



Journal of Applied Sciences

ISSN 1812-5654

science
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Isomerization of M-xylene

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Abstract: In this study, gas-phase isomerization reaction of m-xylene was studied over various catalysts including Ni, Sn, Pt, Ga, Re or Zr over alumina and zeolite carriers. The catalysts prepared over ZSM-5 carriers and consisted of Ga and/or Pt as active components showed high activity and selectivity on p-xylene compared to o-xylene. Kinetics of the reaction was studied over these selective catalysts and it was found that experimental data were pretty well suited to the kinetic model developed.

Key words: Isomerization, m-xylene, o-xylene, ZSM-5 zeolite, disproportionation

INTRODUCTION

Xylenes are C₈ benzene homologues with the molecular formula C₈H₁₀ as seen in Fig. 1. The term mixed xylenes describes a mixture of ethyl benzene and the three xylene isomers, namely p-, m- and o-xylene. They are important chemicals and find wide and various applications in industry. O-xylene is a reactant for the production of phthalic anhydride. M-xylene is used in manufacture of plasticizers, azo dyes, wood preservers, etc. P-xylene upon oxidation yields terephthalic acid used in the manufacture of synthetic textile fibers and poly (p-xylene) which is produced by p-xylene has had economic importance since 1960. Mixed xylenes are largely produced from petroleum such as catalytic reformat, pyrolysis of gasoline, toluene disproportionation and coke-oven light oil. However, as a result of important applications to which the individual xylene isomers are subjected, it is often very important to have high concentrations of a particular xylene.

This can be accomplished by converting a non-equilibrium mixture of the xylene isomers, which is low in the desired xylene isomer, to a mixture which approaches equilibrium concentrations. Numerous catalysts have been proposed for use in xylene isomerization processes. More recently, a number of studies have disclosed the use of crystalline aluminosilicate zeolite containing catalysts for isomerization and conversion of C₈ alkylaromatics^[1].

Most of the studies in the literature for the isomerization of xylenes are related to the isomerization of mixed-xylenes. Only a few are about a pure material such as isomerization of m-xylene and its kinetics. The reaction

of m-xylene isomerization is of great interest for organic chemical industry where the demand for the para and ortho isomers exceeds the supply. The good activity of zeolite catalysts was proved in the gaseous phase isomerization of m-xylene but with respect to kinetics relatively few catalysts were investigated. In spite of the considerable industrial interest on the isomerization and disproportionation of xylenes, especially catalysed by zeolites, no satisfactory correlations have been indicated between catalytic activity and the solid state properties as well. Giordano *et al.*^[2] investigated in particular the interaction of m-xylene with various dealuminated mordenites. The conversion of m-xylene over dealuminated mordenites was found to be a function of the acid strength rather than the number of the acidic sites, as the Si/Al ratio was directly proportional to acid strength. Chatterjee and Ganguli^[3] have investigated the isomerization and associated reactions of o-xylene over 20 catalysts based on a large variety of multicationic (mono to trivalent) zeolite Y samples. All the catalysts showed very high selectivity for m-xylene, but relative improvement in p-xylene yield was obtained with catalysts containing La³⁺ and Ni²⁺. Isuchiya *et al.*^[4], was calculated that AlBr₃/Graphite and AlBr₃/MSC-showed structure selectivity in the isomerization of xylenes in which 1, 2 methyl shift mechanism has been considered and the isomerization of xylenes was almost first order with respect to the pressures of the reactants. Mavradinova *et al.*^[5] have compared the catalytic action of a series of pentasil type zeolites with almost the same Si/Al ratio synthesized by different methods and they have reported that pentasil type zeolites with close chemical composition exhibited pronounced differences

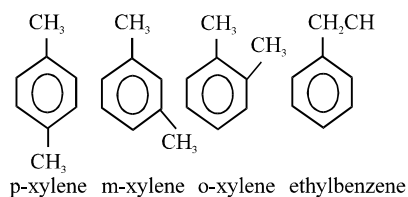


Fig. 1: Mixed xylenes

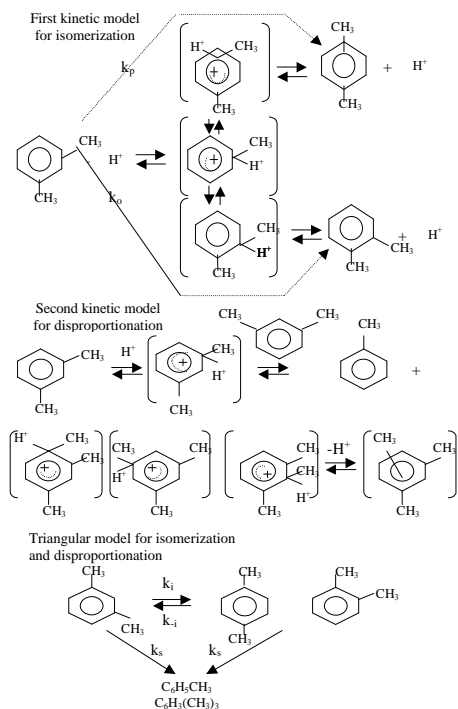


Fig. 2: Different kinetic models for isomerization of m-xylene

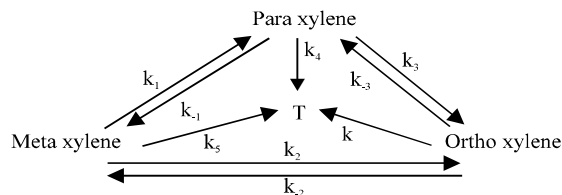


Fig. 3: Reaction network

in crystal morphology, acid function (active site number and strength distributions), catalytic activity and selectivity depending on the method of preparation. It was observed that the disproportionation of m-xylene was more sensitive to the acidic function of the catalysts, whereas their activity and selectivity with respect to the yield of xylene isomers were more consistent with the

presence of differences in the size and morphology of the zeolite crystallites. In a U.S Patent^[6], it is reported that a xylene isomer mixture is treated with hydrogen in the presence of a cracking catalyst comprising a zeolite selected from ZSM-5, ZSM-11, ZSM-12, ZSM-34 and ZSM-48 series at least 20% of its cation site being occupied by a cation of a metal selected from alkali metals and alkaline earth metals such as lithium, sodium and strontium and a refractory inorganic oxide (gamma-alumina) having platinum (in a weight percent of 0.005 to 5% based on the weight of the carrier) supported thereon to suppress side reactions involving a loss of xylenes such as disproportionation and hydrogenation. Dumitriu *et al.*^[7] was found that HZSM-5 had the best selectivity for both the isomerization reaction and p-xylene formation. Acid zeolites catalyse the isomerization of xylenes and also their disproportionation into three methylbenzene and toluene. Two kinetic models, the first taking into account only m-xylene isomerization to p- and o-xylene and the second considering the isomerization and disproportionation reaction of xylene, were adopted. In a triangular model (Fig. 2) involving simultaneous isomerization and disproportionation was also tested and the rate constants were calculated. The calculations of the rate constants indicated that HZSM-5 was a proper catalyst for m-xylene isomerization though its activity was smaller than that of zeolites exchanged with rare earth metals, the selectivity of HZSM-5 was undoubtedly higher. Acid properties of HNaZSM5 [Si/Al=47 and Na/Al=0.85] zeolites of various exchange degrees (0-98%) were studied^[8]. Isomerization of o-xylene and alkylation of toluene with methanol were chosen as the test reactions, both of them known as proceeding on the Brönsted acid sites, to investigate the catalytic activity of zeolite. The strength of the acid centres and their concentrations were studied by IR spectroscopy. In the zeolites of exchange degrees higher than 11%, the conversion increased linearly with the number of OH groups of 3609 cm⁻¹ which were strong Brönsted acid sites. Conversion of m-xylene was also studied on H-faujasite and on several acid zeolites with ten- or twelve-membered rings^[9,10]. It was reported that in the m-xylene conversion, activity of H-faujasite depended strongly on its degree of dealumination and p/o selectivity was always high for ten-membered ring zeolites with crystals bigger than 1 µm although twelve-membered rings showed much more disproportionation. Leu and Chao studied^[11] the properties of crystalline microporous molecular sieve AlPO₄ modified by incorporating B, Si, Fe, Ca, Mg or Zn element into its framework. The incorporation of magnesium in the AlPO₄ structure gives high preference of p-xylene, whereas the incorporation of

