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Preparation and characterization of template-free mordenite type zeolite and comparison of m-xylene isomerization reaction over mordenite and SAPO-11

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ABSTRACT

In this work, Mordenite zeolite was successfully synthesized with Si/Al ratio of 18 in absence of organic template. The hydrothermal method was applied for synthesis under optimum conditions: 24 h synthesis time, 180°C temperature and 2 days aging time. The obtained zeolite was characterized by X-ray powder diffraction (XRD), Brunauer-Emmett-Teller (BET), X-ray fluorescence (XRF), Fourier Transforms infrared Spectroscopy (FT-IR) and Scanning Electron Microscopy (SEM). The prepared sample had total (BET) surface area of 331.63 m^2g^{-1}, whereas total pore volume was 0.278 cm^3g^{-1}. The catalytic performance of this catalyst was investigated for meta-xylene isomerization reaction in a fixed bed reactor at the 10 bars Pressure, 380°C temperature and 3.35 h^{-1} Weight hourly space velocity (WHSV) of feed. The results compared with a commercial SAPO-11 catalyst (Si/Al = 20) and showed that the mordenite gave better Para/Ortho ratio (63%) and fewer amount of xylene loss (2.11%) compared to SAPO-11.

***Keywords**: Mordenite zeolite, Catalyst, m-Xylene isomerization, SAPO-11.*

1. Introduction

The C_8 aromatic fraction in a refinery consists mainly of four isomers, ortho-xylene (o-xylene), meta-xylene (m-xylene), para-xylene (p-xylene) and ethylbenzene [1]. The xylene mixtures result from the catalytic reforming of petroleum NAFTA and the isomers of xylenes usually obtain from this mixture by separation. After separation of the more ortho-isomers and p-isomers, the remainder that is richer from m-xylene, needs to be subjected to isomerization [2]. Xylene isomerization has received growing attention because of the increased demand for para-xylene [3]. Production of para-xylene is a petrochemical process of great importance, since its oxidation yields terephthalic acid, which is a major component in the production of polyester fibers, synthetic resins, vitamins and pharmaceuticals [4]. The xylene isomerization occurs simultaneously at the acidic sites of the catalyst [2].

Zeolites are aluminosilicates containing exchangeable cations that act as Lewis acid sites. The framework oxygen atoms of alkali exchanged zeolites bear partial negative charge and behave as Lewis base [5]. They are well known microporous materials that widely used as catalysts in the petrochemical industry because of their large surface area, high adsorption capacity, charged framework, shape selectivity and controllable acidity [6,7]. Dispersion of molecules in the zeolitic intra-crystalline space is an added advantage [8]. In addition, Zeolites are crystalline aluminosilicates containing pores and cavities of molecular dimensions [9], whose sizes can vary in the range from one to several tens of nanometers depending on the type of aluminosilicates framework, Si/Al ratio and origin of ion exchange cations, etc. [5] which leads to high surface area. Since catalysis is a surface process, the catalyst with the highest possible surface area is of great importance [9].

Heterogeneous catalysts in insoluble form have many advantages over liquid acid systems, because they cause a lower corrosion rate, ensure safer handling of the catalyst, simple catalyst regeneration [10]. The metals can support on zeolites and affecting its properties. They can be used for many reactions [11].

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Among of the various zeolites, mordenite types were found to possess better isomerization activity due to their shape selectivity, high thermal and acid stability [3,12,13]. The structure of mordenite determined by Meier in 1961 [14]. The micropore system of mordenite has a one-dimensional pore system that consists of two-pore channels, 12-membered oxygen ring channel with pore opening 6.7 × 7 Å which is interconnected to 8-membered oxygen ring channel with opening 2.6 × 5.7 Å [6,13,15]. The pore system of mordenite is shown in Fig. 1.

