

The effect of Y-zeolite acidity on *m*-xylene transformation reactions

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Abstract

m-Xylene transformation has been studied on as-prepared H-Y and a series of dealuminated Y-zeolite catalysts. The conversion of *m*-xylene was found to increase initially with acidity, however, decreases subsequently. It was proposed that the high concentration of acid sites in the H-Y catalyst increases paring reaction, in addition to the well-known isomerization and disproportionation pathways. A significant decrease in trimethyl-benzenes (TMBs) yields was observed with both reaction temperature and catalyst acidity. The *p*-xylene/*o*-xylene (P/O) ratio was found to be independent of zeolite acidity. A higher coke deposition was found in the transformation of *m*-xylene over the parent H-Y as compared to the highly dealuminated USY zeolite. The formation of benzene and C₂–C₄ gases was found to be proportional to zeolite acid concentration.

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1. Introduction

Xylenes are important starting materials for some industrial processes like the production of synthetic fibers, plasticizers and resins. The major sources of these aromatic hydrocarbons are naphtha reforming and pyrolysis gasoline, which have a higher ratio of low-valued *m*-xylene. A convenient way to upgrade the low-valued *m*-xylene consists of its transformation to *o*- and *p*-xylene. In this context, the transformation of *m*-xylene has been studied over different types of zeolite catalysts [1–8].

There is increasing interest in ultrastable Y-type zeolites (USY) for *m*-xylene transformation, partly because of their increased chemical and thermal stability. Y-zeolite is made ultrastable by the removal of aluminum from the framework. The dealumination can be accomplished through the use of steam [9], acid leaching [10], or by chemical treatment with hexafluorosilicate or silicon tetrachloride [11–13]. However, the most common procedure is hydrothermal treatment at el-

evated temperatures under controlled atmosphere (steaming). The resulting USY zeolite has modified framework Si/Al ratio, structure and acidity. It usually exhibits improved reactivity, selectivity and coking behavior for a catalytic reaction, which is of great interest to the petroleum refining industry.

m-Xylene isomerization (I) and/or disproportionation (D) have been used to correlate the intrinsic properties of zeolites [14], their diffusion characteristics [15], protonic acidity [1,5], pore geometry and architecture [16]. Both the isomerization and disproportionation reactions were reported to be catalyzed by Brönsted acid sites [1–6]. Disproportionation, being a bimolecular reaction, requires higher concentration of acid sites [1,3,7]. However, these reactions do not produce benzene and gases. Recently, Iliyas and Al-Khattaf [17,18] studied the kinetics of *m*-xylene transformation over FCC catalyst.

Paring reaction was first proposed by Sullivan et al. [19] for the hydrocracking of hexamethylbenzene over a NiS-Al₂O₃-SiO₂ catalyst. It involves a sequence of reactions to apparently pare methyl groups from polymethylated aromatics. The pared methyl groups join together to form longer side chains, and subsequently these chains split off to form low

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chain olefins without disrupting the parent aromatic ring. Several researchers used the mechanism of paring reaction to explain the distribution of products during the disproportionation of 1,2,4-trimethylbenzene [20], isomerization of 1-cyclohexyloctane mixed with dodecane [21], and formation of ethyltoluene during the isomerization of trimethylbenzenes [8]. Also, Tsai et al. [22] showed that trimethylbenzene (TMBs) can transform through paring reaction to produce gases, benzene and toluene.

Several studies have been conducted on the effect of Y-zeolite acid properties on isomerization and disproportionation of *m*-xylene reactions [1,5,7]. However, studies correlating the intrinsic properties of Y-zeolite to other reaction pathways, apart from isomerization and disproportionation are somewhat limited. Therefore, the present work discusses the effect of acid properties of Y-zeolite on products selectivity and various reaction pathways during *m*-xylene transformation in a fluidized-bed reactor. Modified H-Y-zeolites using systematic hydrothermal treatment to obtain varying concentration of acid sites were employed for the study. Mechanisms were proposed for the formation of the various products. Furthermore, the stability and deactivation of the sites responsible for the proposed pathways were investigated for the H-Y and the highly steamed USY zeolite.