silicon and ferric cations results in a value of p-/o-xylene ratio less than unity. The incorporation of cobalt into AlPO_4 , leads to the o-xylene/ p-xylene yield in a state of equilibrium. Sastre *et al.*^[12] investigated the conversion of m-xylene over offretites with different levels of ion exchange. The main conclusion of that study is that the catalytic activity increases monotonically upon exchange of K^+ cations. By removal of these cations, the concentration of protons increases as the accessibility to the internal porosity of the zeolite with the result that the selectivity for isomerization is promoted at the expense of disproportionation. Pere'Z Parientence^[13], studied the relationship between the pore structure and Si/Al ratio of zeolite β , which is twelve-membered ring zeolite, with its catalytic activity and selectivity in the conversion of m-xylene was elaborated. The isomerization and disproportionation activity of zeolite β depend strongly on the aluminum content, decreasing with increasing framework aluminum content. Maximum activity is found for Si/Al ratios between 14 and 15, while the p/o selectivity remains constant. It was seen that the p/o selectivity in m-xylene isomerization is ca. 1.2, independent of the Si/Al ratio of zeolite β and of the conversion. The studies of Shashikala *et al.*^[14] showed that conversion increased with temperature, but para selectivity decreased and much higher m-xylene conversion, as well as higher stability of the catalyst is achieved by using platinum-exchanged HZSM-35 (0.05wt.% platinum). Li *et al.*^[15] used a pulse microreactor-chromatography technique to study the xylene isomerization reaction on HZSM5 zeolite catalyst. The kinetic parameters of the reaction network proposed, (Fig. 3), were calculated. The catalytic properties of zeolites ZSM-5 dealuminated by HCl were investigated for isomerization of m-xylene^[16]. Besides the increase of the Si/Al ratio, the dealumination leads to an inversion of the Si/Al concentration gradient in crystallites, to a shift of acidity spectrum and consequently to a change in catalytic activity and selectivity. A theoretical model modified by Wugeng *et al.*^[17] was used to explain and predict the high para-selectivities in toluene disproportionation and xylene isomerization. The reaction of m-xylene is a useful tool for characterising zeolite structures especially for all range of pore sizes^[18]. The selectivity of these reactions gives information allowing one to estimate pore diameter and architecture for medium through extra-large pore zeolites. As one-dimensional large and extra large pore zeolites give a p/o ratio < 1, likely due to a significant occurrence of the bimolecular isomerization mechanism, multi-dimensional large pore zeolites such as USY and beta and the low-silica, uni-dimensional zeolite LTL give a p/o ratio > 1.

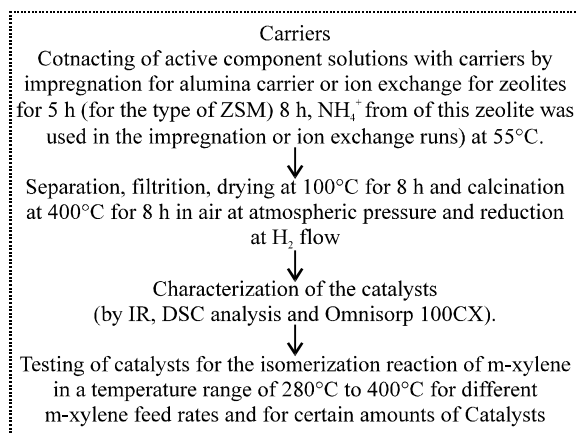


Fig. 4: Preparation steps of the catalysts

The straight channel uni-dimensional zeolites SSZ-24, -31, SIT5, UTD-1, ZSM-12, -48 have the lowest p/o ratios over the range of pore size studied. Morin *et al.*^[19] examined influence of coke deposits on the selectivity of m-xylene transformation on the isomerization mechanism over HFAU zeolites and found the stronger the acid sites the faster their deactivation by coke deposits.

As understood from the given literature, much attention has been focused on the shape selective catalysts, especially ZSM-5 type zeolites, for the isomerization of m-xylene. On the other hand, the kinetics of xylene isomerization over some zeolite based catalysts has been studied by several researchers. To understand the kinetic behaviour of xylenes in isomerization reaction on the catalyst, the knowledge of detailed kinetic parameters must be available. It means that more theoretical and experimental study is needed. The aim of this work is to investigate kinetics of m-xylene isomerization over a selective catalyst determined after a selectivity screening-test, to calculate the kinetic parameters of the model and to compare them with the values in the previous studies.

Catalyst preparation: Eighteen different catalysts depending on the information about the catalysts in literature for the isomerization of m-xylene were prepared. Alumina, natural zeolite (rich in clinoptilolite) and several synthetic zeolites such as MEM5766, MEM1510, ZSM5(Na) and ZSM5(H)-Pentasil were employed as carriers and aqueous solutions of salts of metals such as Ni, Sn, Re, Pt, Ga, Zr, Sn were used to add the active components to the carriers. Preparation steps of the catalysts are given in Fig. 4. Origins of materials used in the catalyst preparation and some physical properties of the catalyst were presented in Table 1.

Table 1: Origins of materials used in the catalyst preparation

Catalyst name	Carrier		Active component solution	
	Name	Producer firm	producer firm (Merck(Pure))	
Ni/Alumina	Alumina	CR 240	Pechiney	Ni/NiNO ₃
Ni/MEM5766	M.S.M-5766	Ca/Na/Al silicate	Sigma (Mol. Sieve)	Ni/NiNO ₃
Ni/Clinop.	Cinoptilolite	Natural zeolite*	Etibank/Bigadic-TR	Ni/NiNO ₃
Sn/Alumina	Alumina	CR 240	Pechiney	Sn/SnCl ₂ .2H ₂ O
Sn/MEM5766	M.S.M-5766	Ca/Na/Al silicate	Sigma (Mol. Sieve)	Sn/SnCl ₂ .2H ₂ O
Sn/Clinop.	Cinoptilolite	Natural zeolite*	Etibank/Bigadic/TR	Sn/SnCl ₂ .2H ₂ O
Ni/MEM1510	M.S.M-1510	Ca/Na/Al silicate	Sigma (Mol. Sieve)	NiNiNO ₃
Sn/MEM1510	M.S.M-1510	Ca/Na/Al silicate	Sigma (Mol. Sieve)	Sn/SnCl ₂ .2H ₂ O
ReNi/Alumin	Alumina	CR 240	Pechiney	Re/Re and Ni/NiNO ₃
Pt/Clinop.	Cinoptilolite	Natural zeolite*	Etibank/Bigadic/TR	Pt/H ₂ (PtCl ₆).6H ₂ O
Pt/MEM5766	M.S.M-5766	Ca/Na/Al silicate	Sigma (Mol. Sieve)	Pt/H ₂ (PtCl ₆).6H ₂ O
Pt/MEM1510	M.S.M-1510	Ca/Na/Al silicate	Sigma (Mol. Sieve)	Pt/H ₂ (PtCl ₆).6H ₂ O
ZSM5Pt-Ga	ZSM5(Na)	Synth. zeolite.**	Süd-Chemi AG	Pt/H ₂ (PtCl ₆).6H ₂ O and Ga/GaN ₃ O ₉ .9H ₂ O
ZSM5Pt-Zr	ZSM5(Na)	Synth. zeolite.**	Süd-Chemi AG	Pt/H ₂ (PtCl ₆).6H ₂ O and Zr/ZrO ₂
ZSM5Pt	ZSM5(Na)	Synth. zeolite.**	Süd-Chemi AG	Pt/H ₂ (PtCl ₆).6H ₂ O
ZSM5Pt-Sn	ZSM5(Na)	Synth. zeolite.**	Süd-Chemi AG	Pt/H ₂ (PtCl ₆).6H ₂ O and Sn/SnCl ₂ .2H ₂ O
ZSM5Ni3	ZSM5(Na)	Synth. zeolite.**	Süd-Chemi AG	Sn/SnCl ₂ .2H ₂ O
ZSM5H-Pent.	ZSM5(H)	Synth. zeolite.**	Süd-Chemi AG	-

