AROMATIC TRANSFORMATION IN FLUIDIZED BED REACTORS

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In this work three important aromatic transformations, namely: toluene disproportionation, toluene methylation and *m*-xylene isomerization, were investigated in a riser simulator which closely mimics the operation of commercial fluidized bed reactors. The transformations were studied over a ZSM-5 based catalyst with medium acidity of 0.23 mmol/g and a series of Y zeolites of acidities between 0.55 and 0.03 mmol/g. For pure toluene feed, it was observed that conversion over the ZSM-5 based catalyst and the weakly acidic Y zeolite (USY-1) was very low. However, with the highly acidic Y zeolite (H-Y), significant toluene conversion was observed with paring reaction more prominent than disproportionation. On the other hand, when toluene was alkylated with methanol, higher toluene conversions were achieved over both the ZSM-5 based and the weakly acidic USY-1 catalysts as compared to when pure toluene feed was used. In addition, *p*-xylene/*o*-xylene (P/O) ratios higher than the equilibrium values were obtained in the reaction product over both catalysts. Finally, for *m*-xylene isomerization it was found that *m*-xylene conversion increased initially as the acidity of the catalyst increased up to 0.1 mmol/g beyond which any further increase in acidity resulted in a slight decrease in the *m*-xylene conversion.
Keywords: Toluene disproportionation; Toluene methylation; *m*-Xylene isomerization; Fluidized bed reactors; Zeolite catalyst.

Aromatic compounds such as benzene, toluene and xylene produced from naphtha reforming find a wide range of applications in the production of polymers and numerous consumer goods such as solvents, paints, polishes and pharmaceuticals etc.[1,2]. Consequently, the demand for these aromatic compounds is always on the increase. *p*-Xylene in particular shows a huge demand since it is an important raw material for the production of terephthalic acid, a key intermediate in the production of the world's most important polymer (polyethylene terephthalate, PET). As a result, efforts are continuously been made to improve the yield of *p*-xylene obtained from naphtha reforming. A promising way of achieving this goal is the transfor-

mation of the low-valued aromatics such as toluene and *m*-xylene into *p*-xylene. Such transformations are typically carried out over solid acid catalysts like zeolites; a class of microporous crystalline solids based on silica and alumina tetrahedra[3]. Compared with other solid catalysts, zeolites have a well defined pore structure which can be exploited to enhance the yield of *p*-xylene resulting from these aromatic transformations. Several zeolites differing in pore sizes and structures have been employed in aromatic transformations. However, the most commonly used zeolites are based on the ZSM-5 and zeolite Y structure.

In addition to *m*- and *o*-xylene isomerization, present alternatives to the production of *p*-xylene are the toluene conversion processes comprising of toluene disproportionation and toluene alkylation with methanol over zeolite based catalysts. Although both reactions have been employed in the selective production of xylene and *p*-xylene in particular, several side reactions have posed serious problems. A number of catalyst modifications have been reported in literature to control these side reactions. The most commonly adopted catalyst modifications include incorporation of oxides such as MgO, B_2O_3 or P_2O_5 into the zeolite catalyst framework[4], steaming[5], pre-coking by high-temperature, anaerobic treatment with a carbonaceous material[6] and chemical vapor deposition (CVD)[7,8]. Comprehensive reviews of some of the most important aromatic reactions including toluene alkylation with methanol, xylene isomerization and toluene disproportionation have been written by Čejka et al.[2] and Corma et al.[9].

It should be mentioned that more than 95% of the above mentioned aromatic transformation processes are carried out in fixed bed reactors and that the catalyst modification approach has not been entirely successful in solving the problems of undesirable reactions, which usually jeopardize the selectivity of required reaction products. The main problem encountered with catalyst modifications is that they lead to a considerable decrease in conversion and in some cases instability of the catalyst framework. Another problem associated with these aromatic transformations is that catalyst deactivation due to coking results in a considerable decrease in the catalyst activity with time-on-stream. In this work, we attempt to address the problems associated with these aromatic transformations from a different perspective by attempting to optimize the process variables of the reaction instead of the catalyst modification approach. This can be achieved specifically by minimizing the undesirable secondary reactions and catalyst deactivation by reducing the contact time between the catalysts and the aromatic reactants. This can offer a superior route to high xylene yield and high *p*-xylene selectivity compared with multiple pre-treatment of the zeo-