2. Experimental

2.1. The riser simulator

All experimental runs were carried out in a riser simulator. This reactor is a novel bench scale equipment with internal recycle unit invented by de Lasa [23] to overcome the technical problems of the standard micro-activity test (MAT). The riser simulator is fast becoming a valuable experimental tool for reaction evaluation involving model compounds [24,25] and also for testing and developing new fluidized catalytic cracking (FCC catalysts) for vacuum gas oil cracking [26,27]. The riser simulator consists of two outer shells, the lower section and the upper section, which allow one to load or to unload the catalyst easily. The reactor was designed in such a way that an annular space is created between the outer portion of the basket and the inner part of the reactor shell. A metallic gasket seals the two chambers with an impeller located in the upper section. A packing gland assembly and a cooling jacket surrounding the shaft provide support for the impeller. Upon rotation of the shaft, gas is forced outward from the center of the impeller toward the walls. This creates a lower pressure in the center region of the impeller, thus inducing flow of gas upward through the catalyst chamber from the bottom of the reactor annular region where the pressure is slightly higher. The impeller provides a fluidized bed of catalyst particles as well as intense gas mixing inside the reactor. A detailed description of various riser simulator components, sequence of injection and sampling can be found in work by Kraemer [28].

2.2. Materials

Commercial Y-zeolite with a Si/Al atomic ratio of 2.6 was provided by Tosoh Co. Japan. The as-synthesized Na-Y-zeolite was ion exchanged with NH_4NO_3 to replace the Na cation with NH_4^+ . Following this, NH_3 was removed and the H form of the zeolite was spray-dried using kaolin as the filler and a silica sol as the binder (both materials were obtained from Catalysts and Chemicals Industries Co., Japan). The resulting 60 μm catalyst particles contained: 30 wt.% zeolite, 50 wt.% kaolin, and 20 wt.% silica. The process of Na removal was repeated for the pelletized catalyst. Following this, the catalyst was calcined at 600 °C for 2 h. Finally, the fluidizable catalyst particles (60 μm average size) were treated with 100% steam at different temperatures and time to obtain the dealuminated Y-zeolites. The steaming conditions of the different USY zeolites are presented in Table 1.

2.3. Catalyst characterization

The BET surface area was measured according to the standard procedure ASTM D-3663 using Sorptomatic 1800 Carlo Erba Strumentazione unit, Italy. The acid property of the catalyst was characterized by NH_3 temperature-programmed desorption (NH_3 -TPD). In all the experiments, 50 mg of sample was outgassed at 400 °C for 30 min in flowing He and then cooled down to 150 °C. At that temperature, NH_3 was adsorbed on the sample by injecting pulses of 2 μl /pulse. The injection was repeated until the amount of NH_3 detected was the same for the last two injections. After the adsorption of NH_3 was saturated, the sample was flushed at 150 °C for 1 h with He to remove excess NH_3 , and then the temperature was programmed at 30 °C/min up to 1000 °C in flowing He at 30 ml/min. Flame ionization detector was used to monitor the desorbed NH_3 .

2.4. Procedure

An 80 mg of the catalyst sample was loaded into the riser simulator basket. The system was then sealed and tested for any pressure leaks by monitoring the pressure changes in the system. The reactor was heated to the desired reaction temperature. The vacuum box was also heated to around 250 °C and evacuated at around 0.5 psi to prevent any condensation of hydrocarbons inside the box. The heating of the riser simu-

Table 1
Physico-chemical properties of the as-prepared H-Y and dealuminated Y-zeolites

	Zeolite				
	H-Y	USY-1	USY-2	USY-3	USY-4
Steaming temperature (°C)	–	800	600	710	600
Steaming time (h)	–	6	5	3	2
Average crystal size (μm)	0.9	0.9	0.9	0.9	0.9
BET surface area (m^2/g)	187	155	172	175	177
Total acidity (mmol/g)	0.545	0.033	0.1	0.14	0.2

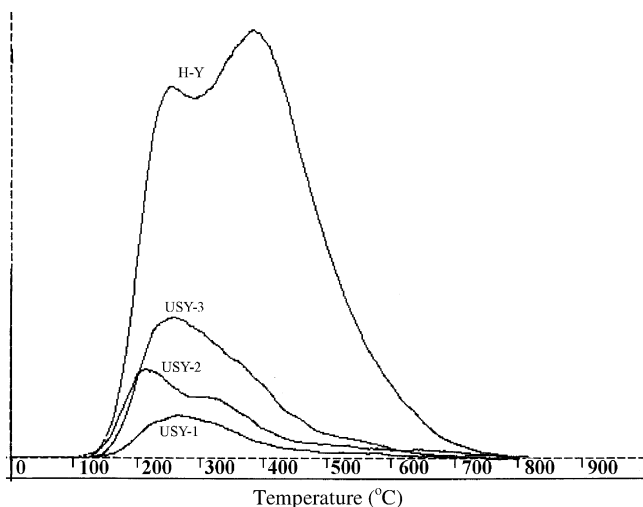


Fig. 1. Temperature programmed desorption of ammonia over the different catalysts.