* Composition: 74.86% SiO₂, 0.42% Fe₂O₃, 0.70% MgO, 0.5% Na₂O, 2.71% K₂O, 9.074% H₂O, 2.42% CaO, 9.35% Al₂O₃

** It was on ZSM5(NH₄) structure and pretreated with NH₄Cl

Table 2: Percent composition, surface areas and bulk densities of the catalysts used in the experiments

Catalyst/Carrier	Active components	Weight percent of active components (based on the mass of catalyst) (Atomic Abs)		Size producer firm (PF)	Surf. area Omn isorp 100 CX	Bulk density PF or Measured	
		I	II				
Name	-	I/II	I	II	m ² /g	g/L	
Ni/Alumina	Al	Ni	3	-	1.7 mm Spheric *	250	905
Ni/MEM5766	Si/Al	Ni	3	-	8-12 Mesh	390	1005
Ni/Klinop.	Si/Al	Ni	3	-	2-3 mm Particle *	24	780
Sn/Alumina	Al	Sn	3	-	1.7 mm Spheric *	233	905
Sn/MEM5766	Si/Al	Sn	3	-	8-12 Mesh	417	1005
Sn/Klinop.	Si/Al	Sn	3	-	2-3 mm Particle *	20	780
Ni/MEM1510	Si/Al	Ni	3	-	1/16 inch Pellet *	321	945
Sn/MEM1510	Si/Al	Sn	3	-	1/16 inch Pellet *	300	945
ReNi/Alumina	Al	Re/Ni	3	-	1.7 mm Spheric *	240	905
Pt/Klinop.	Si/Al	Pt	3	-	2-3 mm Particle *	21	780
Pt/MEM5766	Si/Al	Pt	3	-	1.7 mm Spheric *	250	1005
Pt/MEM1510	Si/Al	Pt	3	-	1/16 inch Pellet *	270	945
ZSM5Pt-Ga	Si/Al	Pt/Ga	1.810 ⁻³	3.0410 ⁻²	0.5-1.5 mm Particle	258	600
ZSM5Pt-Zr	Si/Al	Pt/Zr	1.810 ⁻³	2.8510 ⁻³	0.5-1.5 mm Particle	270	600
ZSM5Pt	Si/Al	Pt	1.810 ⁻³	-	0.5-1.5 mm Particle	335	600
ZSM5Pt-Sn	Si/Al	Pt/Sn	1.810 ⁻³	2.0110 ⁻⁴	0.5-1.5 mm Particle	290	600
ZSM5Ni3	Si/Al	Ni	5.410 ⁻³	-	0.5-1.5 mm Particle	280	600
ZSM5H-Pent.	Si/Al	-	-	-	0.5-1.5 mm Particle	447	600
ZSM5	Si/Al	-	-	-	0.5-1.5 mm Particle	417	600

*Divided into 1-2 mm of particles for this study

The chemical compositions of the catalysts prepared were determined by gravimetric and volumetric (atomic absorption spectrometer) methods and were given in Table 2. Nitrogen adsorption experiments were performed at 77K using a static volumetric apparatus (Coulter Omnisorp 100 CX) up to P/P₀~0.95. The catalyst samples were previously degassed at 400°C for 4 h before nitrogen adsorption measurements. Specific total surface areas and monolayer pore volumes were calculated using Langmuir equation and specific pore volumes were estimated from the nitrogen uptake. Table 3 shows the results of N₂ adsorption measurements of ZSM5, ZSM5PtGa and ZSM5Pt catalysts. An attempt was made

to apply the Dubinin-Astakhov (D-A), Langmuir and BET adsorption models for the characterization of the catalysts. The Dubinin-Astakhov equation is expressed as:

$$\text{Log } W = \text{Log } W_0 - k (\text{Log } P/P_0)^n$$

Where, W is the amount adsorbed at the relative pressure, W₀ is the total micropore adsorption capacity, k is a constant, n is the structural parameter. The value of the adsorption capacity, W₀, can be obtained from the intercept of the D_A plot (Log W) vs. (Log P/P₀)ⁿ. Table 3 shows that surface area of ZSM5 decreases with

Table 3: The results of N₂ adsorption on the catalysts (Degas temperature=400°C)

Methods		Catalysts		
		ZSM5	ZSM5PtGa	ZSM5Pt
Lang-miur	A _{Lang} (m ² g ⁻¹)	569.90	357.26	458.98
	V _m (cc g ⁻¹)	131.01	82.12	105.51
	b	0.0000098	0.00013	0.00934
BET	A _{BET} (m ² g ⁻¹)	414.74	258.51	335.04
	V _m (cc g ⁻¹)	95.43	59.38	77.02
	C	107.17	79.78	120.98
Dubinin-Asthakov	A _D (m ² g ⁻¹)	523.47	341.85	409.29
	W ₀ (ccTP g ⁻¹)	120.34	78.59	94.09
	n	2.47	1.95	2.55
	X _{mean} (Å°)	1.59±0.53	1.72±0.42	1.71±0.48
	V _{max} (cc g ⁻¹)	380.50	300.25	260.25

impregnation of Ga and/or Pt. In the Table 3, A_{Lang}, A_{BET} and A_{D-A} are surface areas, V_m is monolayer capacity, b and c are constants, X_{mean} is half width of pores and V_{max} is the maximum amount adsorbed. Impregnation with Ga and/or Pt causes a decrease in the pore volume of original ZSM5, resulting in the increase of half width of pores.

Experimental set-up: Set-up is given in Fig. 5. Nitrogen was used as the hydrocarbon carrier. It was cleaned from dust, CO₂ and moisture by passing through a series of glass wool, KOH and silica gel, respectively and was metered with a rotameter before fed to the reactor. The hydrocarbon stream from the saturator was fed to the reactor through a pyrex tube that was kept over 140°C in order to prevent xylene condensation. M-xylene was kept in the saturator located in a constant temperature oven and the gas flow leaving the system was also measured with a flow meter. The hydrocarbon heated at constant temperature was carried by the nitrogen flow to the reactor. The amount of hydrocarbon stream carried is dependent on both the velocity of the carrier gas and the temperature of the saturator. During the experiments the temperature of the saturator was kept constant at 70°C, but the gas feed rate was changed between 1 and 2.5 mL sec⁻¹ to carry hydrocarbon in different amounts to the reactor.

The amount of hydrocarbon carried to the reactor at each experiment was sensitively measured by weighing the saturator at the beginning and at the end of the experiment. The tubular reactor employed in the experiments was in 26 mm in diameter, made of pyrex glass. It was located in an electrical oven and heated by radiation. A Fe-constant thermo element was located in the middle of the catalyst bed to measure the temperature of the catalyst and the temperature was recorded continuously during the experiment and it was kept constant. The product stream from the reactor passed through two cold traps was connected in series. The cold traps were kept in salt-ice mixture and liquid

nitrogen, respectively. The products and unreacted m-xylene collected in two traps were analyzed by a gas chromatography (GC) Hewlett Packard 5890/2; on a capillary column of HHP-FFAP using flame ionization detector (FID).

Selectivity studies: These experiments were carried out with a molar flow rate of m-xylene varied 0.00392 and 0.08 mole h⁻¹, at a temperature range of 270-380°C, with a constant fresh catalyst amount (1 or 4 g.) for a reaction time of 4 h. At the end of each experiment, used catalyst was regenerated under nitrogen flow at 380°C for 4 h (Table 4).