lite catalyst. Furthermore, to ensure that significant aromatic conversion can be achieved in the proposed short reaction time, a fluidized bed process will be used in contrast to the more commonly used fixed bed process. It is expected that fluidization, which enhances the catalyst-reactant contact will lead to a high aromatic conversion in a short time. The overall result of the process will be a high aromatic conversion while maintaining high xylene yield and high *p*-xylene selectivity. Another important potential advantage, which the fluidized bed process can have over the fixed bed process, is better heat distribution resulting in a more uniform product quality in contrast to the fixed bed processes where large temperature gradients in the reactor can negatively affect the quality of the product. Finally, the relative easy transportation of deactivated catalyst between the reacting and regeneration zones makes catalyst regeneration much easier in the fluidized bed reactor than in the fixed bed reactor where catalyst regeneration is usually laborious, time-consuming and very expensive.

In the following sections, we present the results obtained from three different aromatic transformations over zeolite catalysts (based on the ZSM-5 and Y zeolite) in a riser simulator which mimics the operation of commercial fluidized bed reactors. These transformations are toluene disproportionation, toluene methylation and *m*-xylene isomerization.

EXPERIMENTAL

The Riser Simulator

All experimental runs in this work were performed in a riser simulator invented by de Lasa[10]. The riser simulator is a novel bench-scale apparatus with an internal recycle unit to overcome the technical problems of the standard microactivity test (MAT), and it is fast becoming a valuable experimental tool for evaluation of the reaction involving model compounds[11,12] and also for testing and developing new fluidized catalytic cracking (FCC) in vacuum gas oil (VGO) cracking. A detailed description of the various riser simulator components, and the sequence of injection and sampling, can be found in the work by Kraemer[13].

Materials

The Y zeolite used in this work was obtained from the Tosoh Company in the Na form. The zeolite was ion-exchanged with NH_4NO_3 to replace the sodium cation with NH_4^+. NH_3 was then removed by calcination to form H zeolite. For use in fluidized bed reactors, zeolite catalysts are usually made in forms, which are readily fluidizable. This is most preferably achieved by composting the zeolites with binders and fillers such that the resulting composite catalyst particles are characterized by a combination of size, shape, and density to be classified as Geldart Type A powders. Therefore, the catalyst used was formed by mixing 30 g of the H-form of the zeolite with 20 g of silica (binder) and 50 g of kaolin (filler). The resulting slurry was then spray-dried to form catalyst pellets having average particle size ca.

60 μm and the composition 30 wt.% zeolite, 50 wt.% kaolin, and 20 wt.% silica sol. The process of sodium removal was repeated for the pelletized catalyst. Following this, the catalyst was calcined at 600 °C for 2 h. This calcined catalyst, which is very acidic, was labeled H-Y. A portion of the H-Y (fluidizable catalyst particles, 60-μm average size) was treated with steam at 600 °C for 5 h forming a catalyst designated as USY-1, with very low acidity. Other catalysts USY-2, USY-3 and USY-4 with varying acidity were also prepared from H-Y using steaming conditions which were less severe compared with those used in preparing USY-1.

The as-prepared ZSM-5 zeolite used in this work was obtained from Grace Division. Similar to the Y zeolite, the ZSM-5 zeolite was spray-dried using kaolin as the filler and a silica sol as the binder. The resulting 60-μm catalyst particles had the following composition: 30 wt.% zeolite, 50 wt.% kaolin and 20 wt.% silica. The catalyst was then calcined at 600 °C for 2 h. This catalyst was labeled GKF-3.

Procedure

Regarding the experimental procedure in the riser simulator, 0.8 g of 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. Afterwards, the reactor was heated to the desired reaction temperature while the vacuum box was heated to ca. 250 °C and evacuated to a pressure of ca. 0.035 bar in order to prevent any condensation of the reaction products inside the box. The riser simulator was heated under continuous flow of argon; the process usually takes a few hours until thermal equilibrium is finally attained. Meanwhile, before the initial experimental run, the catalyst was activated with air at 620 °C for 15 min. After thermal equilibrium was reached, the temperature controller and timer were set to the desired reaction temperature and reaction time, respectively. At this point the GC was started and set to the desired conditions.

