

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 has been 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 was observed with respect to disproportionation/paring (D/Pa) ratio versus reaction temperature. This indicates that higher activation energy is required for paring as compared to disproportionation reaction. The p-xylene/o-xylene (P/O) was established to be independent of zeolite acidity. A higher coke deposition was found for 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 were found to be proportional to zeolite acid concentration.

Keywords: m-Xylene transformation, Y zeolite, isomerization, disproportionation, paring reaction.

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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 the 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 interest in ultrastable Y-type zeolites for m-xylene transformation, partly because of their increased chemical and thermal stability, with respect to other zeolites. 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 elevated temperatures under controlled atmosphere (steaming). The resulting material, USY (ultrastable Y) zeolites, being modified in the framework Si/Al ratio, structure and acidity, usually exhibits improved reactivity, selectivity and coking behavior for a catalytic reaction, which is of great interest to the petroleum 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 have been reported to be catalyzed by Brønsted acid sites [1-6]. Disproportionation being a bimolecular reaction has been established to require 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] in the early sixties 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 splits off to form low chain olefins without disrupting the parent aromatic ring. Moreover, some researchers have employed the mechanism of paring reaction to explain the obtained 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. With this in mind, the present work reports the effect of acid properties of Y-zeolite on products selectivity and various reaction pathways during m-xylene transformation in a fluidized-bed reactor. As prepared H-Y zeolite modified through systematic hydrothermal treatment to obtain varying concentration of acid sites were employed for the study. Mechanisms will be proposed for the formation of the various products. Furthermore, the stability and deactivation of the sites responsible for the proposed pathways will be investigated for the H-Y and the highly steamed USY zeolite.

2. Experimental Section

2.1 The Riser Simulator

All the experimental runs were carried out in the riser simulator. This reactor is 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). For example, the low olefinitivity obtained from MAT reactor, due to its higher reaction time (> 75 s) as compared to the riser (< 15 s), non uniform coke deposition (150 mm long catalyst bed), and temperature/concentration gradient, which are eliminated by the well-mixed characteristics and intense fluidization of the riser simulator. 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 in 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, as illustrated in Fig. 1. 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 having a Si/Al atomic ratio of 2.6 provided by Tosoh Co. Japan was used in this work. The as-synthesized Na 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 are supplied by Catalysts and Chemicals Industries Co. Japan. The resulting 60 μm catalyst particles had the following composition:

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 (designated USY) zeolites. The steaming conditions of the different catalysts are reported 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 NH₃ temperature-programmed desorption (NH₃-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, NH₃ was adsorbed on the sample by injecting pulses of 2 µl/pulse. The injection was repeated until the amount of NH₃ detected was the same for the last two injections. After the adsorption of NH₃ was saturated, the sample was flushed at 150°C for 1 h with He to remove excess NH₃, 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 NH₃.

2.4 Procedure

Regarding the experimental procedure in the riser simulator, a 80 mg portion of the catalyst was weighed and 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. Furthermore, 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 simulator was conducted under continuous flow of inert gas (Ar), and it usually takes a few hours until

thermal equilibrium is finally attained. Meanwhile, before the initial experimental run, the catalyst was activated for 15 min at 620°C in a stream of Ar. 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 GC is started and set to the desired conditions.

Once the reactor and the gas chromatograph have reached the desired operating conditions, the feedstock was injected directly into the reactor via a loaded syringe. After the reaction, the four-port valve immediately opens, ensuring that the reaction was terminated and the entire product stream sent online to the analytical equipment 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, one to inject reactants and withdraw products in short periods of time. The products were analyzed in an Agilent 6890N gas chromatograph with a flame ionization detector and a capillary column INNOWAX, 60-m cross-linked methyl silicone with an internal diameter of 0.32 mm.

3. Results and Discussion

3.1 Catalyst Characterization

The physico-chemical properties of the catalyst used in this study are presented in Table 1. The NH₃-TPD spectra of the parent H-Y and the dealuminated Y zeolites catalysts are shown in Fig. 2, 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 most likely to be associated with the 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. Also, the area of HT peak decreases with increasing steaming temperature.

3.2 *Products distribution*

The degree of m-xylene conversion as a function of total number of acid sites for the catalysts under study, are compared at 450°C as shown in Fig. 3. The activity of the catalysts taken in terms of conversion increases with reaction time, as expected. Moreover, it can be noticed that conversion passes through a maximum for all the reaction times studied, with an initial increase below 0.11 mmol/g, however it decreases 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 observed is as a result of the deactivation of the active sites needed in converting m-xylene at higher acidity. Among the examined catalysts, the lowest conversion of m-xylene was obtained over highly dealuminated catalyst (USY-1) inline with the preceding explanation. H-Y and USY-4 showed nearly the same initial activity, but different product selectivity, as shown in Fig. 4.

The product distribution during the transformation of m-xylene over the parent and the dealuminated Y zeolites are compared in Fig. 4 at constant conversion level of 10%. It is clear from these plots that toluene has the highest yield over the catalysts, except with USY-1, which gave a slightly lower yield of toluene than some other products. On the other hand, the yields of tetramethylbenzenes (TTMBs) seemed to be the lowest at 10 % conversion. Furthermore, the yields of p- and o-xylene are 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. However, H-Y catalyst appeared to give the lowest selectivity toward TMBs particularly at higher reaction temperatures. This is better depicted by the plot of product yields versus reaction temperature over this catalyst (Fig. 5). As shown in this figure, substantial decrease in the yields of TMBs can be noticed with increasing reaction temperature. This decrease suggests that it undergoes secondary reactions. Moreover, the simultaneous increase in the yields of benzene and C₂ - C₄ gases over this catalyst further indicates that these 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 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 used in the present study, an appreciable amount of benzene was not observed, and toluene seemed unreactive. Moreover, the steady increase in toluene yield with reaction time at all reaction temperatures studied, further 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 the highly acidic catalyst, 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. 6.

Regarding paring reaction pathway, it is proposed that the high concentration of strong acid sites on the parent H-Y (Fig.2) and the mildly dealuminated catalysts (USY-4) initiates paring reaction of the produced TMBs, following the mechanism shown in Fig. 6 [22]. A similar conclusion regarding

the formation of benzene via paring reaction was reached 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, thus, it is further proposed 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. These might further lead to the formation of gases and benzene.