lator was conducted under continuous flow of inert gas (Ar), and it usually takes few hours until thermal equilibrium is finally attained. Before the initial experimental run, the catalyst was activated for 15 min at 620 °C in a stream of Air. The temperature controller was set to the desired reaction temperature, and in the same manner, the timer was adjusted to the desired reaction time. At this point the gas chromatograph is started and set to the desired conditions.

Once the reactor and the gas chromatograph have reached the desired operating conditions, the *m*-xylene was injected directly into the reactor via a loaded syringe. After the reaction, the four-port valve opens immediately, ensuring that the reaction has been terminated and the entire product stream has been sent to gas chromatograph via a preheated vacuum box chamber.

2.5. Analysis

The riser simulator operates in conjunction with a series of sampling valves that allow, following a predetermined sequence, to inject reactants and withdraw products in short periods of time. The products were analyzed in Agilent 6890N gas chromatograph equipped with a flame ionization detector and a capillary column INNOWAX, 60 m cross-linked methyl silicone with an internal diameter of 0.32 mm. The carbonaceous deposit on the catalysts was measured by carbon analyzer CS244 (Leco).

3. Results and discussion

3.1. Catalyst characterization

The physico-chemical properties of the catalysts are presented in Table 1. The NH₃-TPD spectra of the parent H-Y and the dealuminated Y-zeolites catalysts are shown in Fig. 1, while the amounts of desorbed NH₃ (total acidity) are summarized in Table 1. H-Y catalyst showed two main desorption peaks at 265 and 390 °C and had a long tailing. The high temperature (HT) peak, at $T > 300$ °C of TPD spectra of H-Y is associated with water desorption as a result of dehydroxylation of surface hydroxyl groups. The HT peak is shifted to lower temperature in USY-2 at 310 °C and is not distinct for USY-3 catalyst. The area of HT peak decreased with increasing steaming temperature.

3.2. Products distribution

The degree of *m*-xylene conversion as a function of total number of acid sites were compared at 450 °C as shown in Fig. 2. The activity of the catalysts measured in terms

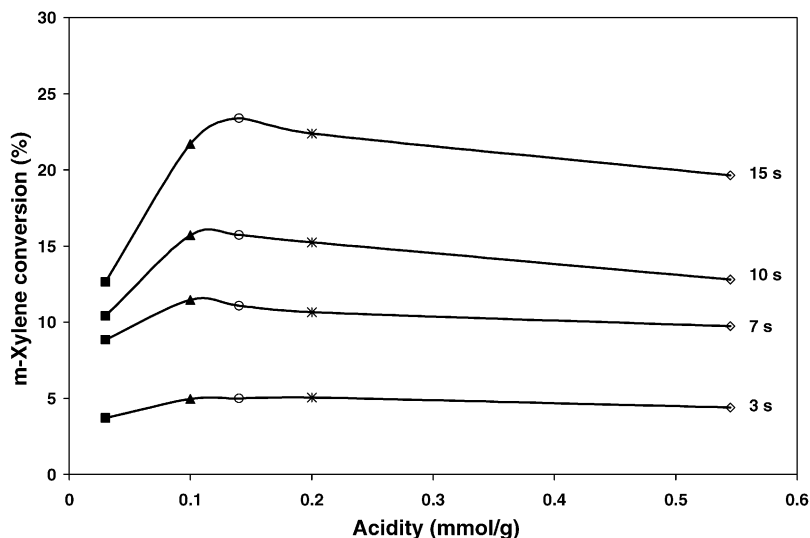


Fig. 2. *m*-Xylene conversion over the different catalysts vs. total acidity at various reaction times at 450 °C: (■) USY-1, (▲) USY-2 (○) USY-3, (✱) USY-4 (◇) USY-4.