Once the reactor and the gas chromatograph reached their desired operating conditions, 200 μl (~0.166 g) of the feedstock was injected directly into the reactor with a loaded syringe while stirring at 6000 rpm. After the reaction, a four port valve connecting the reactor to the vacuum box opened immediately ensuring that the reaction was terminated and the entire product stream sent on-line to the gas chromatograph via the preheated vacuum box chamber. The products were then analyzed by the GC. The catalyst was regenerated after each experimental run under conditions similar to initial activation.

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 with an Agilent 6890N gas chromatograph equipped with flame ionization detection (FID) and a capillary column (INNOWAX, 60 m crosslinked methyl silicone with an internal diameter of 0.32 mm).

Coke deposited on spent catalysts was determined by a common combustion method with a carbon analyzer (multi EA 2000, Analytikjena). Oxygen is supplied to the unit directly. A small amount of the spent catalyst (0.35 g) was used for the analysis. The coke formed on the catalyst during the reaction experiments was burned, completely converting the carbonaceous deposit to carbon dioxide (CO_2). The coke formed was determined by measuring the amount of CO_2.

Catalyst Characterization

The catalysts used in this work were characterized for BET surface area, total acidity and crystal size. The BET surface area was determined according to the standard procedure ASTM D-3663 using a Sorptomatic 1800 unit (Carlo Erba Strumentazione, Italy). The acid properties were characterized by NH_3 temperature-programmed desorption (NH_3-TPD). The unit cell size of the catalysts was determined using X-ray diffraction following ASTM-D-3942-80. Tables Ia and Ib summarize the physiochemical properties of the prepared catalysts.

TABLE I
Catalyst characterization
(a) Y Zeolite based catalysts

Steaming conditions/properties	Catalysts				
	H-Y	USY-1	USY-2	USY-3	USY-4
Steaming temperature, °C	–	600	600	600	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	0.550	0.033	0.100	0.140	0.200

(b) ZSM-5 based catalysts

Catalyst	Surface area m^2/g	Na_2O %	Acidity mmol/g	% of weak acid site	% of strong acid site
GKF-3	70	negligible	0.23	62.5	37.5

RESULTS

Toluene Disproportionation

Toluene disproportionation (Scheme 1) was studied in the riser simulator at temperatures of 400, 450 and 500 °C for reaction times of 3, 5, 7, 10, 13, and 15 s using a catalyst/toluene ratio of 5 (catalyst weight 0.81 g, reactant weight 0.162 g). The reaction was initially studied over the weakly acidic Y zeolite based (USY-1) catalyst and the ZSM-5 based (GKF-3) catalyst. Thereafter, the reaction was also studied over the other three prepared samples of the Y zeolites; H-Y, USY-2 and USY-3 for the purpose of comparison.
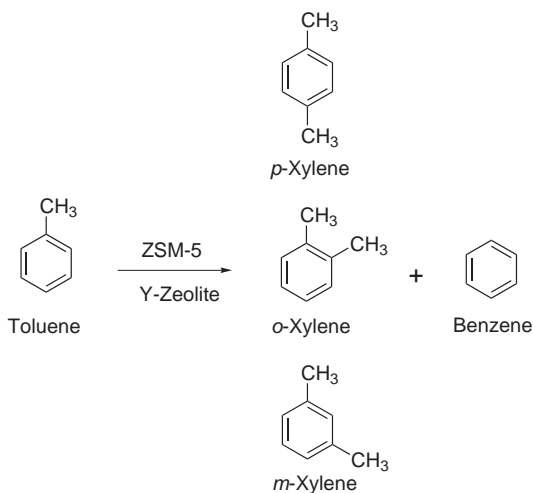
SCHEME 1

Toluene Conversion and Product Distribution

Table II shows the variation of toluene conversion with reaction conditions over the five different catalysts used. From the table, it can be observed that only very low toluene conversion (maximum 1.7%) was achieved using the USY-1 catalyst. The low conversion can be attributed to the very low acidity of the catalyst (0.033 mmol/g). Similarly, in spite of the relatively higher acidity of the ZSM-5 based catalyst (almost seven times of USY-1), toluene conversion over this catalyst was also low with a maximum of only 5.5% obtained at a reaction temperature of 550 °C and reaction time of 15 s. This indicates that the conversion of toluene in the riser simulator is not only dependent on the catalyst acidity, but also on the operation conditions of the riser simulator. Specifically, the low conversion over the ZSM-5 based GKF-3 catalyst can be attributed to the low operation pressure of the riser simulator (ca. 1.01 bars). In general toluene disproportionation is carried out in fixed bed reactors at high hydrogen pressures (ca. 30 bars).