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. 6, m-xylene may undergo paring reaction in addition to the isomerization and disproportionation reactions over highly acidic zeolite catalyst. The selectivity 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. 7 – 9, respectively at 450°C, as a function of reaction time for the parent and dealuminated catalysts. The highly dealuminated (USY-1) catalyst showed the highest isomerization selectivity, which is around 50% higher than the parent H-Y catalyst (Fig. 7). From this result, it is evident that the low concentration of acid centers in the USY-1 catalyst catalyzes above all, the isomerization reaction. This is in agreement with the well-established fact that isomerization being a monomolecular reaction requires weaker acidic sites.

Indeed it has been established that increase in concentration of Brønsted sites facilitates disproportionation reaction. Since disproportionation is a bimolecular reaction, it requires higher amount of acid sites for its catalysis [7]. Following this, one would expect that the parent H-Y catalyst should give the highest disproportionation selectivity, since it has the highest concentration of Brønsted acid sites. However, Fig. 8 shows that the moderately dealuminated catalysts (USY-2 and USY-3) appeared to be the most active catalyst for m-xylene disproportionation, with selectivity values being about 1.45 times greater than parent H-Y catalysts at 7 s reaction time. 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 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, suggesting that bimolecular reaction, such as disproportionation reaction is more sensitive to this effect than isomerization.

Furthermore, it is clear from Fig. 8 that disproportionation selectivity increases with time over the highly dealuminated catalyst (USY-1), remains constant 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 could be explained by fact that TMBs, which are necessary 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 greatly depending on the catalysts, as shown in Fig. 9. 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 earlier

discussion, the high amount of acid sites of H-Y catalyst results 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 temperature and conversion

In an attempt to study the role of temperature and conversion on the different ratios, a plots of disproportionation/paring (D/Pa) and p-xylene/o-xylene (P/O) ratios are made under various conversion and temperature levels as shown in Figs. 10 and 11, respectively. A significant result was obtained with regard to the variation of D/Pa ratio versus reaction temperature. As depicted in Fig. 10, it is clear that reaction temperature has a pronounced influence on D/Pa ratio. An increase in temperature from 350 to 500°C results in a corresponding decrease in D/Pa ratio by 80 % over the parent H-Y catalyst. A similar result was observed over the partially dealuminated catalysts. This phenomenon indicates that the energy of activation is higher for paring as compared to disproportionation reaction. As a consequence, disproportionation dominates at lower temperatures, while paring at higher temperatures, as indeed found experimentally. In contrast to temperature, conversion has a negligible effect on D/Pa ratio over the catalyst examined and under the reaction conditions used.

The result presented in Fig. 11 indicates that under the conditions of this study, all the catalysts exhibits 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.

3.5 Influence of acidity

The effect acidity on P/O and D/I ratio was investigated at 10% conversion, as presented in Fig. 12. Indeed, the data presented in this figure indicate 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 the Y zeolite used in this work is not affected by either acid strength or acid site density. Thus, weak as well as strong acid sites should give the same P/O ratio. As mentioned 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.

3.6 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 the parent H-Y and the highly dealuminated Y zeolite (USY-1) were measured under different reaction conditions of the present work. Both catalysts were chosen as they represent the most and least deactivated catalyst, respectively. Table 2 reveals that carbon deposition on the as prepared H-Y catalyst is initially 15 times greater than that of USY-1 catalyst and increases by twice this value with increasing time on stream. Similarly, the amount of coke deposited on H-Y catalyst increases with reaction temperature, while temperature has a mild effect of coke deposition on USY-1 catalyst.

The more pronounced coke deposition measured over the as prepared H-Y zeolite as compared to USY-1 could be due to its stronger acid sites. It has been reported that coke is formed preferentially on stronger acid sites which results in their faster deactivation rate than on weaker acid sites [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 contributing to the low coking rate observed for the highly delaminated catalyst.

Conclusions

The transformation of m-xylene was successfully investigated over as-prepared H-Y zeolite and a series of USY zeolites dealuminated to different extent. It was found that the zeolite acidity plays an important role in the conversion, products selectivity and reaction pathways during transformation of m-xylene. The activity of the catalysts taken in terms of conversion was found to increase initially with acidity, however, decreases subsequently due to the rapid deactivation of the catalysts having higher total acidity.

Paring reaction is proposed as a secondary reaction pathway with m-xylene transformation over the as-prepared H-Y zeolite and the partially dealuminated catalysts. The increase in the selectivity towards paring reaction with increase zeolite acidity suggests that high concentration of strong acid sites facilitates this reaction pathway. On other hand, the low concentration of acid sites in USY-1 enhances isomerization pathway. Also, the pronounced decrease in disproportionation/paring (D/Pa) ratio with reaction temperature indicates higher activation energy for paring as compared to disproportionation reaction.

The mild influence of acidity on p-xylene/o-xylene (P/O) ratio confirms earlier proposition 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. A higher coke deposition was measured over H-Y as compared to the USY zeolites. This again could be related to its higher concentration of strong acid

sites. Moreover, the presence of extraframework aluminium species in USY zeolites may prevent the formation of the bulky coke intermediates, thus, reducing their deactivation rate.

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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	177	175
Total acidity (mmol/g)	0.545	0.033	0.1	0.14	0.2

Table 2. Coke deposited on the catalysts at various conditions

temp. (°C)	time (s)	total coke deposited (wt %)	
		<i>USY-1</i>	<i>H-Y</i>
400	3	0.044	0.63
	7	0.035	1.00
	10	0.039	1.30
	15	0.059	1.66
450	3	0.065	0.67
	7	0.051	1.17
	10	0.050	1.44
	15	0.041	1.72
500	3	0.041	0.59
	7	0.046	1.09
	10	0.075	1.35
	15	0.056	1.77