It has an orthorhombic crystal structure and 5-membered rings stacked in columns parallel to the [001]-direction framework [16]. Mordenite is an industrially important zeolite and also used as a solid catalyst for many reactions such as alkylation, disproportionation, trans-alkylation, hydrocracking, hydroisomerization, dehydration, steam reforming, polymerization, dewaxing and xylenes isomerization [12,17]. It also widely used in separation and purification due to its uniform, small pore size, flexible framework and high internal surface area [14]. Uni-dimensional pore system with small side-pockets of mordenite catalysts cause that they be not accessible for reactant molecules to enter and confine the free diffusion of intermediate and product molecules that make it appropriate for xylene isomerization [18].

In this work, we reported the synthesis of the mordenite type catalyst without an organic template. The prepared catalyst characterized by several methods. The catalytic performance of this catalyst was investigated for meta-xylene isomerization reaction in a fixed bed reactor and compared with a commercial SAPO-11 catalyst.

2. Experimental

2.1. Materials and equipment

SiO_2 as a source of silica, sodium aluminate as an alumina source and sodium hydroxide were purchased from Sigma-Aldrich (USA).

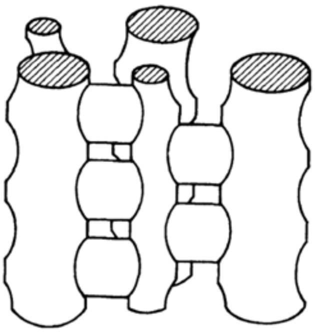

Fig. 1. The pore system of mordenite [16].

X-ray powder diffraction pattern was recorded on a FILIPS PW1800 instrument using CuK_α radiation from 4 to 90° (2θ). The SiO_2/Al_2O_3 ratio was accomplished by the FILIPS PW1480 X-ray Fluorescence Spectrometer. The surface area and pore volume of the sample were calculated using BET (JWGB K132F) equation. SEM (VEGA\\TESCAN) was used for determination of morphology and size of the synthesized mordenite with an acceleration voltage of 15.0 kV. The lattice vibration in the inorganic framework was determined with FT-IR (BomemMB). Crystallization was carried out in a Teflon coated stainless steel autoclave in a conventional oven. The analysis of products was performed using gas chromatograph (Varian 3800).

2.2. Synthesis of catalyst

Mordenite zeolite was prepared using the procedure as described in the literatures [14,19,20]. This reaction contains the following steps:

At the first, 4.75 g of NaOH was dissolved in 10 ml water and then 3.57 g of sodium aluminate was added to this solution and the mixture was stirred until dissolution. Finally, 24.55 g SiO_2 and 161.25 ml water was added and the mixture was stirred for 2 days. The molar composition of the prepared gel was 6 Na_2O: 1 Al_2O_3: 30 SiO_2: 780 H_2O. In order to crystallization of the compound, the obtained gel was transferred to a reactor made of stainless steel coated with Teflon and heated to 180°C for 24 hours. The precipitate was filtered, washed with the water until the filtrate pH reached about 9 and dried at 110°C. In order to the conversion of Na-Mordenite to H-Mordenite, the product was ion-exchanged with a 1M of NH_4NO_3 solution for 1h at 60°C. This ion-exchange procedure repeated three times and the sample calcined at 450°C.

2.3. Catalyst activity measurements

Meta-xylene isomerization was carried out in a fixed bed reactor according to the following conditions:

Pressure: 10 bars, temperature: 380°C, the amount of catalyst: Ca 4 g of H-mordenite catalyst (6-10 mm mesh), space velocity (WHSV) of feed: 3.35 h^{-1}, catalyst depth: 1.2 mm. The hydrogen gas co-feed into the reactor for hydrogenation of ethylbenzene to xylenes [21]. The catalyst was placed in the center of a stainless steel reactor and heated by a furnace. The composition of the feedstock is shown in Table 1.

The analysis of products was performed using gas chromatograph every 6h. Fig. 2 shows the catalytic setup.

Table 1. Composition of the feedstock (wt. %).