In the presence of the non-steamed (H-Y) and the partially steamed catalysts (USY-2 and USY-4), toluene conversions were significantly higher than when the fully steamed catalyst (USY-1) was used. The highly acidic H-Y catalyst in particular gave the highest conversion of 27.1% at 500 °C and reaction time of 15 s. Furthermore, it was observed that at low temperatures (around 350 °C), the conversion of toluene occurred mainly through disproportionation producing xylene and benzene with a very small amount of gases. Although an increase in temperature from 400 to 500 °C

increased conversion over the H-Y catalyst from 9.3 to 27.1% (i.e. three times), the high temperatures also enhanced undersirable side reactions like dealklylation which resulted in an appreciable increase in the gas yield and a consequent decrease in the yield of xylene. Figures 1, 2 and 3 depict the influence of toluene conversion and temperature on the yield of xylene, gases and benzene respectively over the H-Y catalyst. It is apparent that while xylene yield decreased with increasing reaction temperature, the yield of gases increased. Since benzene is a product of both the primary reaction (disproportionation) and the secondary reaction (dealkylation), the yield of benzene also increased with temperature.

Comparison of H-Y, USY-2 and USY-4 Catalysts

As can be seen from Table II, the conversion of toluene increases with the acidity of the Y zeolite based catalysts. Hence the activities of the catalysts for toluene conversion decrease in the following order H-Y > USY-4 > USY-2 > USY-1 with H-Y the most acidic of the catalyst (0.55 mmol/g) showing the

TABLE II
Comparison of toluene conversions for ZSM-5, H-Y, USY-1, USY-2 and USY-4

Temperature °C	Reaction time, s	Toluene conversion, %				
		ZSM-5	USY-1	USY-2	USY-4	H-Y
550	15	5.5				
500	15		1.7	22.1	24.0	27.1
500	10	1.6	0.9	14.6	17.6	20.3
500	5			5.5	6.7	11.2
450	15		0.8	17.2	20.0	26.1
450	10	0.9	0.5	12.0	14.3	19.6
450	5			5.4	7.2	10.7
400	15		0.8	8.8	13.0	23.3
400	10	0.5	0.4	6.0	8.0	17.1
400	5			3.6	5.7	9.3
350	15					
350	10	0.3				

highest activity. It should be mentioned however that although H-Y gave higher toluene conversion, it shows a lower selectivity to disproportion-ation reaction resulting in lower xylene yields compared with the other catalyst samples.
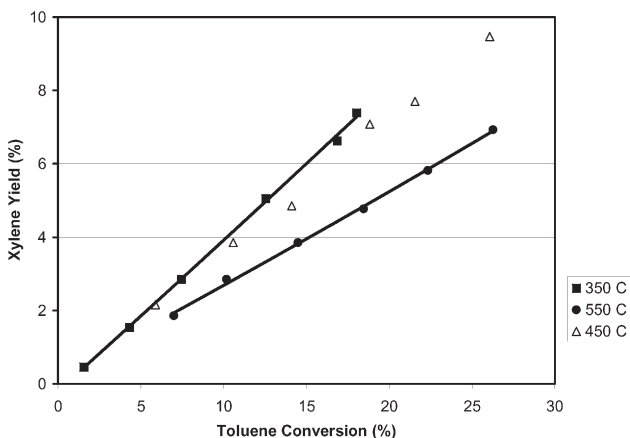
Effect of temperature on the yield of xylene during toluene transformation using H-Y
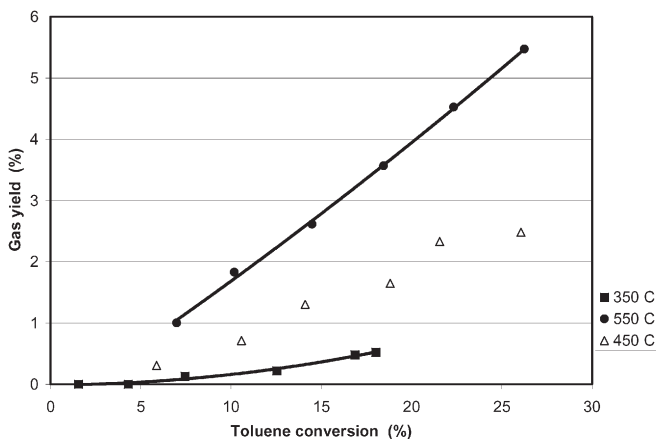
Effect of temperature on the yield of gaseous hydrocarbons during toluene transformation using H-Y
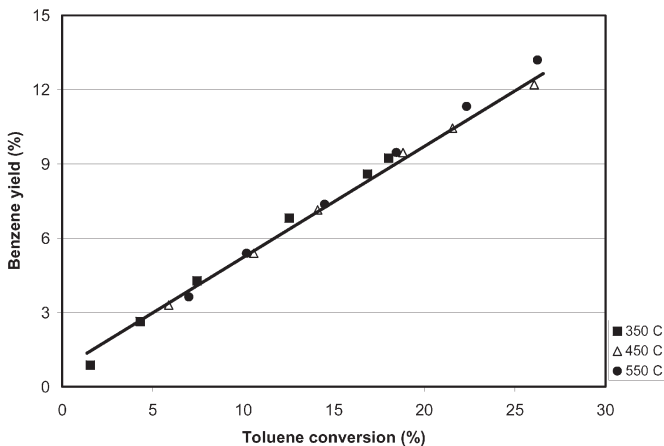
Fig. 3
Effect of temperature on the yield of benzene during toluene transformation using H-Y