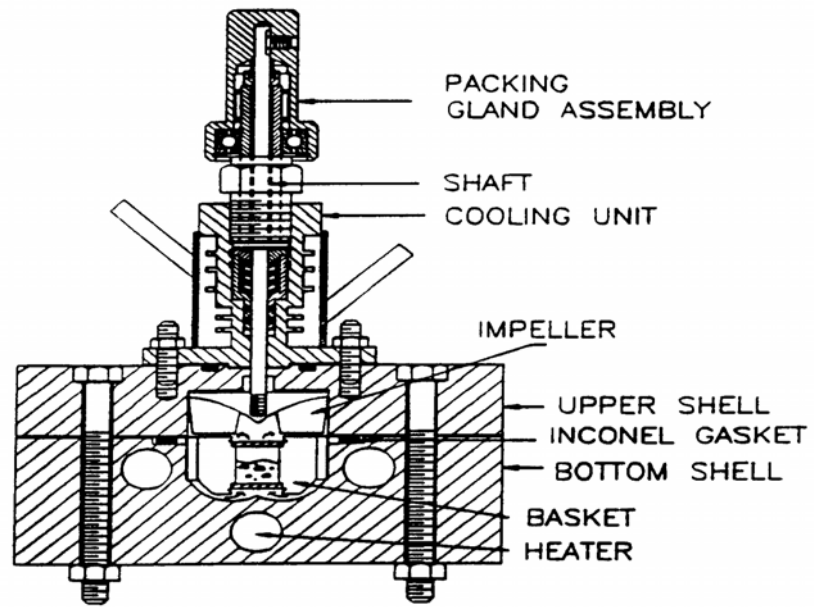


Fig. 1 Schematic diagram of the riser simulator.

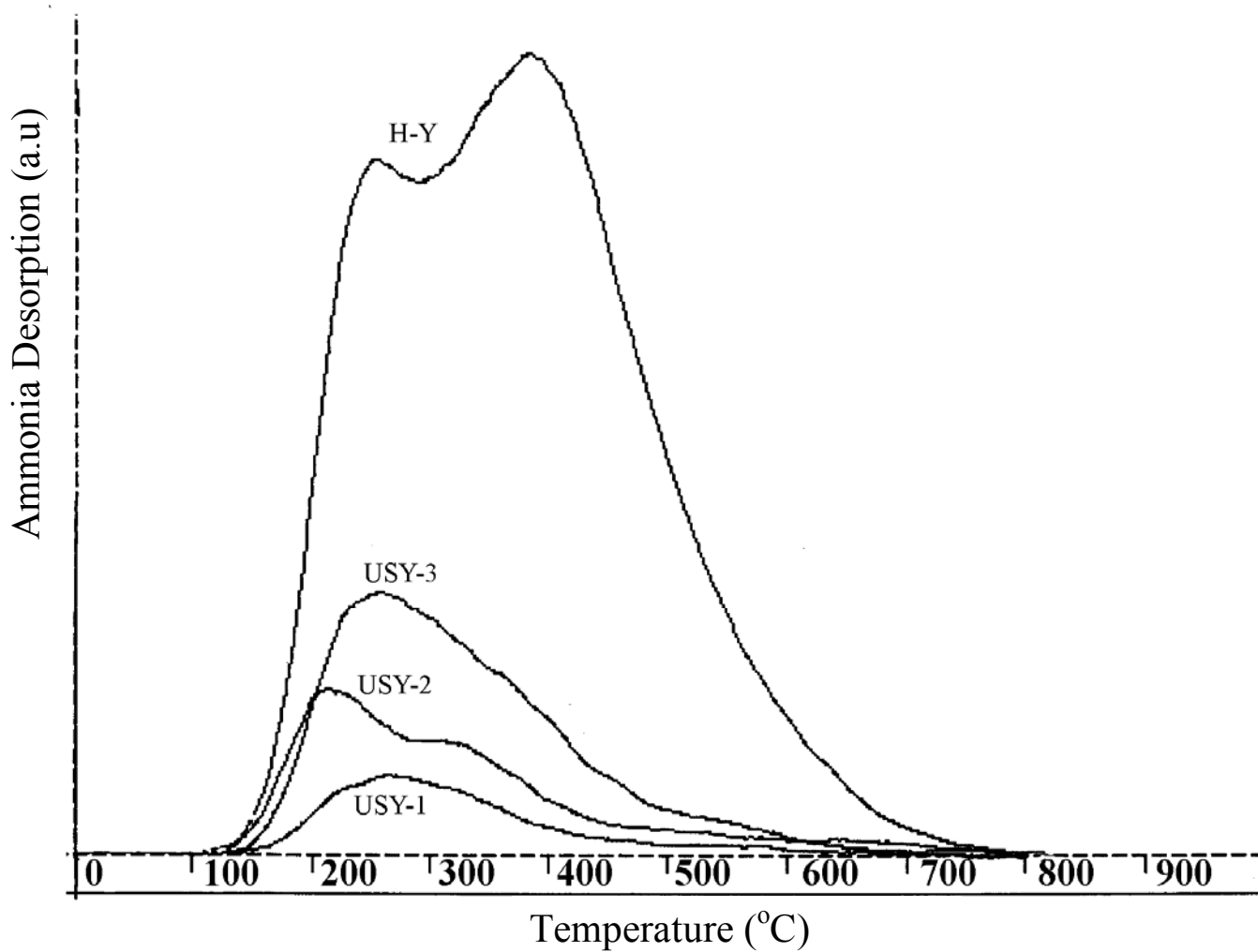


Fig. 2. Temperature programmed desorption of ammonia over the different catalysts