Table 2
Coke deposited on the catalysts at various conditions

Temperature (°C)	Conversion (%)		Total coke deposited (wt.%)	
	USY-1	H-Y	USY-1	H-Y
400	2.2	4.0	0.044	0.63
	4.45	9.83	0.035	1.00
	5.1	13.11	0.039	1.30
	8.5	19.744	0.059	1.66
450	3.92	6.4	0.065	0.67
	9.1	11.11	0.051	1.17
	11.2	14.81	0.050	1.44
	13.3	20.88	0.041	1.72
500	8.17	6.3	0.041	0.59
	13.2	11.4	0.046	1.09
	15.5	15.1	0.075	1.35
	20.7	20.5	0.056	1.77

of conversion increased with reaction time. Moreover, it was noticed that conversion passed through a maximum for all reaction times studied, with an initial increase below 0.11 mmol/g. However the conversion slightly decreased subsequently. The initial increase in conversion with acidity can be explained easily, since transformation of *m*-xylene over Y-zeolite is enhanced with total acidity [1–3]. However, the subsequent decrease in conversion was due to the deactivation of active sites needed in converting *m*-xylene at higher acidity. In addition, Fig. 2 is explained according to the concept of “next nearest neighbors” (NNN). It has been reported that the isolated framework aluminum atoms (0-NNN) have the strongest acidity [29,30]. Ino and Al-Khattaf [31] showed that acidity is directly proportional to framework aluminum atom.

Since the H-Y catalyst has the highest acidity, it has less 0-NNN sites and abundant 1,2,3,4-NNN sites. These sites (1,2,3,4-NNN) have been reported to have high coke-making and less cracking and isomerization tendency [31]. This was further substantiated by the high coke yield measured over

H-Y catalysts compared to USY-1, as shown in Table 2. On the other hand, USY-2 and USY-3 with 0.1 and 0.14 mmol/g acidity, respectively were expected to have the highest number of 0-NNN sites as shown in a previous study [31], which explains their relatively higher conversion. Accordingly, the lowest conversion of *m*-xylene was obtained over highly dealuminated catalyst (USY-1). H-Y and USY-4 showed nearly the same initial activity, but different product selectivity, as shown in Fig. 3.

The product distribution during the transformation of *m*-xylene (at 450 °C) over the parent and the dealuminated Y-zeolites are compared in Fig. 3 at constant conversion level of 10%. The results show that toluene has the highest yield over the catalysts, except with USY-1, which gave a slightly lower yield of toluene than other products. The yields of tetramethylbenzenes (TTMBs) seemed to be the lowest at 10% conversion. Furthermore, the yields of *p*- and *o*-xylene were closely identical over all the catalysts, with the highest value being around 2.4% for each isomer over USY-1 catalyst.

It is worth mentioning that TTMBs, benzene, and C₂–C₄ gases were not observed over USY-1 catalyst at all conversion levels, and were formed with relatively low yields over USY-3 catalyst. In contrast, significant amounts of benzene and C₂–C₄ products were obtained over the parent H-Y as compared to the dealuminated catalysts. H-Y catalyst, however, gave the lowest selectivity toward TMBs particularly at higher reaction temperatures. This is better depicted by the plot of product yields versus reaction temperature for H-Y catalyst (Fig. 4). Substantial drop in the yields of TMBs were observed at higher reaction temperature. This drop suggests that TMBs undergoes secondary reactions. Moreover, the simultaneous rise in the yields of benzene and C₂–C₄ gases indicates that they are probably the products of such secondary reactions.

Pamin et al. [5] and Sulikowski et al. [6] attributed the secondary formation of benzene to simple dealkylation reaction. However, as observed by Roger et al. [20] methyl

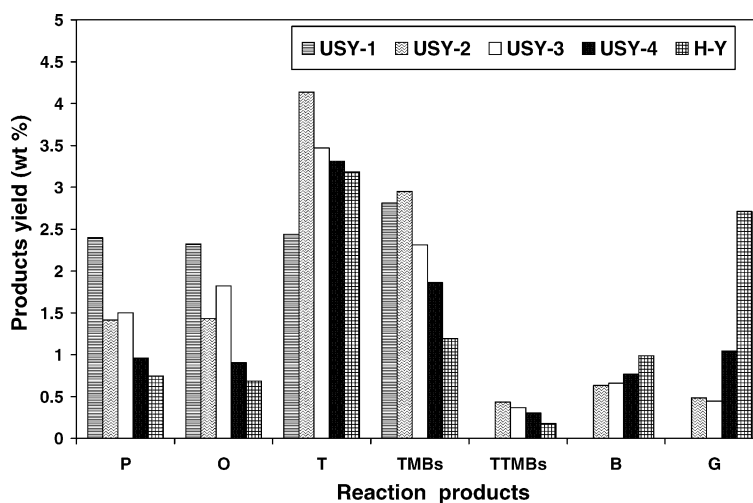


Fig. 3. Products distribution of *m*-xylene transformation over the different catalysts at 10% conversion and 450 °C reaction temperature.