Coke Formation

The amount of coke formed in the transformation of toluene is a function of gaseous hydrocarbons produced. It has been found that the condensation of gaseous hydrocarbons in the pores of the zeolite leads to the formation of main coke precursors. Consequently, higher amounts of coke deposits were observed over the H-Y zeolite since it produced the highest amount of gaseous hydrocarbons. Table III shows that the amount of coke deposited over H-Y zeolite varies with both reaction temperature and time. A maximum coke deposit of 1.67% was obtained at 550 °C for the reaction time of 15 s.

Kinetic Model

Experimental data for the transformation of toluene over the H-Y zeolite at 350, 400, 450, 500 and 550 °C and reaction times 3, 5, 7, 10, 13 and 15 s were used to derive kinetic models based on the classical time-on-stream (TOS) approach and also based on the reactant conversion (RC) approach proposed by Al-Khattaf and de Lasa[14]. The activation energy for the transformation of toluene was found to be 14.50 kJ/mol according to the former approach and 16.7 kJ/mol based on the latter. It may not be appropriate to compare the value of the activation energy in this work with those men-

TABLE III
Variation of amount of coke deposited with reaction conditions during toluene disproportionation over H-Y

Temperature/time	Conversion %	Amount of coke wt.%	Amount of coke/Toluene conversion
400 °C/5 s	9.3	0.57	0.06
400 °C/7 s	11.6	0.77	0.07
400 °C/10 s	17.1	0.93	0.06
400 °C/15 s	23.3	1.42	0.06
450 °C/5 s	10.7	0.65	0.06
450 °C/7 s	14.3	0.93	0.07
450 °C/10 s	19.5	1.1	0.06
450 °C/15 s	26.1	1.53	0.06
500 °C/5 s	11.2	0.80	0.07
500 °C/7 s	11.5	1.1	0.07
500 °C/10 s	20.3	1.38	0.07
500 °C/15 s	27.1	1.67	0.06

tioned in most literatures. The reason for this is due to the great difference between our system which is a fluidized bed and the systems used in most other works which is usually the fixed bed reactor. The increased reactant–catalyst contact due to fluidization can be a major contributory factor for the low activation energy.

Toluene Methylation

Toluene methylation (Scheme 2) is usually accomplished by reacting toluene and methanol over zeolite based catalysts. In this study, toluene methylation was carried out at 375, 400, 425 and 450 °C. At each of these temperatures, the reaction was carried out for reaction times of 3, 5, 7, 10, 13 and 15 s over the ZSM-5 based (GKF-3) and the weakly acid Y zeolite based (USY-1) catalysts. The following sections present some of the results of the study.