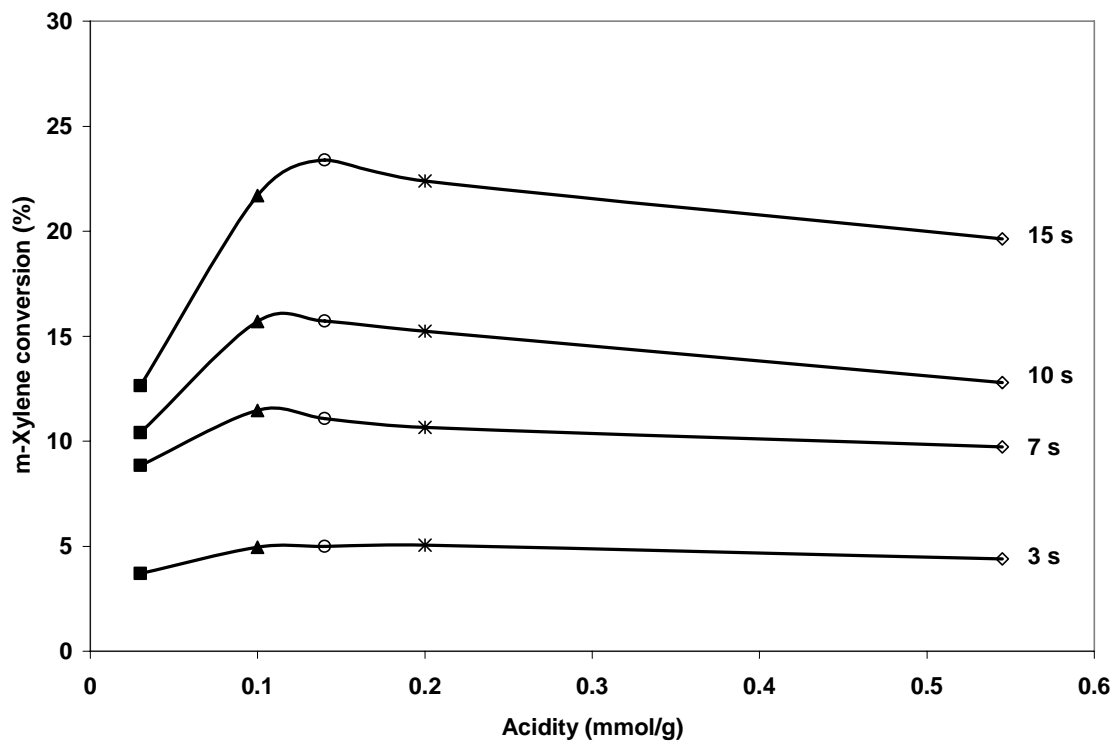


Fig.3. m-Xylene conversion over the different catalysts versus total acidity at various reaction times at 450°C ; (■) USY-1, (▲) USY-2 (○) USY-3, (✱) USY-4 (◇) USY-4

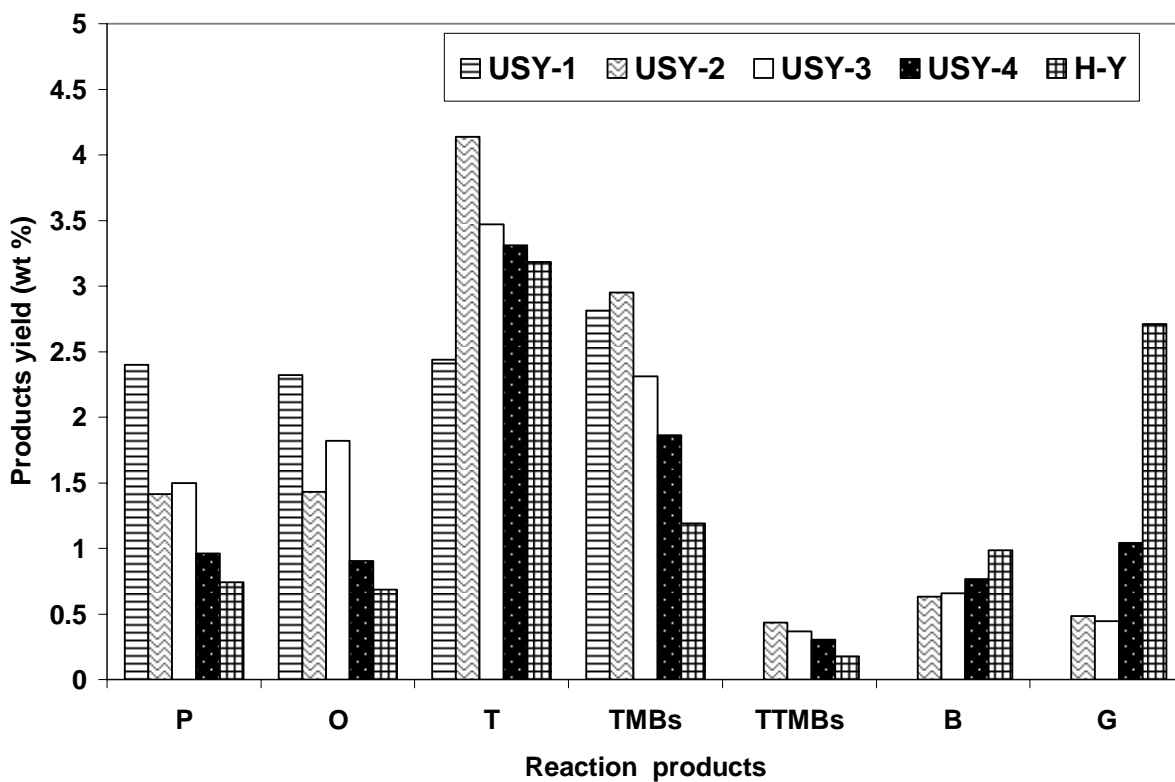


Fig. 4. Products distribution of m-xylene transformation over the different catalysts at 10% conversion.