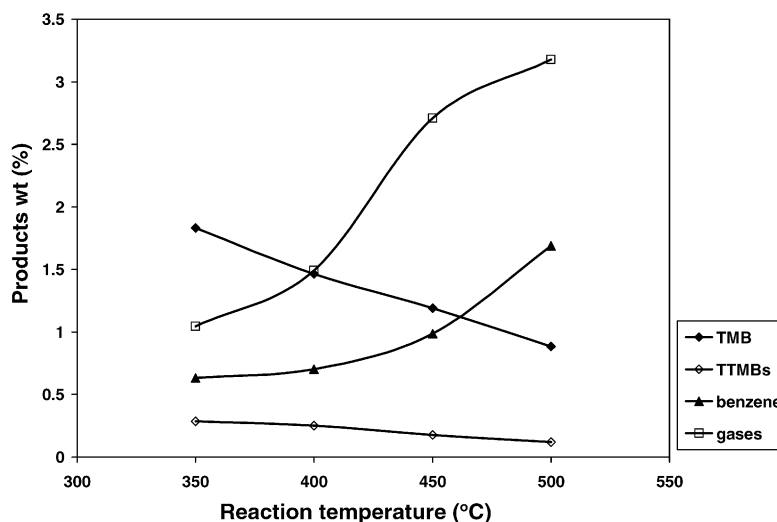


Fig. 4. Products yield vs. reaction temperature over H-Y catalyst at 10% *m*-xylene conversion.

groups do not dealkylate readily over acid catalysts. Moreover, this step needs hydrogen and forms methane, which was not reported in these studies. On the other hand, Laforge et al. [8] suggested that the produced benzene during the conversion of *m*-xylene over H-MCM-22 is likely the result of the transalkylation between *m*-xylene and toluene. However, when toluene and *m*-xylene were reacted under the conditions of the present study, an appreciable amount of benzene was not observed, and toluene was not converted. Moreover, the steady increase in toluene yield with reaction time at all reaction temperatures supports the fact that toluene does not undergo secondary reaction. Thus, it can be concluded that benzene is not formed from this route. Consequently, it is possible that over highly acidic catalysts, an alternative pathway, so-called paring reaction is initiated in addition to the well-known isomerization and disproportionation pathways, as shown by path 3 of Fig. 5.

Regarding paring reaction pathway, it is suggested that the high concentration of acid sites on the parent H-Y (Fig. 1) and the mildly dealuminated catalysts (USY-4) initiate the paring reaction of the produced TMBs, according to the mechanism

shown in Fig. 5 [22]. A similar conclusion regarding the formation of benzene via paring reaction was reported by Roger et al. [20] in their study of 1,2,4-trimethylbenzene conversion over H-ZSM5 zeolite. Moreover, since TMBs is formed via disproportionation route of the three xylene isomers, which suggests that they all undergo a similar paring reaction pathway. Moreover, the surplus toluene observed in the present study may have been formed from the alternate step of paring reaction. In addition, due to the high coke formation over H-Y, an appreciable amount of hydrogen will be formed as a consequence. This might further lead to the formation of gases and benzene via dealkylation.

3.3. Selectivity to different reaction pathways

The comparison of the product distribution over the different catalysts gives additional information about other possible reaction pathways in the course of *m*-xylene transformation. As shown in Fig. 5, *m*-xylene may undergo paring reaction in addition to the isomerization and disproportionation reactions over highly acidic zeolite catalyst. The se-