PX	MX	OX	EB	C_3	C_4	C_5	C_6^{N+P}	C_7^{N+P}	C_8^{N+P}	C_9^{A+n}	C_{10}^{A+n}	C_{11}+H	T	B
3.282	51.452	24.151	12.004	0.006	0.006	0.021	0.193	0.507	5.967	1.417	0.040	0.073	0.881	0.00

Notes: PX: p-xylene, MX: m-xylene, OX: o-xylene, EB: ethylbenzene, C_6^{N+P}: C_6 naphthenes and paraffin, C_7^{N+P}: C_7 naphthenes and paraffin, C_8^{N+P}: C_8 naphthenes and paraffin, C_9^{A+n}: C_9 Aromatic and nonaromatic, C_{10}^{A+n}: C_{10} Aromatic and nonaromatic, H: hydrocarbons, T: toluene, B: benzene.

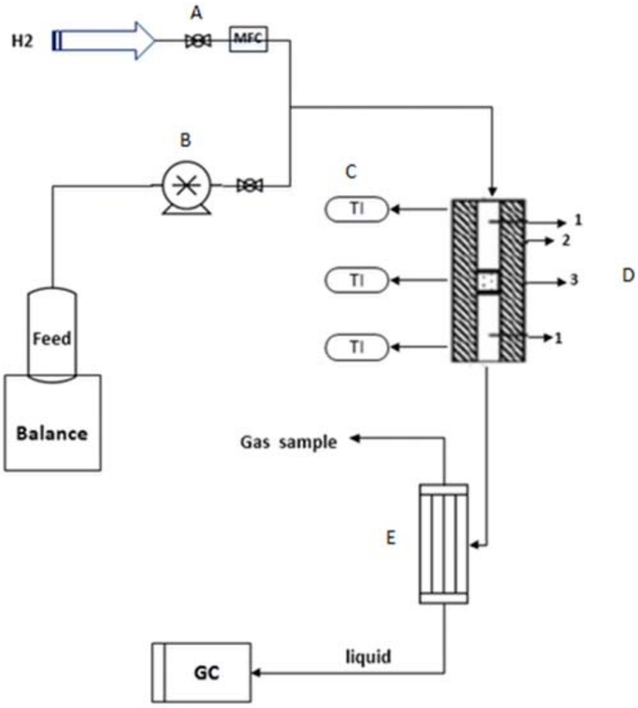

Fig. 2. The catalytic setup of m-xylene isomerization reaction (A) ball value, (B) HPLC pump, (C) temperature indicator, (D) isothermal reactor, (E) condenser, (1) quartz, (2) wool, (3) catalyst.

m-xylene conversion, p-xylene/o-xylene ratio and xylene loss were calculated according to the following equations:

MX conversion (%) = [(mass fraction of MX in a feedstock – mass fraction of MX in products) ÷ mass fraction of MX in feedstock] × 100 (1)

PX/OX (%) = (mass fraction of PX in products ÷ mass fraction of OX in products) × 100 (2)

Xylene loss (%) = {[mass fraction of (OX + MX + PX) in a feedstock – mass fraction of (OX + MX + PX) in products] ÷ mass fraction of (OX + MX + PX) in feedstock} × 100 (3)

(Mass fraction is based on wt. %)

3. Results and Discussion

3.1. FT-IR studies

Mordenite can be characterized by its infrared spectrum. FT-IR spectra of Na-mordenite sample is shown in Fig. 3. It has some main absorption regions, the peak around to 1083 cm^{-1} ascribed to the asymmetric stretching vibration of Si-O bond and another peak near to 810 cm^{-1} referring to symmetric stretching vibration of Al-O bond.