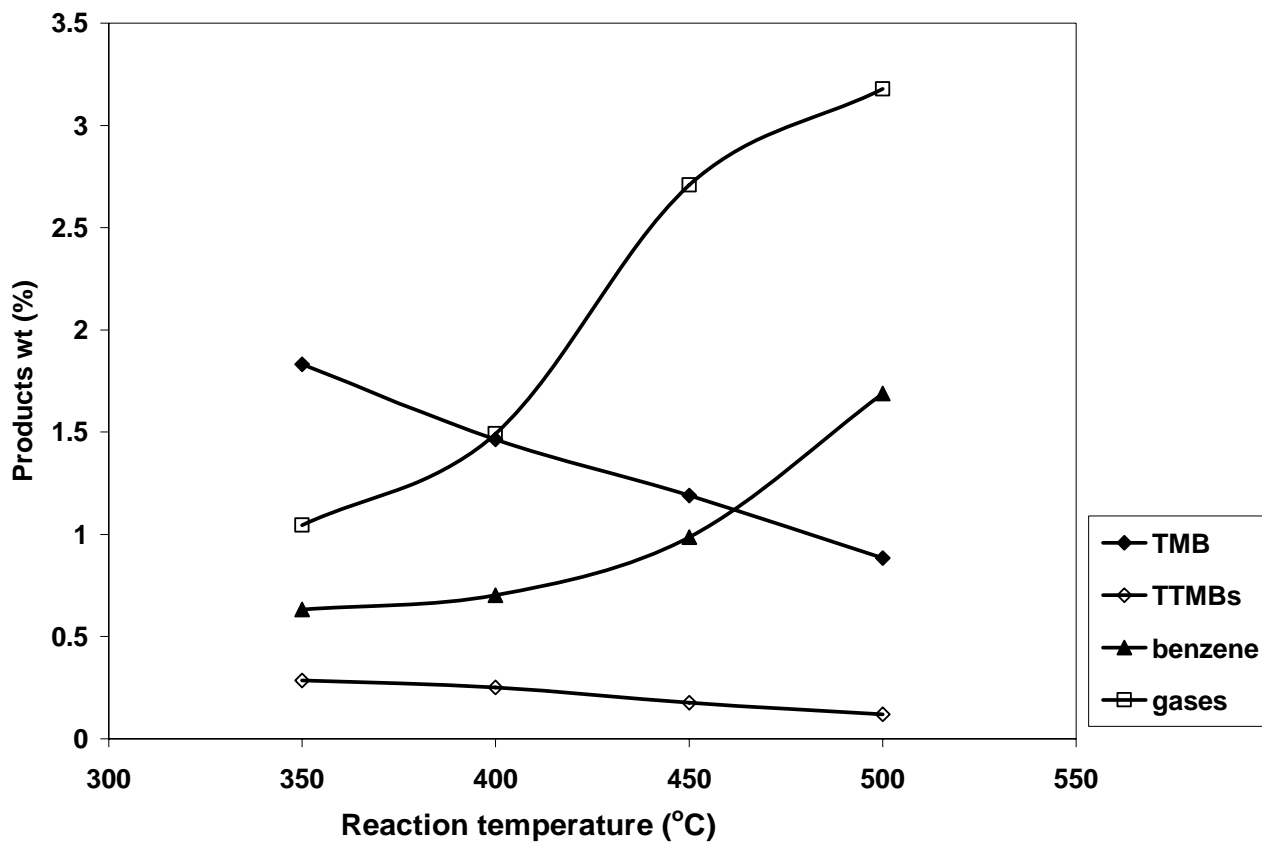


Fig. 5. Products yield versus reaction temperature over H-Y catalyst at 10% m-xylene conversion.

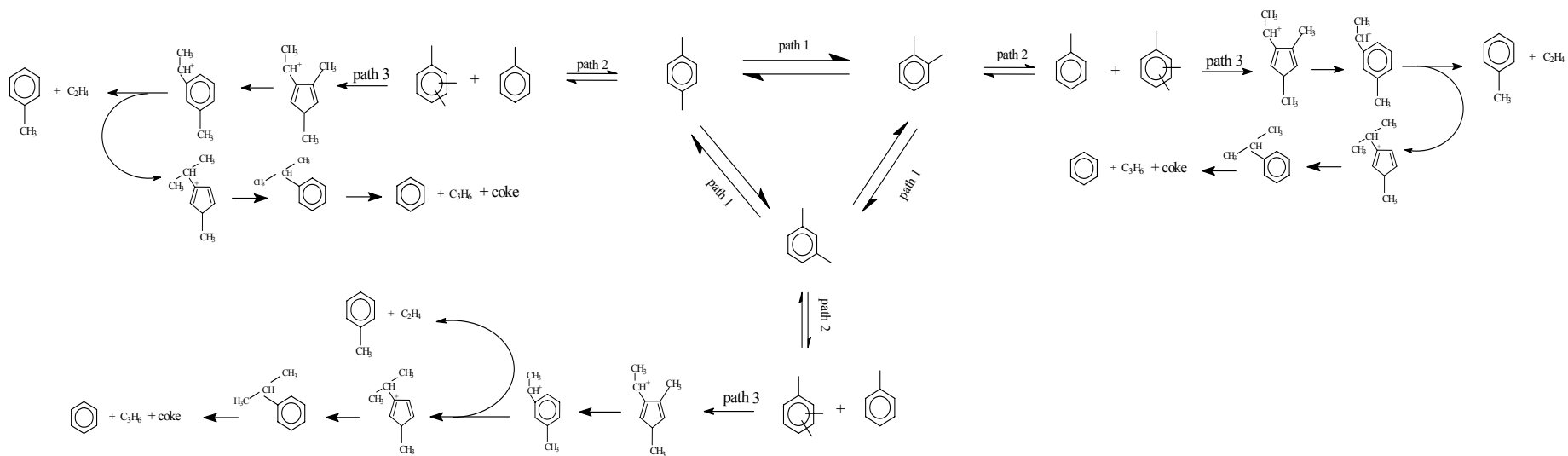


Fig. 6. Proposed overall reaction scheme and pairing reaction mechanism during m-xylene transformation.

