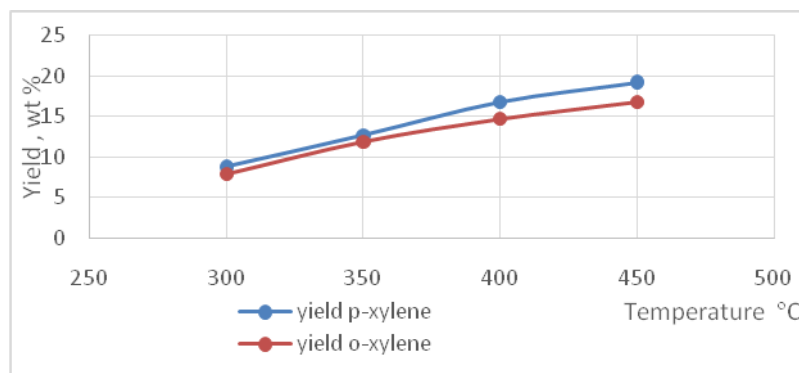


Fig. 1. Temperature Dependence of p-xylene and o-xylene yield during isomerization of m-xylene over 0.83 H Mordenite

Zeolite type mordenite containing transition metal of Gd demonstrates the intensive involvement over the isomerization of m-xylene. General observation is more based on the enhancement of p-xylene conversion rate during the application of previously indicated catalyst. Additionally, convenient temperature gap for proper implementation of this catalyst stands for $300\text{--}450^\circ \text{C}$ interval. Conversion of p-xylene for that special condition accounts for 14.8-24.8 wt. % (Fig.2). Among the liquid products, amount of o-xylene floats near to 9 % (8.7-9.7 %).

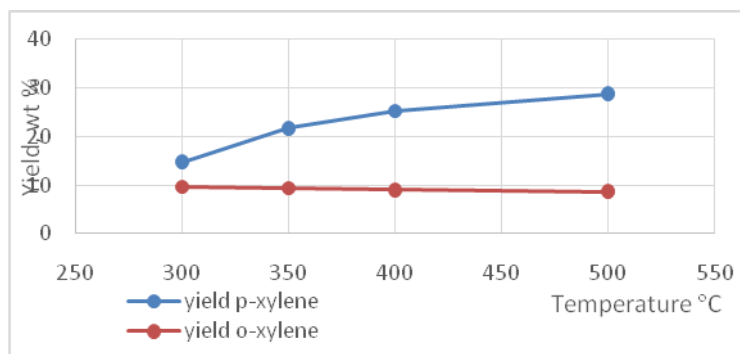


Fig. 2. Temperature dependence of p-xylene and o-xylene over 0.78 Gd Mordenite

Almost the same behavior is observed via application of Ni and Mn separately based on catalyst of mordenite. 0.74 Ni Mordenite catalyst presence makes the reaction to proceed with the conversion of m-xylene to p-xylene which increases from 18.6 % to 27.7 wt. % caused by the



temperature growth from 300 to 450° C. The same catalyst activity towards the formation of o-xylene from isomerization of m-xylene is non-critical because it increases the conversion rate from 7.2 to 8 wt. % (Fig.3).