CH₃

p-Xylene

CH₃
+ CH₃OH → ZSM-5 / Y-Zeolite → o-Xylene + H₂O
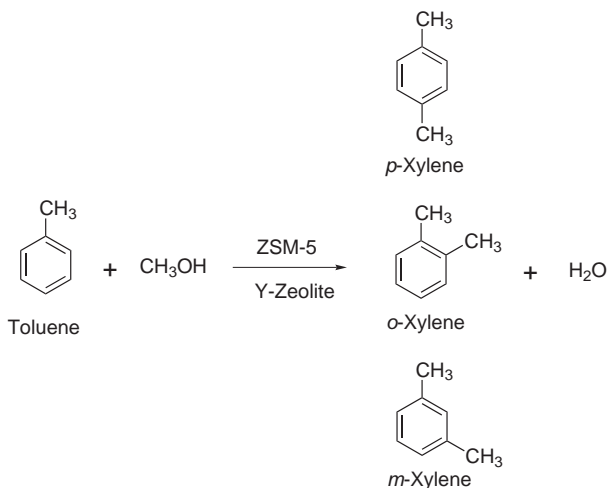
Toluene

m-Xylene

SCHEME 2

Toluene Conversion

Over both catalysts, the main products of toluene methylation were the three isomers of xylene (*p*-, *o*-, *m*-) and trimethylbenzenes. Negligible amounts of benzene, ethylbenzene, cumene and gaseous hydrocarbons were also detected. It is important to note that in spite of the short contact times used and very low acidity of the USY-1 catalyst, appreciable toluene conversion was observed. Figure 4 shows that toluene conversion over the
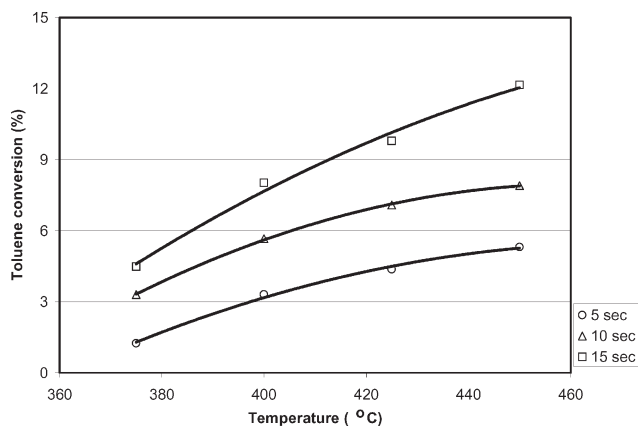
FIG. 4
Effect of time and temperature during toluene methylation over USY-1 catalyst

USY-1 catalyst increased with both reaction temperature and time reaching a maximum of about 12.1% at 450 °C for the reaction time of 15 s. With the more acidic GKF-3, toluene conversions were much higher. As depicted in Fig. 5, toluene conversion varies with temperature and reaction time in a similar way with USY-1. However, the maximum toluene conversion in this case was 16.81%.
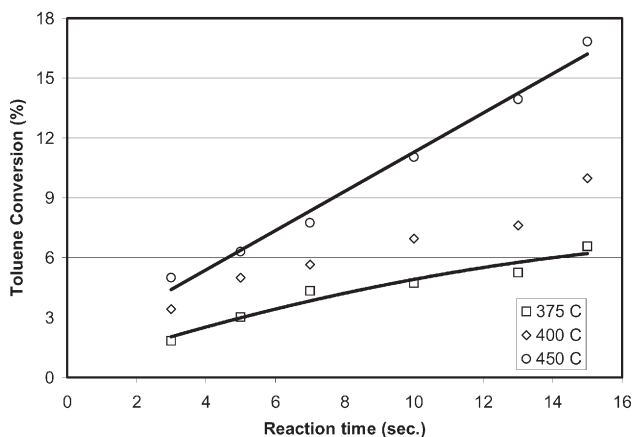

Fig. 5
Effect of time and temperature during toluene methylation over ZSM-5 based (GKF-3) catalyst

Product Distribution

p-Xylene/o-xylene ratio (P/O ratio). Generally, when toluene and methanol are passed through a fixed bed of a shape selective catalyst like the ZSM-5, an equilibrium mixture of xylene is formed with the *p*-xylene/*o*-xylene ratio (P/O) being around 0.9. It should be mentioned that in such cases, the initial primary product of the reaction may be very rich in *p*-xylene (i.e. high P/O ratio) due to its relatively higher diffusion rate in the pores of zeolite compared with the other isomers[15]. However, with time secondary isomerization of the formed *p*-xylene into the *o*- and *m*-isomers occurring on the surface of the catalyst where shape selectivity is absent causes the P/O ratio to drop drastically. Consequently, a number of modifications are made on the catalyst to minimize these secondary reactions[4–8]. A major disadvantage of these catalyst modifications as mentioned above is a decrease in toluene conversion and in some cases loss of catalyst stability. In the present work, we have been able to achieve P/O ratios higher than the equilibrium value over both catalysts without having to perform any of the conventional cat-