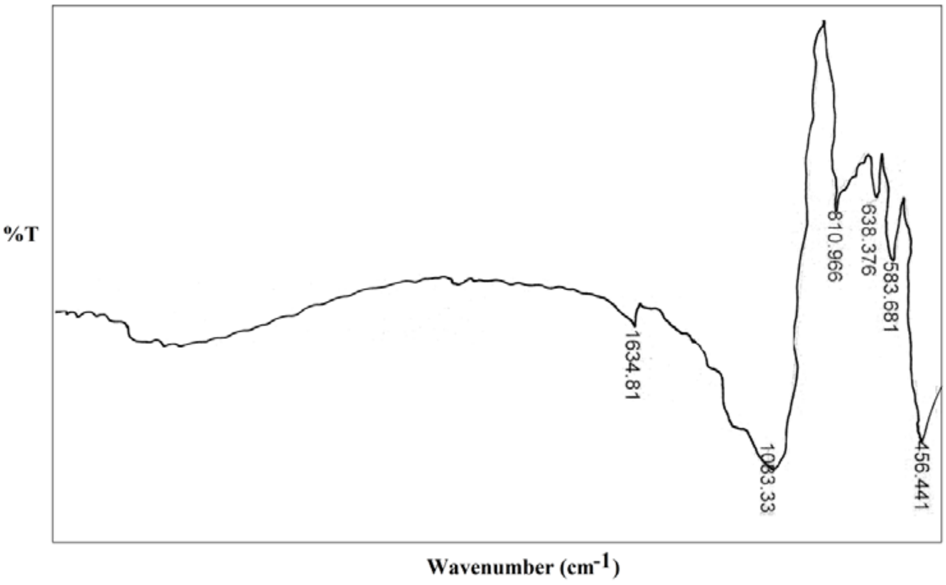

Fig. 3. FT-IR spectrum the prepared sample.

It also has a peak at 638 cm^{-1} belonged to SiO_4 and AlO_4 tetrahedral and a peak centered at 583 cm^{-1} related to the vibration of five-membered rings. The located peak at 456 cm^{-1} corresponding to bending vibration of T-O bond [12,13]. As shown in the previous references [13,22-24], all zeolitic vibration modes are present at the spectra of raw and H-form of sample, confirming that there was no significant difference between Na-mordenite and protonated form (H-form not shown).

3.2. X-ray diffraction studies

Fig. 4 shows the X-ray pattern of synthesized Na-mordenite. The strong diffraction peaks located at 2θ values range of 9° to 36° in the pattern, correspond to the reflections of mordenite structure [25]. The reflection peaks at 2θ values of 9.77°, 13.45°, 19.61°, 22.20°, 23.16°, 25.63°, 26.25°, 27.67°, 27.87°, 30.89° and 35.61° in XRD pattern of prepared zeolite were in agreement with the literature [13,19,25] and crystalline phases were identified using the Joint Committee on Powder Diffraction Standards (JCPDS) files (29-1257 corresponds to mordenite). This indicated that a highly crystalline and pure sample was formed. The XRD pattern of the H-form zeolites is essentially identical to those of the corresponding Na-form zeolites [26].

3.3. Surface area and SEM studies

The obtained data of prepared mordenite sample such as Si/Al ratio, surface area and pore volume are listed in Table 2. The BET results indicate that the synthesized mordenite has a large surface area.

The morphological characters of the synthesized mordenite were obtained by SEM. As shown in Fig. 5, the morphology and size of the synthesized mordenite is similar with other studies as reported already [13,19,27]. The average size of the sample was estimated about 5-7 μm.

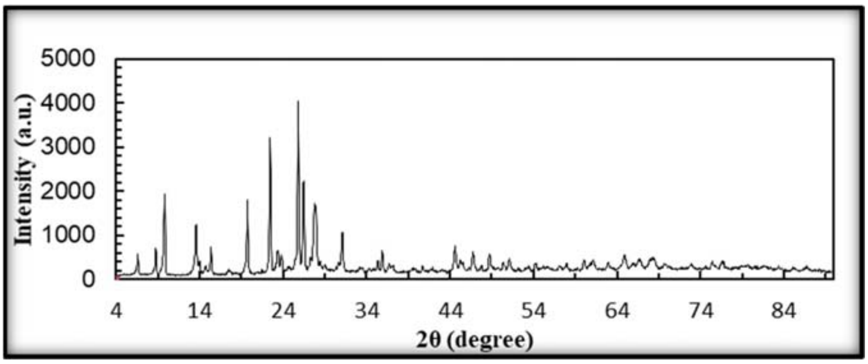

Fig. 4. XRD pattern of mordenite.

Table 2. Properties of mordenite.