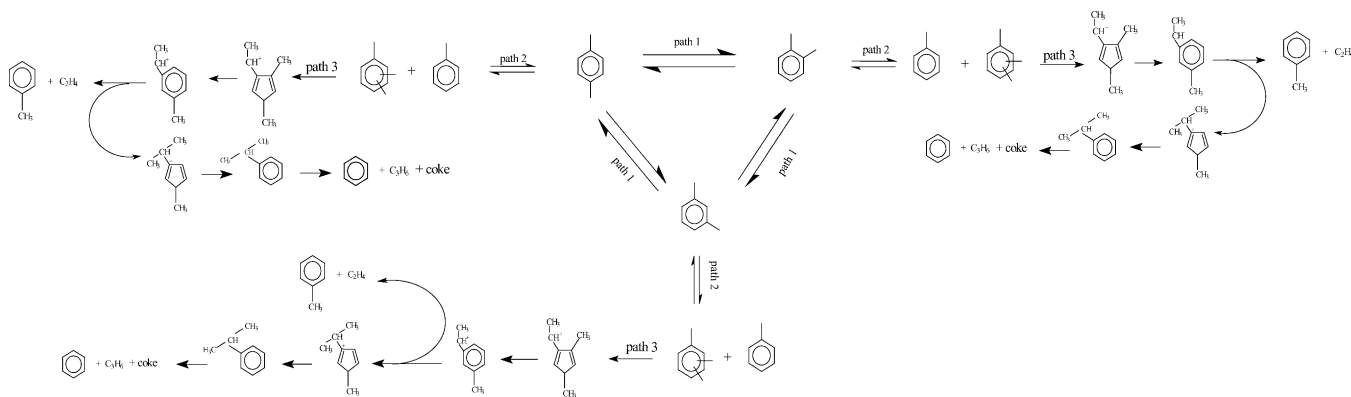


Fig. 5. Proposed overall reaction scheme and paring reaction mechanism during *m*-xylene transformation.

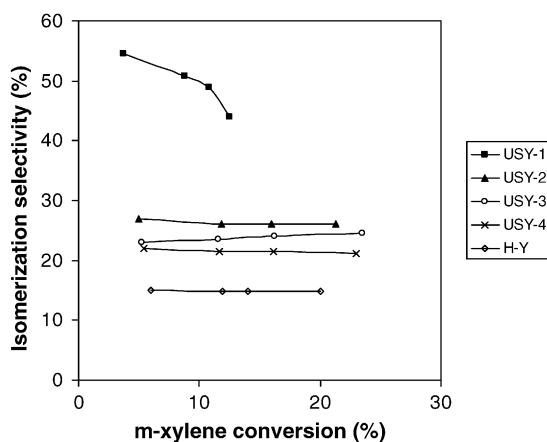


Fig. 6. Isomerization selectivity as a function of *m*-xylene conversion at 450 °C.

lectivity of *m*-xylene along these reaction pathways reflects, at least to a first approximation, the intrinsic properties of the catalysts, particularly the strength and concentration of acid sites. It may also provide indirect information on the relative stability and deactivation of the sites responsible for these reactions [1]. Thus, the selectivity of *m*-xylene transformation toward isomerization, disproportionation and paring pathways are plotted in Figs. 6–8, respectively at 450 °C, as a function of *m*-xylene. The highly dealuminated (USY-1) catalyst showed the highest isomerization selectivity, which is around 50% higher than the H-Y catalyst (Fig. 6). This result suggests that the low concentration of acid centers in the USY-1 catalyzes above all, the isomerization reaction. This is in agreement with the well-established fact that isomerization being a monomolecular reaction requires lower acid site density than bimolecular reactions.

Indeed it has been established that the increase in concentration of Brönsted sites facilitates disproportionation reaction. Since disproportionation is a bimolecular reaction, it requires higher amount of acid sites [7]. Based on this, the H-Y catalyst should give the highest disproportionation selectivity, since it has the highest concentration of Brönsted acid sites. However, Fig. 7 shows that the moderately dealuminated catalysts (USY-2 and USY-3) appeared to be the most active catalysts for *m*-xylene disproportionation, with selectivity values being about 1.45 times greater than parent H-Y catalysts at 12% *m*-xylene conversion. This is probably due to secondary transformation of TMBs, a major disproportionation product to coke precursors and paring reaction products, as evident from the relatively higher amount of both secondary products over this catalyst. Moreover, the high coke formation over the H-Y catalyst results in the decrease in the density of these sites. Thus, it is concluded that disproportionation reaction is more sensitive to this effect than isomerization.