Selectivity studies showed that the catalysts numbered from 1 to 12 are almost inactive catalysts in isomerization of m-xylene. Disproportionation products such as toluene (TOL) and threemethylbenzene (TMB) are not present in the reaction mixture over these catalysts even for severer reaction conditions, when compared with catalysts 13-18, higher temperature, higher m-xylene feed and four-fold catalyst amount. Catalysts prepared on ZSM5(Na), numbered from 13 to 18, represent better activity than the above ones. ZSM5Pt (numbered 15) is the most active catalyst under the reaction conditions studied. In the reaction mixture various TMB isomers, toluene are formed as disproportionation products. ZSM5Pt-Ga, ZSM5Pt-Zr and ZSM5Pt exhibit higher selectivity on p-xylene compared to o-xylene, S_{p/o}, than the others. These catalysts possess the catalytic activity in the order:



Catalysts ZSM5Pt and ZSM5PtGa, which are the ones composed of 1.8*10⁻³ (in w%) Pt and 3.04*10⁻³ (in w%) Ga, 1.8*10⁻³ (in w%) Pt over ZSM5 support, respectively, were chosen for kinetic analysis, due to the their higher activities.

Kinetic study: Kinetic runs were performed under the similar conditions to those in selectivity studies. A kinetic run took 8 h. One gram of catalyst (except one group of experiments, which were carried out to find the effect of catalyst amount on reaction rate) was placed to the reactor. During the runs with different flow rates of m-xylene, the change in the feed rate of m-xylene was obtained by varying the flow rate of nitrogen (between 1 and 2.5 mL sec⁻¹) which is used to carry hydrocarbon to the reactor.

After each run, the reaction mixture collected in the traps was analysed by the gas chromatography. In the reaction mixture p-, o-xylene as isomerization products,

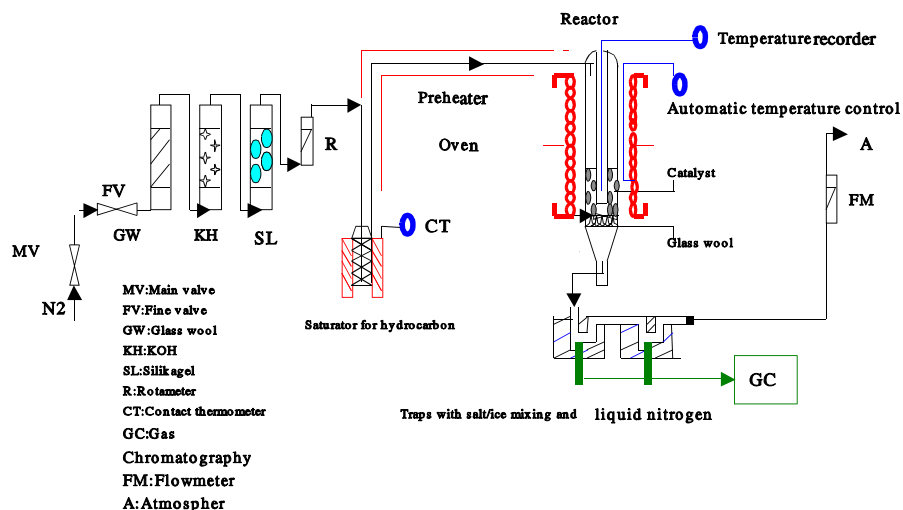


Fig. 5: Experimental set-up for the isomerization reaction of m-xylene in gas phase

Table 4: Results of the selectivity experiments

Exp No	Catalyst			Feed (HC) Mole/h	T, °C	[Mole fraction in the reaction mixture, %]					
	No	Name	W (g)			m-X	p-X	o-X	Tol	TMB	Sel p/o
1	01	Ni/Alumina	4	0.02600	330	99.81	0.038	0.15	0.00	0.00	0.25
2	01	Ni/Alumina	4	0.08000	330	99.75	0.045	0.18	0.00	0.00	0.25
3	01	Ni/Alumina	4	0.05700	360	99.80	0.045	0.15	0.00	0.00	0.30
4	01	Ni/Alumina	4	0.07800	380	99.76	0.046	0.19	0.00	0.00	0.24
5	02	Ni/MEM5766	4	0.04200	250	99.81	0.038	0.15	0.00	0.00	0.25
6	02	Ni/MEM5766	4	0.08000	330	99.61	0.076	0.31	0.00	0.00	0.24
7	02	Ni/MEM5766	4	0.02900	360	99.61	0.077	0.31	0.00	0.00	0.25
8	02	Ni/MEM5766	4	0.02000	380	99.50	0.100	0.40	0.00	0.00	0.25
9	03	Ni/Clinop.	4	0.01700	330	99.77	0.045	0.18	0.00	0.00	0.25
10	04	Sn/Alumina	4	0.05600	330	99.55	0.090	0.36	0.00	0.00	0.25
11	04	Sn/Alumina	4	0.03000	400	99.77	0.045	0.18	0.00	0.00	0.25
12	05	Sn/MEM5766	4	0.04000	280	99.70	0.060	0.24	0.00	0.00	0.25
13	06	Sn/Clinop.	4	0.01700	330	99.82	0.033	0.14	0.00	0.00	0.23
14	06	Sn/Clinop.	4	0.07400	380	99.62	0.075	0.30	0.00	0.00	0.25
15	07	Ni/MEM1510	4	0.05400	330	99.71	0.057	0.23	0.00	0.00	0.24
16	07	Ni/MEM1510	4	0.04400	380	99.63	0.071	0.29	0.00	0.00	0.24
17	08	Sn/MEM1510	4	0.06600	330	99.73	0.052	0.21	0.00	0.00	0.25
18	09	ReNi/Alumina	4	0.01500	350	99.61	0.078	0.31	0.00	0.00	0.25
19	09	ReNi/Alumina	4	0.04600	390	99.24	0.150	0.61	0.00	0.00	0.24
20	10	Pt/Clinop.	4	0.05000	350	99.60	0.080	0.32	0.00	0.00	0.25
21	10	Pt/Clinop.	4	0.06300	380	99.66	0.068	0.27	0.00	0.00	0.25
22	11	Pt/MEM5766	4	0.01000	330	99.16	0.060	0.24	0.00	0.00	0.25
23	12	Pt/MEM1510	4	0.01000	380	99.67	0.065	0.26	0.00	0.00	0.25
24	13	ZSM5Pt-Ga	1	0.00796	340	59.29	16.920	13.73	6.53	3.46	1.23
25	13	ZSM5Pt-Ga	1	0.01166	270	90.66	4.670	3.71	0.56	0.38	1.25
26	13	ZSM5Pt-Ga	1	0.01166	340	76.12	11.720	8.93	1.87	1.35	1.31
27	13	ZSM5Pt-Ga	1	0.01615	340	80.51	9.950	6.98	1.47	1.06	1.42
28	14	ZSM5Pt-Zr	1	0.00858	340	75.61	11.340	10.02	1.96	1.04	1.13
29	14	ZSM5Pt-Zr	1	0.01178	340	88.10	6.270	4.65	0.67	0.29	1.34
30	14	ZSM5Pt-Zr	1	0.01034	270	85.39	7.210	5.34	1.04	1.00	1.35
31	14	ZSM5Pt-Zr	1	0.01034	340	72.19	13.660	10.31	2.38	1.43	1.32
32	15	ZSM5Pt	1	0.00894	270	64.67	17.840	13.00	2.33	2.14	1.37
33	15	ZSM5Pt	1	0.00894	340	55.77	19.780	18.25	3.65	2.64	1.37
34	15	ZSM5Pt	1	0.01216	340	56.76	16.140	15.15	5.17	6.76	1.06
35	15	ZSM5Pt	1	0.01234	340	64.71	16.310	12.09	3.79	3.07	1.34
36	16	ZSM5Pt-Sn	1	0.00609	340	75.03	10.550	9.72	3.43	1.25	1.08
37	16	ZSM5Pt-Sn	1	0.01207	340	90.44	4.930	3.93	0.68	0.00	1.25
38	16	ZSM5Pt-Sn	1	0.01108	270	96.96	1.400	1.39	0.23	0.00	1.01
39	16	ZSM5Pt-Sn	1	0.01108	340	89.50	5.150	4.15	0.85	0.33	1.24
40	17	ZSM5Ni3	1	0.00392	340	68.60	13.770	11.66	4.23	1.72	1.18
41	17	ZSM5Ni3	1	0.01252	340	85.71	7.260	5.45	1.07	0.49	1.33
42	17	ZSM5Ni3	1	0.00831	340	85.34	6.900	6.24	0.91	0.58	1.10
43	17	ZSM5Ni3	1	0.00831	270	97.21	1.160	1.62	0.00	0.00	0.71
44	18	ZSM5H-Pent.	1	0.00995	340	67.56	15.130	12.16	3.56	1.57	1.24
45	18	ZSM5H-Pent.	1	0.00995	270	82.35	4.820	10.89	1.45	0.47	0.44
46	18	ZSM5H-Pent.	1	0.00779	340	70.60	13.060	11.52	3.40	1.40	1.13
47	18	ZSM5H-Pent.	1	0.01416	340	86.28	6.880	5.78	1.04	0.00	1.18