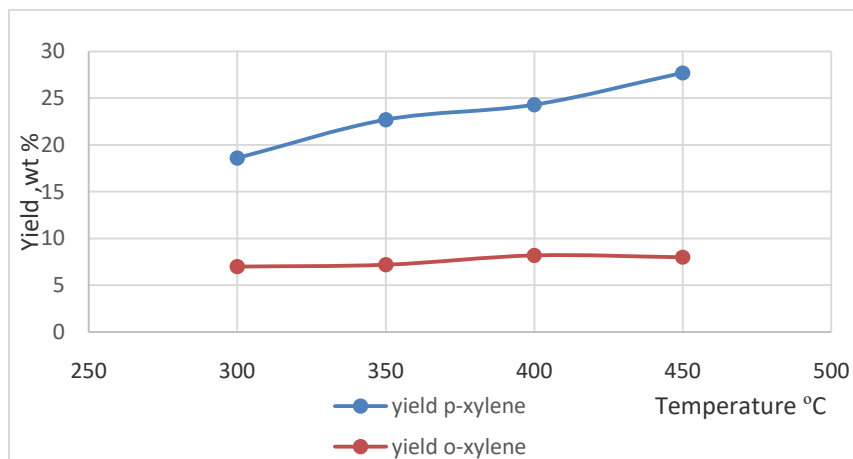


Fig. 3. Temperature Dependence of p-xylene and o-xylene over 0.74 Ni Mordenite

In comparison with 0.78 Gd Mordenite and 0.74 Ni – mordenite catalysts, 0.70 Mn - mordenite catalyst demonstrates slightly lower activity towards isomerization of m-xylene. Application of 0.7 Mn Mordenite makes it possible to rise the conversion of m-xylene to p-xylene in temperature rate 300-450°C to 11.3-21.2 wt. %, yield of o-xylene constitutes 3.2- 8.2 wt. % (Fig.4). The main driving force observed is the presence of modifications on process parameters of which temperature is the most important. It is obvious from the obtained results that unmodified H-mordenite presence makes it possible to convert m-xylene to the direction of production of p and o-xylene. Selectivity between o and p – xylene production is differed by the application of cationic form of mordenit which favor direction of p-xylene formation.

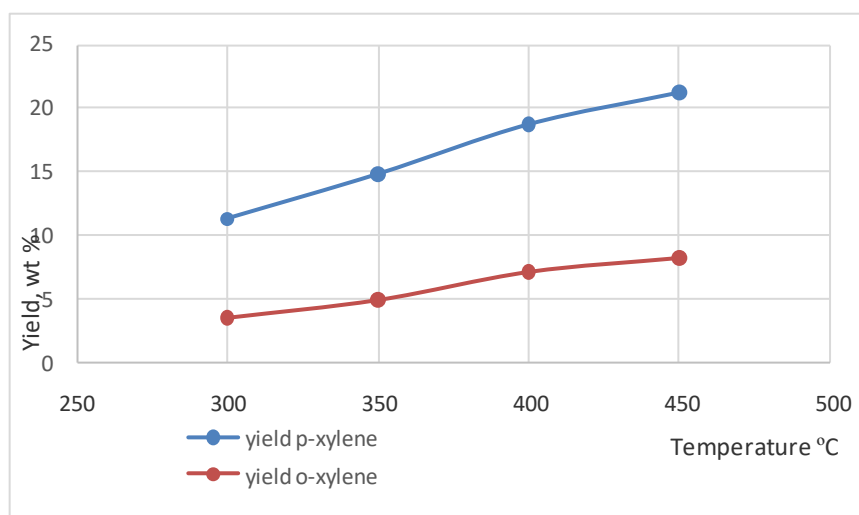


Fig. 4. Temperature Dependence of p-xylene and o-xylene over 0.70 Mn Mordenite

Figure 5 below shows the activity and selectivity of different catalysts in 450°C on o and p – xylene production on mass basis.

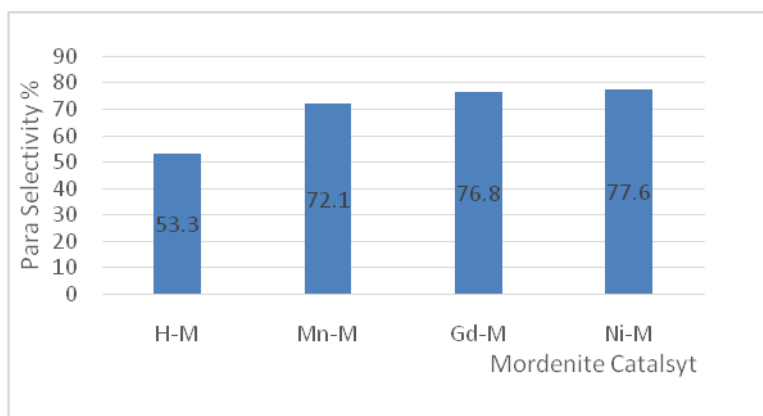


Fig. 5. Para Selectivity % for different mordenite catalysts

Based on the selectivity analysis, it is obvious that modified version of mordenites with transition metal group representatives make the p-xylene conversion enhancement from the isomerization of m-xylene. Least favorable behavior is observed for H-mordenite application 53.3 % for isomerization of m-xylene whereas most desirable activity involved utilization of Ni based catalyst (77.6 %). The order of para selectivity could be arranged in the following way based on the recent outcomes:

Ni- mordenite > Gd- mordenite > Mn-Mordenite > H-mordenite.

Eventually, application of natural mordenite cation forms shows a great selectivity towards for m-xylene isomerization. Together with this, they also demonstrate great compatibility on governing maximum paraxylene production amount.

CONCLUSION

Stated work includes the investigation of conversion of m-xylene into value added p and o-xylene species with the help of synthesized forms of mordenites combined with H and transition metals. Together with advances on conversion, chemical and catalytic characteristics of mentioned type mordenite catalysts were determined for creating large question mark on applicability of them into new processes. It was found out that p-xylene formation from isomerization of m-xylene was enhanced by the use of zeolite type H-modernite catalysts. Moreover, applying different sources of catalyst being as modified versions of mordenites with transition metals conversely helped to maximize the conversion of m-xylene not only to p-xylene but also to o-xylene. Among transition metal type mordenite catalysts, combination with Ni showed the greatest activity on conversion of m-xylene to p-xylene with enhanced selectivity being as 77.6 %.

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MODİFİKASIYA OLUNMUŞ TƏBİİ MORDENİTİN İŞTRAKINDA M-KSİLÖLÜN İZOMERLƏŞMƏSİ

A.Z. Məmmədova, İ.Ə. Qurbanlı

300-400°C temperatur diapazonunda stasionar layda fasiləsiz axın tipli kvarts reaktorunda hidrogenin qazının axınında təbii mordenitin H- və keçid metallarla modifikasiya olunmuş kation formalarının iştirakı ilə m-ksilolun çevrilmə qanunauyğunluqları öyrənilmişdir.

Göstərilmişdir ki, H-mordenitin iştirakında m-ksilol izomerləşməyə məruz qalaraq təxminən bərabər qalaraq təxminən bərabər miqdarda para və orto ksilola çevrilir. Katalizatorun para seçiciliyi 53.3 % təşkil edir. Keçid metal kationların (Gd³⁺, Ni²⁺, Mn²⁺) mordenit zeolitinə promotorlaşdırıcı təsir göstərərək m-ksilolun çevrilməsini əsasən p-ksilolə istiqamətləndirərək onun paraseçiciliyini artırır. Maksimal paraseçicilik (77.6 %) 0.74 Ni-mordenit katalizatorunun iştirakına nail olunur.

Açar sözlər: *təbii mordenit, izomerizasiya, Mn, Ni, Gd, ksilollar, paraseçicilik*

ИЗОМЕРИЗАЦИЯ М-КСИЛОЛА НА МОДИФИЦИРОВАННЫХ ПРИРОДНЫХ МОРДЕНИТАХ

А.З. Мамедова, И.А. Гурбанлы

В интервале температур 300-400° С в проточной установке в присутствии водорода изучены закономерности превращения м-ксилола в присутствии H- и катионных форм природного морденита модифицированных переходными металлами. Показано что в присутствии H-морденита метаксилон примерно в равных количествах подвергается изомеризации в п- и о-ксилолы. Параселективность катализатора составляет 53.3%. Катионы переходных металлов (Gd³⁺, Ni²⁺, Mn²⁺) оказывая промотирующее влияние направляет превращение м-ксилола в сторону образования п-ксилола что приводит в увеличению параселективности катализатора. Максимальная параселективность (77.6%) достигается на 0.74 Ni-морденит при 450° С.

Ключевые слова: *природный морденит, изомеризация, Mn, Ni, Gd, ксилоты, параселективность*