Unit cell parameters (Å)			Si/Al ratio	BET surface area (m^2g^{-1})	Pore volume (m^3g^{-1})
a	b	c			
18.1	20.5	7.5	18	331.63	0.278

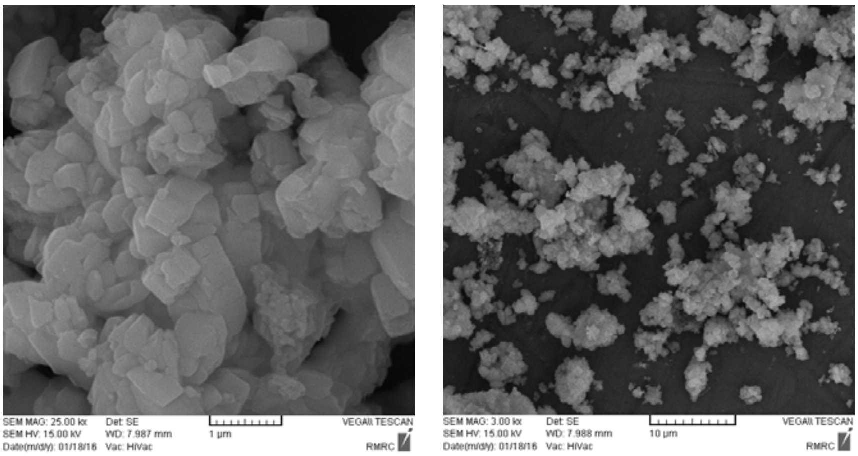

Fig. 5. SEM images of mordenite.

3.4. Catalytic application of synthesized mordenite

In order to investigate the application of the prepared zeolite in m-xylene isomerization reaction, the synthesized mordenite sample was tested in a fixed bed catalytic setup and the results were compared with a commercial SAPO-11 catalyst (Si/Al = 20) provided by Zeolyst International. The results of meta-xylene conversion to para-xylene on two zeolites are shown in Table 3 at pressure of 10 bars and temperature of 380°C in 2 reaction times: 6h and 12h.

According to the results depicted in Table 3, over two catalysts, when the time of reaction increased from 6h to 12h, the amount of para-xylene which was produced was decreased whereas, the amounts of meta-xylene which was produced and xylene loss were increased.

Table 3. Comparison of catalytic activity of prepared mordenite catalyst with commercial SAPO-11 catalyst in m-xylene isomerization reaction.

Catalyst	Mordenite		SAPO-11	
Temp. (°C)	380	380	380	380
Catalyst (g)	4	4	4	4
WHSV (1 h^{-1})	3.35	3.35	3.35	3.35
TOS (h)	6	12	6	12
p-xylene	13.20	10.96	10.07	8.81
m-xylene	43.78	43.97	43.01	44.19
o-xylene	20.74	21.16	21.05	21.81
ethylbenzene	6.63	8.40	9.86	10.35
C_3	0.01	0.01	0.01	0.01
C_4	0.05	0.04	0.06	0.06
C_5	0.26	0.12	0.19	0.15
C_6^P	0.24	0.10	0.14	0.14
C_6^N	0.36	0.24	0.08	0.05
C_7^P	0.25	0.03	0.04	0.06
C_7^N	0.29	0.31	0.43	0.35
C_8^P	2.02	2.53	3.19	3.11
C_8^N	4.39	6.30	7.09	6.12
C_9^n	2.58	3.18	2.67	3.26
C_9^A	2.11	0.08	0.17	0.05
C_{10}^n	0.00	0.00	0.02	0.00
C_{10}^A	0.106	0.076	0.092	0.020
C_{11} + H	0.10	0.08	0.21	0.07
Toluene	1.96	1.42	1.46	1.31
Benzene	0.92	0.55	0.12	0.09
MX conversion (%)	14.91	14.54	16.40	14.11
PX/OX (%)	63	52	48	40
Xylene loss (%)	2.11	3.54	6.03	5.16

[*] Note: TOS is Time-on-stream, The compositions are in wt.%.