Table 5: Results of for kinetic experiments

CAT No	CAT name	CWG g	GAS rate mL sec ⁻¹	T °C	Feed rate Mol H.C h	(W/F _{A0} g cat*h)/ mol H.C	Conversions %				
							X _{TOT}	X _{p-x}	X _{o-x}	X _{TOL}	X _{TMB}
13	PtGa	1	1.13	270	0.00546	182.97	39.33	18.65	13.14	4.525	3.006
13	PtGa	1	1.25	270	0.00579	172.61	37.05	18.18	12.40	4.018	2.451
13	PtGa	1	1.66	270	0.00831	120.27	35.17	18.61	11.54	3.177	1.839
13	PtGa	1	2.08	270	0.01021	97.85	33.23	18.17	10.98	2.699	1.373
13	PtGa	1	2.50	270	0.01989	50.25	27.09	15.54	9.01	1.508	1.030
15	Pt	1	2.50	270	0.01959	51.03	32.02	16.83	10.28	2.943	1.957
15	Pt	1	1.66	270	0.01003	99.68	36.06	17.96	11.92	3.685	2.485
15	Pt	1	1.25	270	0.00737	135.54	37.14	18.00	12.45	3.714	2.964
15	Pt	1	1.00	270	0.00592	168.69	39.11	18.94	13.33	3.906	2.932
13	PtGa	1	1.13	340	0.00546	182.97	45.49	20.85	16.33	4.288	4.023
13	PtGa	1	1.25	340	0.00579	172.61	43.92	19.84	15.14	4.822	4.120
13	PtGa	1	1.66	340	0.00831	120.27	40.94	20.33	14.30	3.893	2.411
13	PtGa	1	2.08	340	0.01021	97.85	37.81	18.94	12.63	4.047	2.176
13	PtGa	1	2.50	340	0.01989	50.25	33.01	18.61	11.50	1.608	1.283
15	Pt	1	2.50	340	0.01959	51.03	36.92	18.39	12.47	3.309	2.748
15	Pt	1	1.66	340	0.01003	99.68	38.21	18.28	13.19	3.355	3.375
15	Pt	1	1.25	340	0.00737	135.54	43.20	19.08	14.41	5.167	4.532
13	PtGa	1	1.13	380	0.00546	182.97	48.77	20.58	17.38	6.182	4.626
13	PtGa	1	1.25	380	0.00579	172.61	43.17	19.40	15.24	4.121	4.408
13	PtGa	1	1.66	380	0.00831	120.27	43.68	20.97	15.18	5.098	2.422
13	PtGa	1	2.08	380	0.01021	97.85	40.47	19.90	14.54	3.511	2.517
13	PtGa	1	2.50	380	0.01989	50.25	37.61	19.34	13.28	2.901	2.085
15	Pt	1	2.50	380	0.01959	51.03	39.54	18.42	12.70	5.176	3.236
15	Pt	1	1.66	380	0.01003	99.68	38.63	17.85	13.48	3.727	3.564
15	Pt	1	1.00	380	0.00592	168.69	46.96	19.03	15.35	7.498	5.079

Table 6: Correlation of x_i versus. W/F_{A0} data (R= Correlation coefficient)

CAT no. and name	T°C	Product	Conversion space time relations x _i = f(W/F _{A0}) _t = a ₃ x ³ +a ₂ x ² +a ₁ x				Reaction rate expressions d [x _i /(W/F _{A0}) _t] = 3*a ₃ x ² +2*a ₂ x+a ₁			
			a ₃	a ₂	a ₁	R ²	3*a ₃	2*a ₂	a ₁	
13	PtGa	270	p-Xyl.	+1E-07	-4E-05	+0.0048	0.9988	+3*(+1E-07)	+2*(-4E-05)	+0.0048
13	PtGa	270	o-Xyl	+6E-08	-2E-05	+0.0028	0.9993	+3*(+6E-08)	+2*(-2E-05)	+0.0028
13	PtGa	270	Tol.	-7E-10	-4E-07	+0.0003	0.9999	+3*(-7E-10)	+2*(-4E-07)	+0.0003
13	PtGa	270	TMB.	+6E-09	-2E-06	+0.0003	0.9904	+3*(+6E-09)	+2*(-2E-06)	+0.0003
15	Pt	270	p-Xyl.	+2E-07	-5E-05	+0.0055	0.9966	+3*(+2E-07)	+2*(-5E-05)	+0.0055
15	Pt	270	o-Xyl	+8E-08	-3E-05	+0.0032	0.9976	+3*(+8E-08)	+2*(-3E-05)	+0.0032
15	Pt	270	Tol.	+2E-08	-7E-06	+0.0009	0.9991	+3*(+2E-08)	+2*(-7E-06)	+0.0009
15	Pt	270	TMB.	+8E-09	-3E-06	+0.0005	0.9931	+3*(+8E-09)	+2*(-3E-06)	+0.0005
13	PtGa	340	p-Xyl.	+2E-07	-6E-05	+0.0060	0.9902	+3*(+2E-07)	+2*(-6E-05)	+0.0060
13	PtGa	340	o-Xyl	+9E-08	-3E-05	+0.0035	0.9948	+3*(+9E-08)	+2*(-3E-05)	+0.0035
13	PtGa	340	Tol.	-2E-08	+3E-06	+0.0002	0.9794	+3*(-2E-08)	+2*(+3E-06)	+0.0002
13	PtGa	340	TMB.	+6E-09	-2E-06	+0.0003	0.9902	+3*(+6E-09)	+2*(-2E-06)	+0.0003
15	Pt	340	p-Xyl.	+3E-07	-8E-05	+0.0069	0.9999	+3*(+3E-07)	+2*(-8E-05)	+0.0069
15	Pt	340	o-Xyl	+2E-07	-5E-05	+0.0046	0.9999	+3*(+2E-07)	+2*(+2E-07)	+0.0046
15	Pt	340	Tol.	+9E-08	-2E-05	+0.0011	0.9999	+3*(+9E-08)	+2*(-2E-05)	+0.0011
15	Pt	340	TMB.	+5E-08	-1E-05	+0.0010	0.9999	+3*(+5E-08)	+2*(-1E-05)	+0.0010
13	PtGa	380	p-Xyl.	+2E-07	-6E-05	+0.0062	0.9919	+3*(+2E-07)	+2*(-6E-05)	+0.0062
13	PtGa	380	o-Xyl	+1E-07	-4E-05	+0.0044	0.9951	+3*(+1E-07)	+2*(-4E-05)	+0.0044
13	PtGa	380	Tol.	-4E-09	-1E-06	+0.0006	0.9425	+3*(-4E-09)	+2*(-1E-06)	+0.0006
13	PtGa	380	TMB.	+3E-08	-7E-06	+0.0007	0.9907	+3*(+3E-08)	+2*(-7E-06)	+0.0007
15	Pt	380	p-Xyl.	+2E-07	-7E-05	+0.0062	0.9999	+3*(+2E-07)	+2*(-7E-05)	+0.0062
15	Pt	380	o-Xyl	+1E-07	-5E-05	+0.0044	0.9999	+3*(+1E-07)	+2*(-5E-05)	+0.0044
15	Pt	380	Tol.	+1E-07	-3E-05	+0.0023	0.9999	+3*(+1E-07)	+2*(-3E-05)	+0.0023
15	Pt	380	TMB.	+4E-08	-1E-05	+0.0011	0.9999	+3*(+4E-08)	+2*(-1E-05)	+0.0011

various trimethylbenzene (TMB) isomers, toluene were formed as disproportionation products. Unreacted m-xylene was measured but no benzene was observed in the reaction mixture. In the Table 5, the total conversion of m-xylene, conversions to p-, o-xylene and conversions to toluene and TMB are represented. The conversions on

Table 5 were obtained from mole fractions of related components in the reaction mixture. The reaction network which was used in kinetic modeling, is presented in Fig. 6.