alyst modifications. This is directly linked to the usage of short reaction times, which suppresses most of the undesirable secondary reactions. Figure 6 shows the effect of toluene conversion and temperature on P/O ratio when the reaction was carried out over USY-1 catalyst. It can be seen that although the P/O ratio was less than the equilibrium value at low temperatures (375 °C) and low toluene conversions, its value increased with both toluene conversion and temperature reaching a maximum of about 1.63 at 450 °C corresponding to a toluene conversion of 12.1%. With regards to the ZSM-5 based (GKF-3) catalyst, P/O ratios were higher than the equilibrium values for all the investigated reaction conditions as shown in Fig. 7. The relative higher P/O ratios obtained with the ZSM-5 based (GKF-3) catalyst is due to its relatively smaller pore sizes when compared with the USY-1 catalyst. This increases diffusional constraints on the two other isomers (*o*- and *m*-) thereby reducing their concentration in the product.

The effect of temperature on P/O ratio over the GF K-3 catalyst was found to be slightly different from that over the USY-1 catalyst. Initially, when the reaction temperature was increased from 375 to 400 °C, the P/O ratio increased. However, beyond 400 °C, the P/O ratio was found to decrease as temperature was further increased. This is due to the fact that at temperatures above 400 °C, the rate of diffusion of *o*-xylene also becomes high and comparable to that of *p*-xylene thereby reducing the diffusional advantage of *p*-xylene over it. Consequently, there is a decrease in the P/O ratio. Fur-
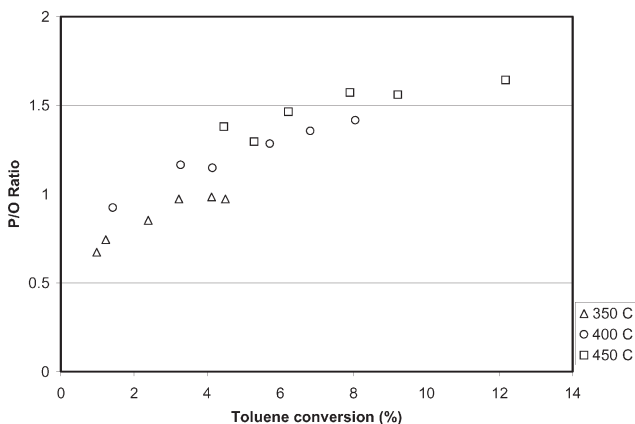

Fɪɢ. 6
Effect of temperature and toluene conversion on P/O ration during toluene methylation over USY-1

thermore, it can be observed from Fig. 7 that while the P/O ratio remains almost unaffected by conversion at 375 and 400 °C, it clearly decreased with increasing conversion at temperatures higher than 400 °C. This observation is due to the fact that at higher temperatures, the rates of secondary reactions like *p*-xylene isomerization which consume *p*-xylene increase.
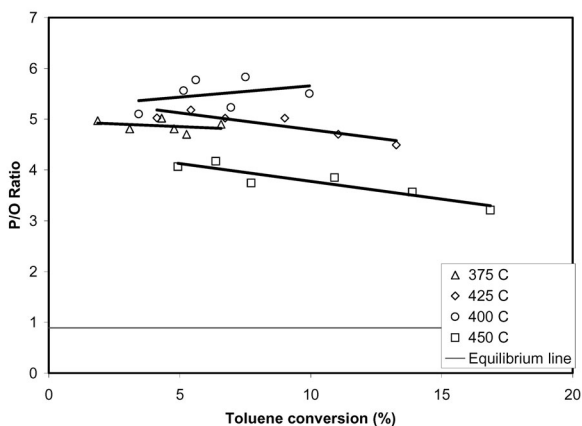

Fig. 7
Effect of temperature and toluene conversion on P/O ration during toluene methylation over ZSM-5 based (GKF-3) catalyst

Effect of catalyst pre-coking. Undesirable secondary reactions like *p*-xylene isomerization leading to other isomers and the reaction of produced xylene with methanol to yield trimethylbenzenes can have adverse effects on the product distribution of toluene methylation. The former reaction for example can significantly reduce the P/O ratio while the latter can reduce the relative amount of xylene compared to trimethylbenzene (xylene/TMB ratio in the reaction product). Since these undesirable reactions take place on the external acid sites of the catalyst, pre-coking the catalyst in order to deposit a given amount of coke on the external surface of the catalyst can help to deactivate these external sites and hence to improve both the P/O ratio and the relative concentration of xylene compared with trimethylbenzene. However, depending on the extent of catalyst pre-coking and the procedure adopted, catalyst pre-coking may result in significant decrease in the toluene conversion.