3.5. Investigation of reaction time on m-xylene conversion over the zeolite catalysts

Conversion of m-xylene over zeolite catalysts is plotted against reaction time in Fig. 6. After the reaction time of 6 hours over mordenite, m-xylene conversion reached to 14.91% compared to 16.40% over SAPO-11. After the reaction time of 12 h, Fig. 6 shows that m-xylene conversion reached to 14.54% compared to 14.11% over the SAPO-11. It can be explained that acidic properties of SAPO-11 which is medium, increased in high temperature (>300°C) and therefore it be suitable for isomerization reaction [28].

According to the Fig. 6, when the reaction time increased from 6h to 12h, m-xylene conversion over two catalysts decreased.

3.6. Investigation of p-Xylene to o-xylene (P/O) ratio over the zeolite catalysts

The para to ortho ratio over mordenite and SAPO-11 are presented in Fig. 7 at both reaction times of 6 and 12h. As shown in Fig. 7, mordenite has a (P/O) ratio of 63% at 6 h that is greater than the SAPO-11 at 6 h (48%) and decrease to 52% at 12 h reaction time over mordenite and to 40% over SAPO-11. The higher P/O ratio over mordenite catalyst is due to the higher diffusivity of p-xylene into the large pore of mordenite compared to the medium pore of SAPO-11 (4 Å × 6.5 Å). p-Xylene quickly diffusion into the mordenite zeolite as soon it forms [29,30]. As can be seen in Fig. 7, with increasing the reaction time over both catalysts, the P/O ratio decreased.

Generally, the best time of this reaction for both catalysts at 380°C was 6h, because the amount of para-xylene which was produced, meta-xylene conversion and PX/OX ratio were higher but the amounts of meta-xylene which was produced and xylene loss were lower compared to 12h reaction time.

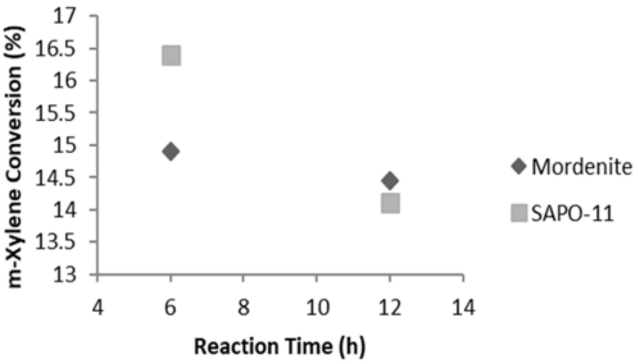

Fig. 6. m-Xylene conversions versus reaction time at 380°C over two catalysts.

4. Conclusions

In this study, the mordenite zeolite was synthesized with high crystallinity in absence of templating agent. The performance of prepared zeolite in meta-xylene isomerization reaction in a fixed bed reactor was investigated and compared with the commercial SAPO-11 catalyst. Based on the results which were obtained from this study, our synthesized catalyst demonstrated higher para/ortho ratio, while keeping the loss of xylene lower compared to SAPO-11. These results are shown that totally, the prepared mordenite is a better catalyst than SAPO-11 in m-xylene isomerization reaction.

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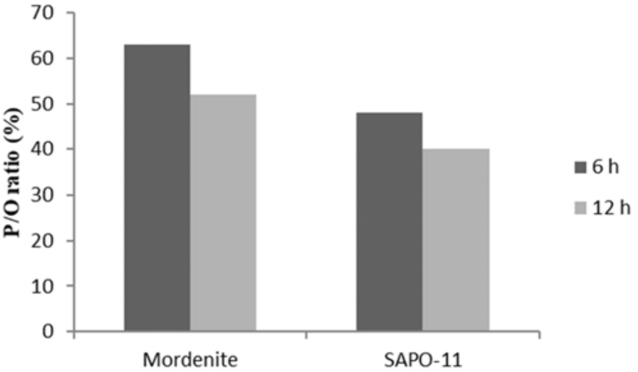

Fig. 7. P/O ratio over two catalysts at 6h and 12h reaction time.

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