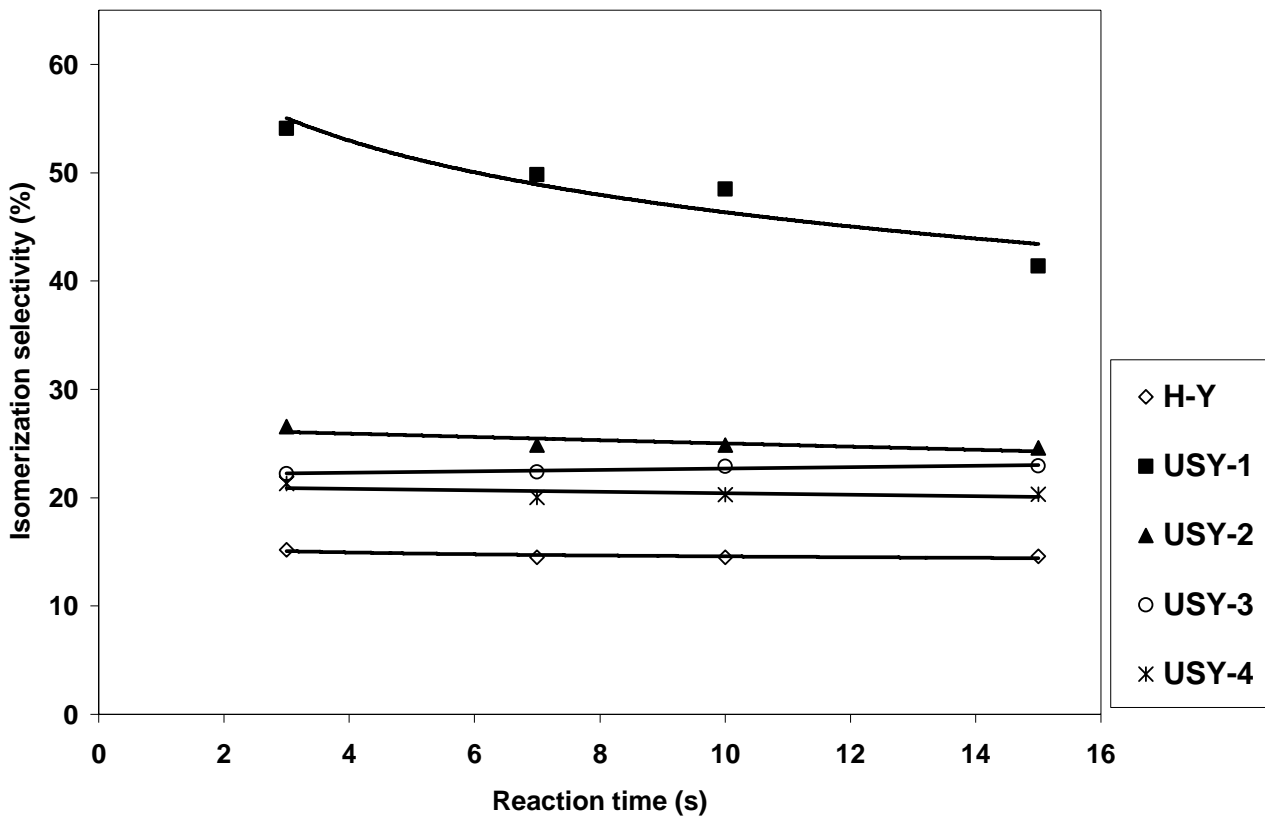


Fig. 7. Isomerization selectivity as a function of reaction time at 450°C.