This model takes into account m-xylene isomerization to p-, o-xylene, disproportionation and demethylation reactions of m-xylene, The reactions between o-xylene

Table 7: Reaction rate constants with data in Table 5

Reaction rate constants						
CAT 1 g	k_{mo}	k_{-mo}	k_{mp}	k_{-mp}	k_{TOL}	k_{TMB}
PtGa	1.22274	0.39962	0.66884	0.19848	0.06238	0.06235
PtGa	1.26211	0.41249	0.68847	0.20430	0.06475	0.06473
PtGa	1.17820	0.38506	0.63324	0.18791	0.06013	0.06011
PtGa	1.19234	0.38968	0.64027	0.19000	0.06117	0.06116
PtGa	0.71215	0.23275	0.38612	0.11458	0.03769	0.03769
Pt	0.84129	0.27495	0.00602	0.00179	0.11482	0.06380
Pt	1.10979	0.36271	0.00276	0.00082	0.14943	0.08303
Pt	1.13284	0.37024	0.00197	0.00058	0.15246	0.08471
Pt	1.14075	0.37282	0.00151	0.00045	0.15179	0.08434
PtGa	1.56914	0.51283	0.86707	0.25730	0.04164	0.06242
PtGa	1.60877	0.52578	0.88763	0.26340	0.04324	0.06479
PtGa	1.50303	0.49122	0.81641	0.24227	0.04014	0.06015
PtGa	1.50339	0.49134	0.81499	0.24185	0.04084	0.06119
PtGa	0.92282	0.30160	0.49592	0.14716	0.02514	0.03770
Pt	1.07473	0.35125	0.66878	0.19846	0.14023	0.12756
Pt	1.39697	0.45656	0.87754	0.26041	0.18251	0.16601
Pt	1.43915	0.47035	0.90783	0.26940	0.18612	0.16936
PtGa	1.61636	0.52826	1.10348	0.32746	0.12482	0.14557
PtGa	1.65366	0.54045	1.11703	0.33148	0.12953	0.15111
PtGa	1.56571	0.51171	1.03670	0.30764	0.12031	0.14030
PtGa	1.57200	0.51376	1.04687	0.31066	0.12238	0.14274
PtGa	0.96209	0.31443	0.63596	0.18872	0.07541	0.08796
Pt	0.96573	0.31562	0.64131	0.19031	0.56009	0.29317
Pt	1.24842	0.40801	0.84203	0.24987	0.38173	0.18262
Pt	1.28618	0.42035	0.87384	0.25931	0.38753	0.18549

Table 8: Activation energies and frequency factors of the rate constants

Arrhenius equation							
$k=A \cdot e^{-E/RT}$ (s ⁻¹) or $\ln k = \ln A - (E/R) \cdot (1/T)$ R=1.987 cal/mole K, E=Cal/mole							
		k_{rx}	k_{-rx}	k_{ox}	k_{-ox}	k_{TOL}	k_{TMB}
13 PtGa	A	4.41	2.07	9.73	2.88	1.12	1.14
	E	1887.65	1887.65	3040.11	3040.11	79.48	99.35
	Corr.	0.98	0.98	0.98	0.98	0.92	0.99
15 Pt	A	3.67	1.29	1.80	3.67	3.67	635.84
	E	1331.29	834.54	1510.12	437.14	1271.68	6358.40
	Corr.	0.92	0.64	0.90	0.90	0.82	0.99

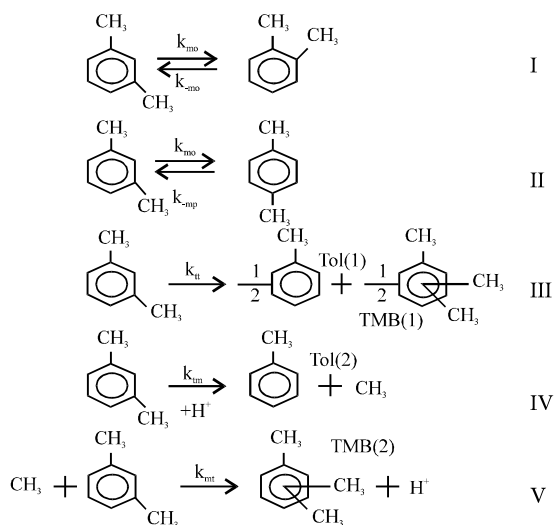


Fig. 6: The reaction network used in kinetic modeling

Table 9: Comparison of the kinetic parameters calculated with those of (D) Dumitriu *et al.*^[7] and (L) Li *et al.*^[15] obtained on several catalysts
Rate constant (k: s⁻¹) and Activation energies (E: kJ/mole)

D.	HNDY			SK-500			HZSM5			HZSM5			ZSM5PtGa			ZSM5Pt		
	673 K	673 K	673 K	L.	628 K	794 K	E	628 K	794 K	E	628 K	794 K	E	628 K	794 K	E		
k _p	7.68*10 ⁻⁵	6.28*10 ⁻⁵	9.62*10 ⁻⁵	k ₁	3.264	7.640	21.43	k _{mp}	0.973	1.344	7.89	1.263	1.578	5.56				
-	-	-	-	k ₁	0.521	2.798	43.72	k _{mp}	0.456	0.625	7.89	0.664	0.764	3.48				
k _o	5.94*10 ⁻⁵	8.53*10 ⁻⁵	3.90*10 ⁻⁵	k ₂	0.081	0.493	46.29	k _{mo}	0.851	1.417	12.71	0.538	0.692	6.31				
-	0.102	0.0861	0.0394	k ₂	0.262	1.023	33.50	k _{mo}	0.252	0.420	12.71	2.591	2.767	1.83				
-	-	-	-	k ₃	0.172	1.505	53.52	k _{po}	-	-	-	-	-	-				
-	-	-	-	k ₃	0.631	1.300	17.87	k _{po}	-	-	-	-	-	-				
-	-	-	-	k ₄	1.488	6.674	47.45	k _{pTol}	-	-	-	-	-	-				
k ₅	0.152	0.102	0.0047	k ₅	-	0.000	0.184	k _{TOL}	1.055	1.069	0.33	1.328	1.642	5.36				
-	-	-	-	k ₆	-	0.026	-0.02	k _{o-Tol}	-	-	-	-	-	-				
-	-	-	-	-	-	-	-	k _{TMB}	1.063	1.078	0.41	3.893	11.13	26.61				