Furthermore, Fig. 7 shows that disproportionation selectivity increases with *m*-xylene conversion over the highly dealuminated catalyst (USY-1). However, it remains constant

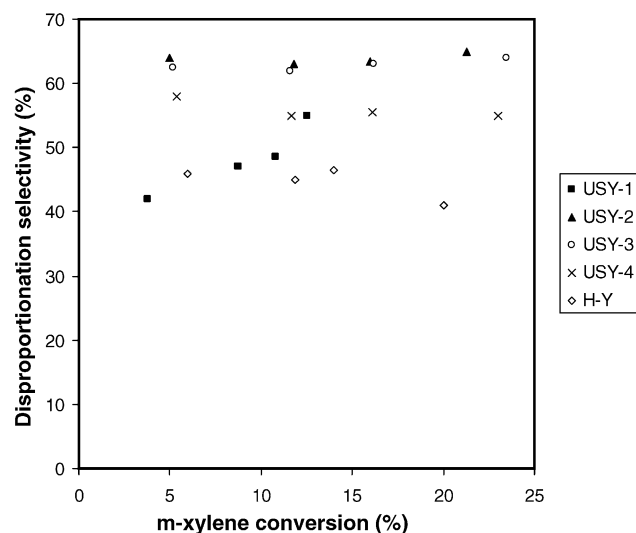


Fig. 7. Disproportionation selectivity as a function of *m*-xylene conversion at 450 °C.

with partially dealuminated catalysts, and decreases with the parent H-Y catalyst. The increase in disproportionation selectivity over USY-1 is consistent with the measured negligible coke deposition over this catalyst. This may be attributed to the fact that TMBs, which are intermediates for the formation of coke precursors, did not undergo any appreciable secondary transformation over USY-1 catalyst as shown in Table 2. In contrast, the observed decrease in the disproportionation selectivity with reaction time over H-Y supports earlier explanation regarding the selective deactivation of this reaction pathway.

It can be noticed that the selectivity to paring reaction differed significantly depending on the type of catalyst, as shown in Fig. 8. The highest selectivity to this reaction pathway was observed over the parent H-Y catalyst, while USY-1 shows no selectivity towards paring pathway. In line with ear-

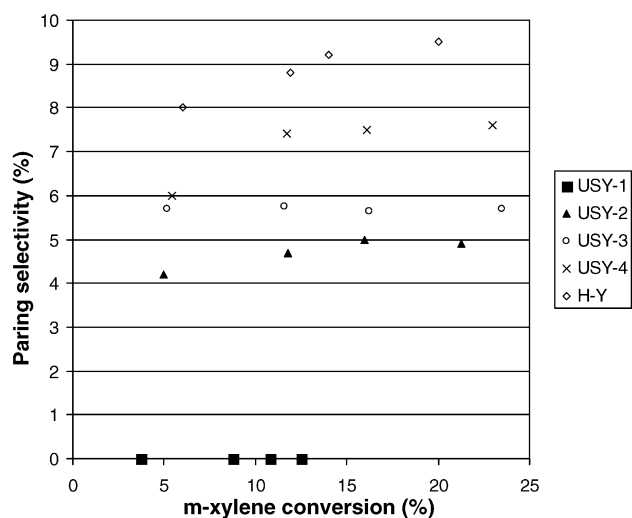


Fig. 8. Paring selectivity as a function of *m*-xylene conversion at 450 °C.

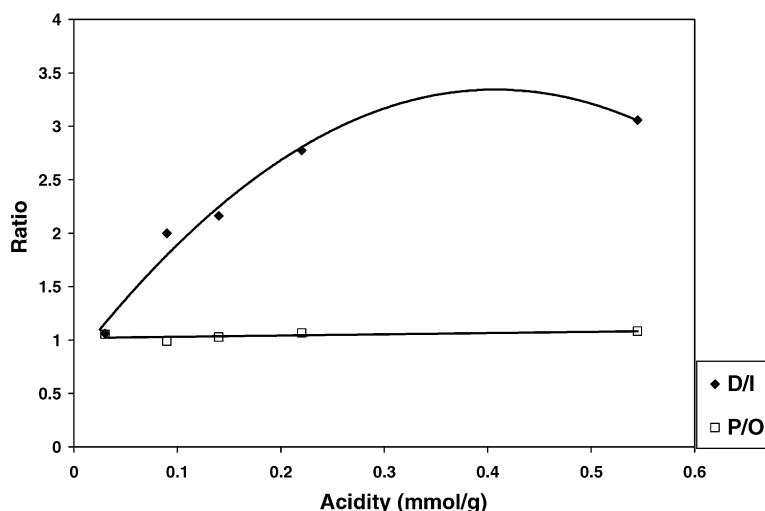


Fig. 9. D/I and P/O ratios vs. total acidity at 10% *m*-xylene conversion.

lier discussion, the high amount of acid sites of H-Y catalyst resulted in its high selectivity toward paring pathway. On the other hand, the decrease in the amount of acid centers with increasing level of dealumination explains the lower selectivity of the USY-zeolites toward this pathway, particularly with highly dealuminated (USY-1) catalyst, which shows no selectivity toward this reaction.