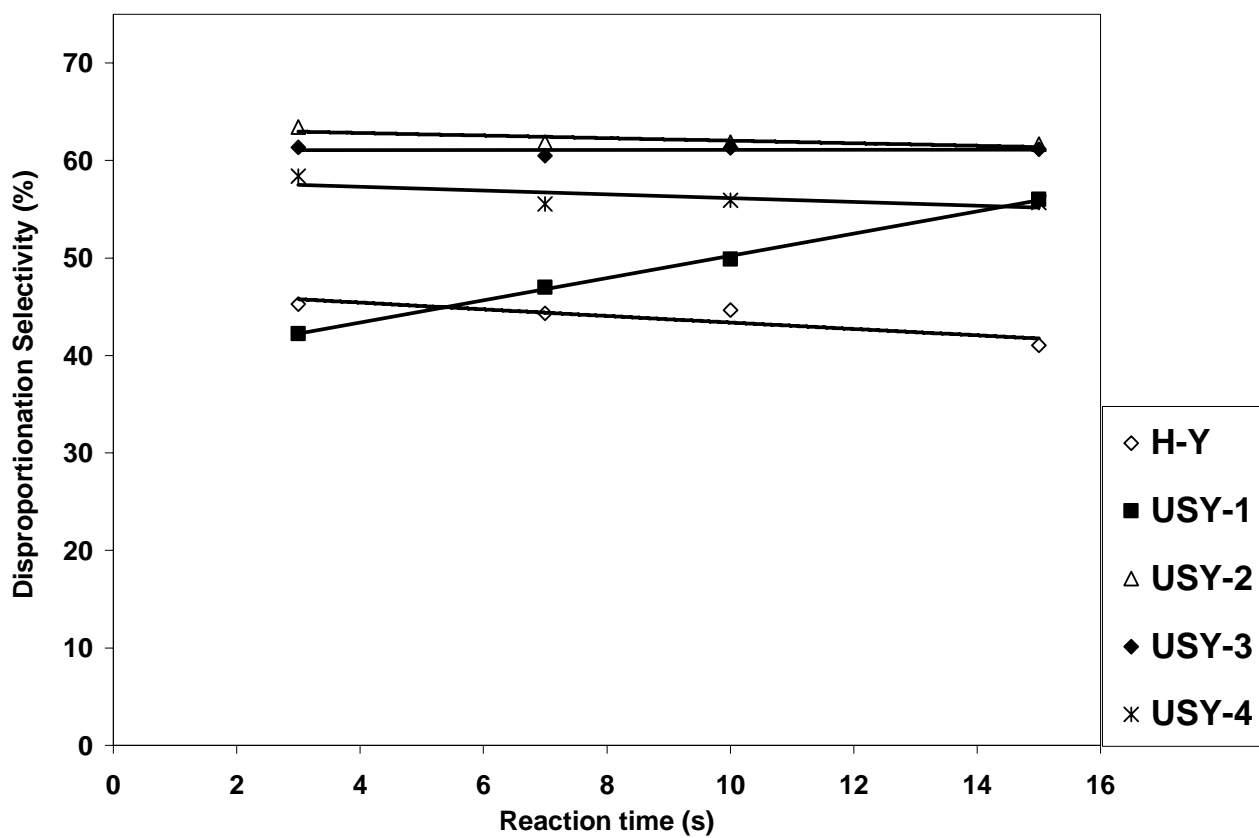


Fig. 8. Disproportionation selectivity as a function of reaction time at 450°C

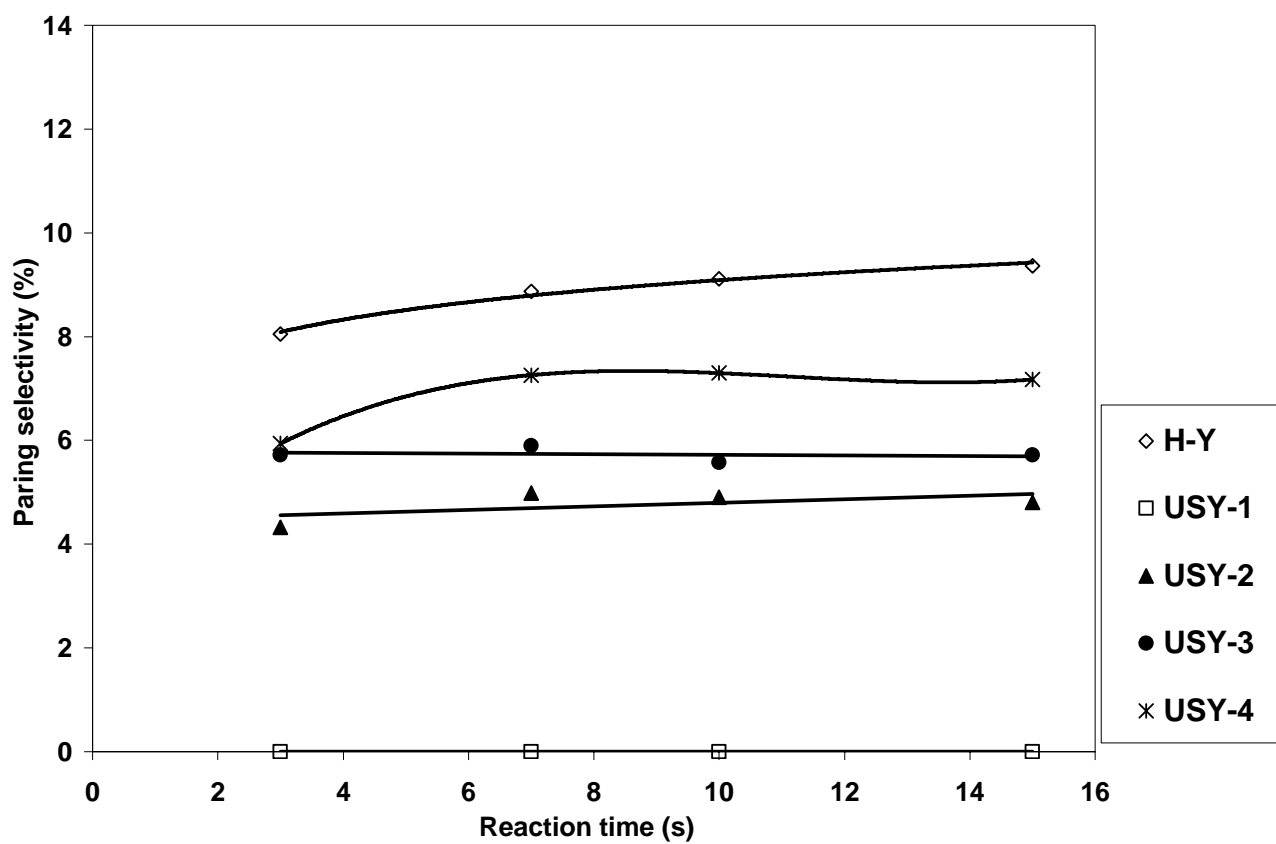


Fig. 9. Paring selectivity as a function of reaction time at 450°C.

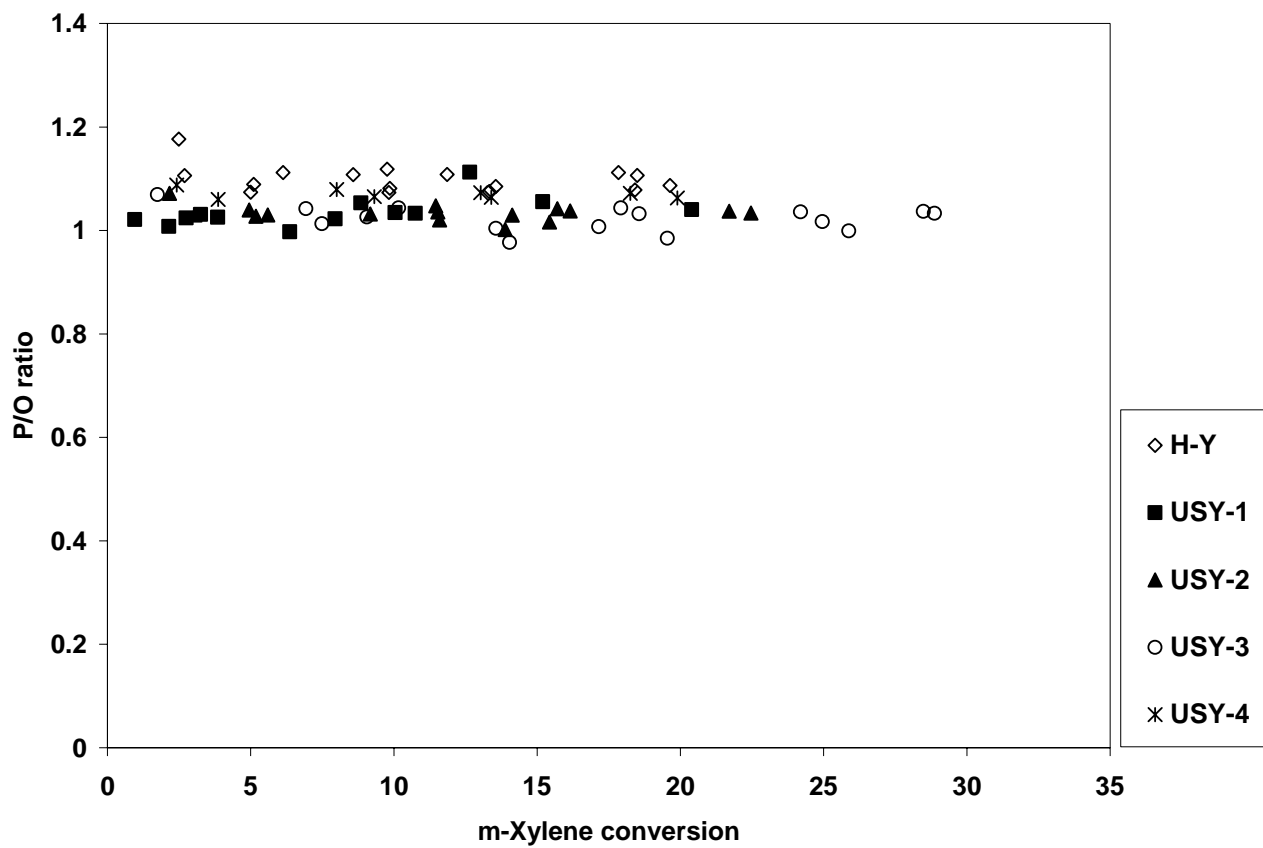


Fig. 10 p-Xylene/o-xylene (P/O) ratio as a function of m-xylene conversion.