k₅=k_{Tol+TMB}

$$\begin{aligned}
 \left[\frac{dC_{o-Xylene}}{dt} \right]_{i=I} &= k_{mo} * C_{m-Xylene} - k_{-mo} * C_{o-Xylene} \\
 \left[\frac{dC_{p-Xylene}}{dt} \right]_{i=II} &= k_{mp} * C_{m-Xylene} - k_{-mp} * C_{p-Xylene} \\
 \dots \dots \dots \left[\frac{dC_{Tol1}}{dt} \right]_{i=III} &= \left[\frac{dC_{TMB1}}{dt} \right]_{i=III} = 2 * k_{tt} * C_{m-Xylene} \\
 \dots \dots \dots \left[\frac{dC_{Tol2}}{dt} \right]_{i=IV} &= \left[\frac{dC_{CH3-}}{dt} \right]_{i=IV} = k_{tm} * C_{m-Xylene} \\
 \dots \dots \dots \left[\frac{dC_{TMB2}}{dt} \right]_{i=V} &= \left[\frac{dC_{H+}}{dt} \right]_{i=V} = k_{mt} * C_{m-Xylene} \\
 \left[\frac{dC_{Tol}}{dt} \right]_{i=III+IV} &= (2 * k_{tt} + k_{tm}) * C_{m-Xylene} = k_{Tol} * C_{m-Xylene} \\
 \left[\frac{dC_{TMB}}{dt} \right]_{i=III+V} &= (2 * k_{tt} + k_{mt}) * C_{m-Xylene} = k_{TMB} * C_{m-Xylene} \\
 - \frac{dC_{m-Xylene}}{dt} &= \sum_{i=1}^V \frac{dC_i}{dt}
 \end{aligned}$$

Fig. 7: The reaction rates used in kinetic modeling

and p-xylene and between methyl groups were neglected, Assuming that the reactions are first order, the rate expressions were given in Fig. 7. Xylene concentrations in the rate equations were expressed in terms of related conversions which were calculated from the mole fractions in the reaction mixture^[20]. Because of the fact that total conversions achieved in all the experiments are greater than ≥10%, the reactor is treated as an integral reactor, By using the continuity equation in a tubular reactor for plug flow behaviour, the ratio of tube diameter/particle diameter should be ≥ 10, which is 19.5 to conclude plug flow behaviour^[21] reaction rates were obtained by differentiating the X_i versus W/F_{A0} curves drawn for all runs for each product where X_i is the conversion to the product, such as o-xylene, p-xylene, toluene and TMB^[20]. First of all, the best curve fitting to the X_i versus W/F_{A0} data, making it pass through the origin is found, For this purpose, several polynomials with different orders are tested for the goodness of fit of the

polynomial with experiment, the best fit is determined and the slope of the curve at any point gives the reaction rate at that point. Table 6 presents the correlation of X_i versus W/F_{A0} data, Table 7 represents reaction rate constants calculated using the experimental data in Table 5. Finally, the activation energies and frequency factors of the rate constants corresponding reactions were estimated by means of Arrhenius equation. Table 8 represents these results with regression coefficients.

DISCUSSION

Partial and total conversions of m-xylene vs, space time (W/F_{A0}) plots were presented in Fig. 8 for ZSM5PtGa and ZSM5Pt catalysts at different reaction temperatures. It is obvious that there is an appreciable increase in conversion to each product as the temperature increases from 270 to 340°C, Above 340°C, such a significant change couldn't be observed in the partial and total

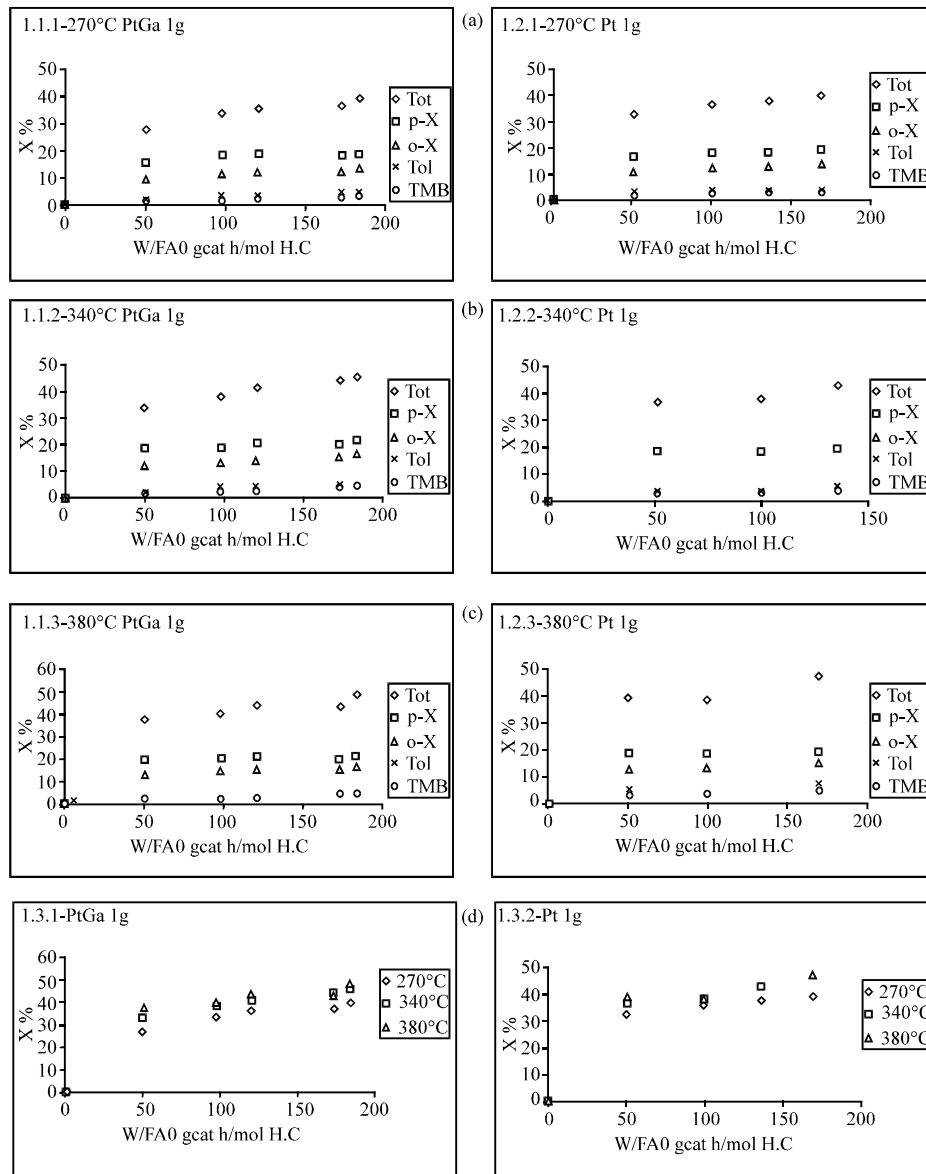


Fig. 8: Partial and total conversions of m-xylene vs space time (W/FAO)

conversions of m-xylene. Figure 9 illustrates the effect of temperature on the selectivities to several products calculated from data in Table 5. Important increases (almost four fold) in the selectivities s_{p-o} -and s_{p-TOT} were obtained over ZSM5PtGa catalyst at 380°C and addition of Ga to ZSM5Pt catalyst improved the selectivity to p-xylene.