3.4. Influence of acidity

All catalysts exhibited a P/O ratio close to the thermodynamic predicted value of 1.09 [1]. This result confirmed the absence of shape selectivity over the Y-zeolite used, since the pore size of this zeolite is larger than the molecular diameter of the bulky *o*-xylene, and thus both isomers can move freely within the pores of the zeolite.

The effect acidity on P/O and D/I ratio was investigated at 10% conversion, as presented in Fig. 9. The data shows that under the conditions of this study, alteration of total acidity has no significant effect on P/O ratio. This result suggests that P/O selectivity during *m*-xylene transformation over large pore zeolite, such as Y-zeolite is not affected either by acid strength or acid site density. Thus, weak as well as strong acid sites should give the same P/O ratio. As reported earlier, P/O ratio is mainly a function of size of the pore channel, and as such has been used as criteria in determining the shapes and dimensions of intracrystalline cavities of zeolites [15,16]. In contrast to P/O ratio, D/I ratio gave a volcano-shaped curve with respect to change in acidity, in agreement with earlier explanation regarding the dependence of isomerization and disproportionation reactions on acidity.

3.5. Coke deposition

Zeolite deactivation during the conversion of organic compounds is mainly due to coke (carbonaceous compounds) deposition, which may cause site coverage or pore blockage. In

order to study the extent of deactivation rate during *m*-xylene conversion, the amount of coke deposited on H-Y and the highly dealuminated Y-zeolite (USY-1) were measured under different reaction conditions. The catalysts were chosen since they represent the most and least deactivated catalyst, respectively. Table 2 reveals that carbon deposition on both H-Y and USY-1 catalysts increases with *m*-xylene conversion. Similarly, the amount of coke deposited on H-Y catalyst increases with reaction temperature, however, temperature has only mild effect of coke deposition on USY-1 catalyst. Furthermore, the data in Table 2 show that at same conversion, H-Y catalyst produces more coke than USY-1. For example, at 500 °C and 20% *m*-xylene conversion H-Y produced 1.77 wt.% coke while USY-1 produced only 0.056 wt.%.

The more pronounced coke deposition measured over the as prepared H-Y-zeolite as compared to USY-1 could be due to its high acid site concentration. It has been reported that coke is formed preferentially on the catalyst with high acid density than on catalyst with low acid density [7]. It is also probable that some of the expelled aluminium atoms which remain in the non framework positions following the steaming of Y-zeolite may inhibit the formation of the bulky intermediates during coke formation. Thus it contributes to the low coking rate observed for the highly delaminated catalyst.

4. Conclusions

The transformation of *m*-xylene was investigated over H-Y-zeolite and a series of USY-zeolites dealuminated to different extent. It was found that zeolite acidity plays an important role in the conversion, products selectivity and reaction pathways during the transformation of *m*-xylene. The activity of the catalysts was found to increase initially with acidity, however, decreases subsequently due to the rapid deactivation of the catalysts with higher total acidity. The concept of “next nearest neighbors” was used to explain this behavior.

Paring reaction was proposed as a secondary reaction pathway with *m*-xylene transformation over the as-prepared H-Y-zeolite and the partially dealuminated USY catalysts. The increase in the selectivity towards paring reaction with increase zeolite acidity suggests that high concentration of acid sites facilitates this reaction pathway. On other hand, the low concentration of acid sites in USY-1 enhances isomerization pathway. Benzene and gases formation can be used as an indication for paring reaction.

The mild effect of acidity on *p*-xylene/*o*-xylene (P/O) ratio confirms earlier findings in the literature that the pore diameter of Y-zeolite is large enough, thus, allowing the xylenes to move freely without shape selectivity. This is obvious from the obtained P/O ratio, which corresponds to the thermodynamic equilibrium value of 1.09. Higher coke deposition was measured over H-Y as compared to the USY zeolites. This could be related to its higher concentration of acid sites. The higher coke yield of H-Y zeolite was accompanied with higher benzene and gases and lower TMBs yields.

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