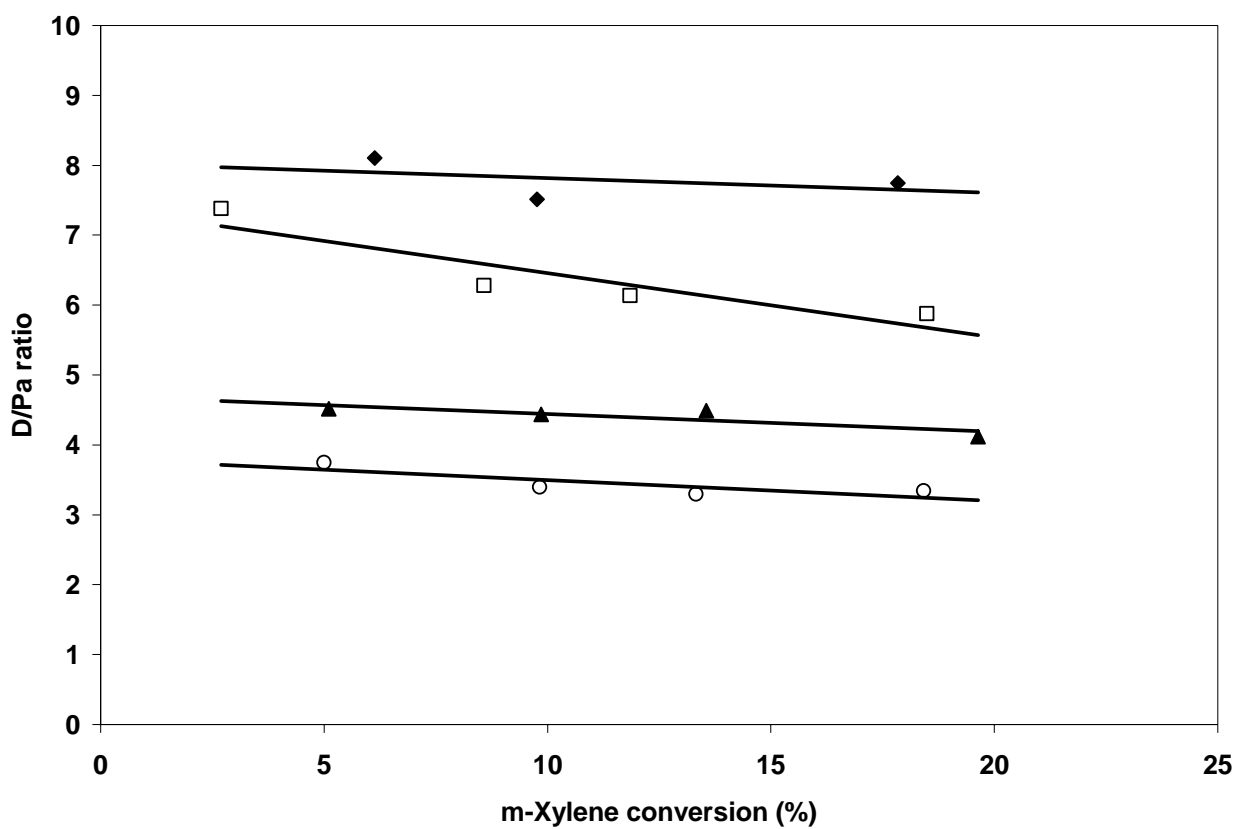


Fig. 11. Disproportionation/paring (D/Pa) ratio as a function of m-xylene conversion over H-Y catalyst at (◆) 350°C, (□) 400°C, (▲) 450°C, (○) 500°C

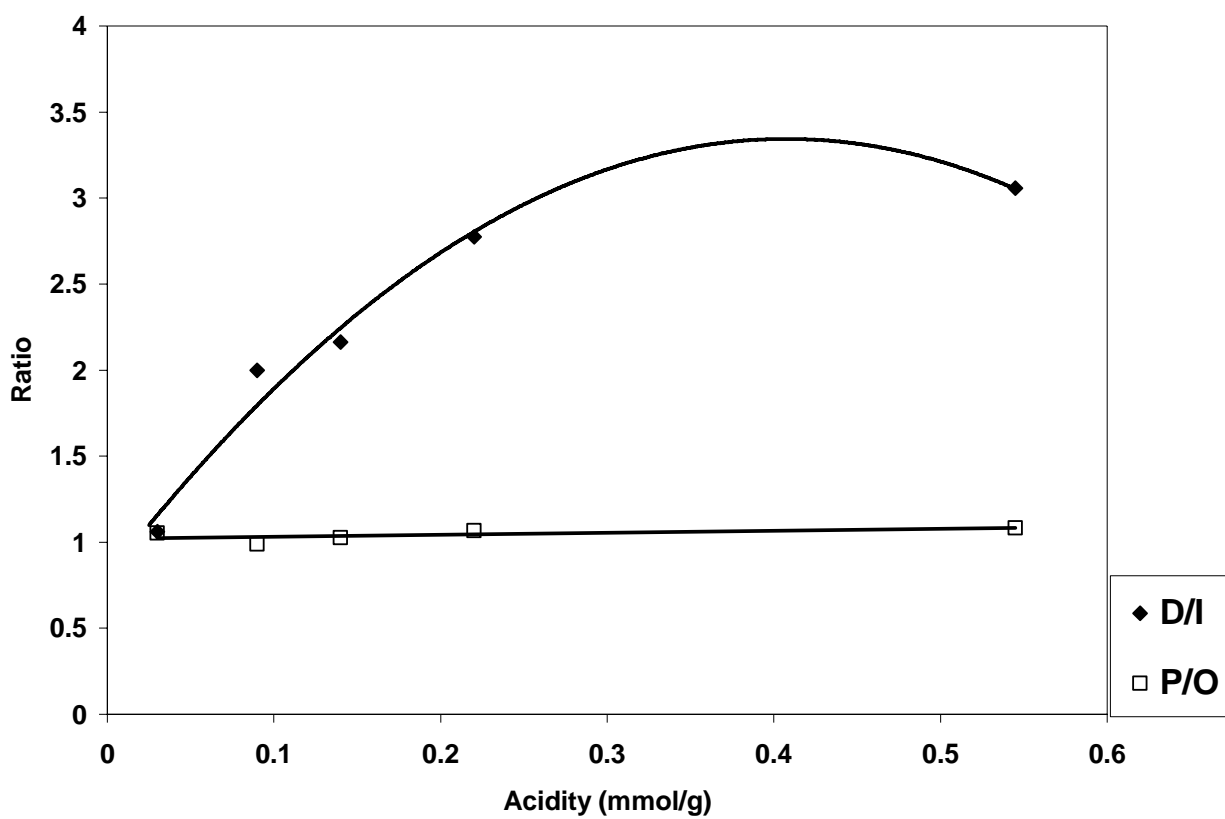


Fig.12. D/I and P/O ratios versus total acidity at 10% m-xylene conversion