P-/o-selectivities remained almost unchanged as the total conversions increased. The Fig. 9 presents p-/o-selectivities at all the temperature studied over the two catalysts and for all the temperatures studied. It was observed that in general p-/o-selectivity has not been affected significantly with increasing temperature from 270

and 340°C over ZSM5PtGa and ZSM5Pt catalysts. It was observed that there was no a significant difference in selectivities over ZSM5PtGa and ZSM5Pt catalysts in the temperature range of 270 and 340°C. The kinetic model taking into account m-xylene isomerization to p- and o-xylene, disproportionation and demethylation reactions of m-xylene fitted the experimental data fairly well. First order reaction mechanism was used and isomerization was taken reversible, but disproportionation and demethylation irreversible^[20]. By use of standard procedures^[22] it was shown that both external and internal diffusion do not influence the reaction rate, External diffusion effects were calculated by use of the generalised

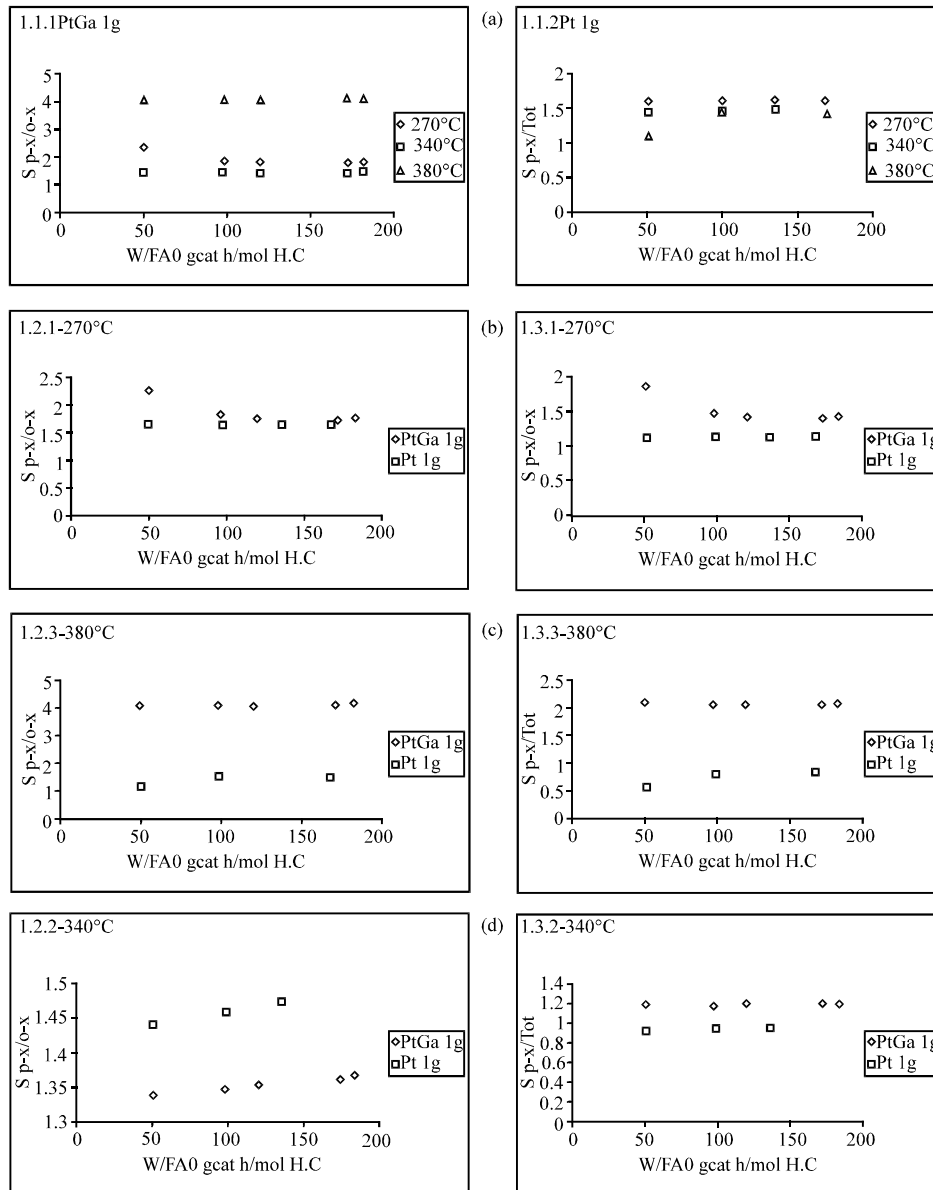


Fig. 9: Effect of temperature on the selectivities to several products

J_D factor and it was found that $(C_b - C_s)/C_b$ was equal to $3.5 \cdot 10^{-4}$ for ZSM5PtGa and $2.1 \cdot 10^{-4}$ for ZSM5Pt catalyst at the maximum reaction temperature of 380°C , so it was assumed that $C_b \approx C_s$. To calculate the internal diffusion effects, the generalised Thiele modulus based on the reaction rate was determined. For this purpose, Weisz's criterion, $r_k^2(r_p^2/D_e C_s) \leq 1.0$, where, r : diameter of catalyst, ρ_c : density of catalyst, D_e : effective diffusion coefficient, C_s : concentration of reactant on the catalyst surface, r_{HC} : reaction rate, was tested for the experiments. The ratio mentioned above was found to be 0.1396 and 0.1351 for ZSM5PtGa and for ZSM5Pt catalysts,

respectively. It means that Weisz's criterion was satisfied. Hence the effectiveness factor can be taken equal to unity which means that internal diffusion resistance can be neglected.

The kinetic parameters calculated in this study were compared with the ones obtained by Dimitriu *et al.*^[7] and Li *et al.*^[15]. Dimitriu *et al.*^[7] tested the zeolites SK-500, HndY and HZSM5 in the reaction of m-xylene isomerization. It was found that HZSM5 had the best selectivity for p-xylene formation. Three kinetic models including isomerization and disproportionation reactions were employed to explain the kinetic data. It was observed

that as the temperature was increased, the rate constants were also increased, as expected, Li *et al.*^[15] used a pulse micro reactor chromatography technique to study the xylene isomerization reaction on HZSM5 zeolite catalyst, A mathematical model including diffusion, adsorption and reaction steps were developed, They also declared that the reaction rate constants increased with increasing temperature, They observed that m-xylene and o-xylene couldn't produce any toluene, i.e. k_5 and k_6 in Fig. 3 had to be small, because m-xylene and o-xylene were strongly adsorbed and dealkylation was very difficult under the experimental conditions used by them, As seen from Table 7 clearly, rate constants calculated in this study also increase with increasing temperature, which is the right trend for the constants, Activation energies obtained in this study are very low with respect to the activation energies given by Li *et al.*^[15]. But there is a good fitness between the values of the reverse reaction rate constants of the isomerization reaction calculated at 628 K in this study by using Arrhenius equation obtained from experimental data (Table 9) over ZSM5PtGa catalyst and by Li *et al.*^[15], over HZSM5 catalyst. It is obvious that the numerical values of the kinetic parameters given by Dumitriu *et al.*^[17] are very different from those given by this study and by Li *et al.*^[15]. It should be kept in mind that the catalyst, the experimental conditions, the kinetic models used in the studies mentioned above have significant differences which cause important deviations in the numerical values of kinetic parameters.

An experimental run took 8 h and no significant catalyst deactivation was noted. Just to have an idea about the magnitude of the deactivation, isomerization of m-xylene was carried out over ZSM5Pt and ZSM5PtGa catalysts for durations longer than the reaction time used in kinetic analysis (8 h) at the same temperature (340°C) and at a constant feed rate of m-xylene. As the reaction time increased from 8 to 40 h, a significant decrease in total conversion of m-xylene (over ZSM5PtGa from 40 to 20% and over ZSM5Pt from 42 to 18%) was observed^[20], but up to a reaction time of 8 h, an appreciable decrease in total conversion was not measured and even a significant change in color was not noted over two catalysts employed. However, it was clearly seen that addition of Ga to catalyst lengthened its life.

CONCLUSIONS

In this study, gas-phase isomerization reaction of m-xylene was studied over various catalysts including Ni, Sn, Pt, Ga, Re or Zr in different compositions over alumina and zeolite catalysts. The catalyst composed of

$1,8 \cdot 10^{-3}\%$ Pt and the one composed of $1,8 \cdot 10^{-3}\%$ Pt and $3,04 \cdot 10^{-3}\%$ Ga, over ZSM5 support were found to be the selective ones to p-xylene, The ZSM5 catalysts including Pt and Zr and the HZSM5 type of zeolite have also given rather good results when compared to the other ones prepared, The kinetic model with first order mechanism taking into account m-xylene isomerization, disproportionation and demethylation fitted the experimental data fairly well.

ACKNOWLEDGMENT

Funding for this work from Ege University Research Fund through Grand 91Müh029 is gratefully acknowledged.

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