To study the effect of catalyst pre-coking on toluene conversion, P/O ratio and xylene/TMB ratio, a comparison between toluene methylation over

the fully regenerated (fresh) GKF-3 and a pre-coked sample of GKF-3 was made at 400 and 450 °C for reaction times of 5, 10 and 15 s. The pre-coked catalyst was prepared by treating 80 mg of the fresh catalyst with 100 ml of carbonaceous 1,3,5-TIPB under mild reaction conditions (temperature 400 °C, reaction of 3 s). 1,3,5-TIPB was used because its kinetic diameter is larger than the pore opening of ZSM-5 thereby restricting coke deposit to the external surface of the catalyst only. Hence, the internal active sites were not affected significantly by pre-coking. The amount of coke deposited on the pre-coked catalyst from 1,3,5-TIPB was found to be ~0.15 wt.%. Total acidities along with the measured BET surface areas for both the fresh and the pre-coked catalyst are summarized in Table IV.

Figure 8 compares toluene conversions over the fresh and pre-coked catalyst at temperatures of 400 and 450 °C for reaction times of 5, 10 and 15 s.

TABLE IV
Comparison between the properties of the fresh and the pre-coked ZSM-5 based (GKF-3) catalysts

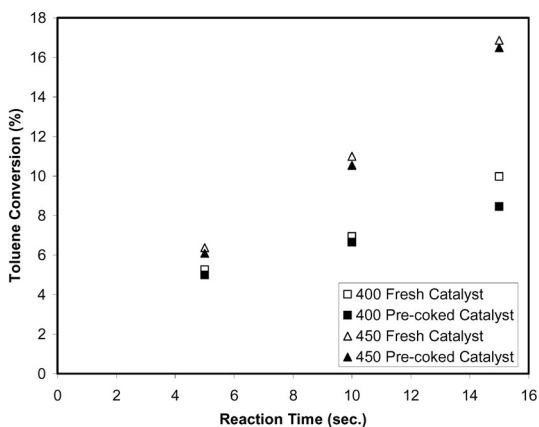| Catalyst	Surface area m^2/g	Na_2O %	Acidity mmol/g	% of weak acid site	% of strong acid site
Fresh	70	negligible	0.23	62.5	37.5
Pre-coked	63	negligible	0.18	66.67	33.33

FIG. 8
Comparison between toluene conversion over fresh and pre-coked ZSM-5 based (GKF-3) catalysts

From this figure it can be seen that at both temperatures 400 and 450 °C, pre-coking of the catalyst had only a mild effect (<5% decrease) on toluene conversion, especially at reaction time less than 10 s. The mild effect of catalyst pre-coking on toluene conversion is an indication that coke deposit was restricted to the external surface of the catalyst only without interfering much with the acid sites within the pores of the catalyst where alkylation largely takes place. The slight decrease in toluene conversion can be attributed to the reduction of the total number of active sites due to partial deactivation and also due to problems of toluene diffusion which may occur as a result of a possible blockage of some of the pore openings of the catalyst by the relatively larger molecules of 1,3,5-TIBP.

Tables Va and Vb show the product distribution of toluene methylation over the fresh (fully regenerated) and the pre-coked GKF-3 catalyst at 400 and 450 °C. As can be clearly seen from these tables, pre-coking of the catalysts was found to increase the ratio of xylene yield to TMB as a result of the partial deactivation of the external surface of the catalyst where xylene alkylation with methanol to produce trimethylbenzene (TMB) is believed to occur during toluene methylation. The formation of trimethylbenzenes within the pores of ZSM-5 has been reported to be highly hindered especially at low methanol concentration and short contact time[16]. Figure 9 compares the ratio of xylene yield/TMB yield for the fresh and pre-coked catalyst at 400 and 450 °C at toluene conversion of 8%. From Fig. 9 it can be seen that at 400 °C, pre-coking of the catalyst increased the ratio from
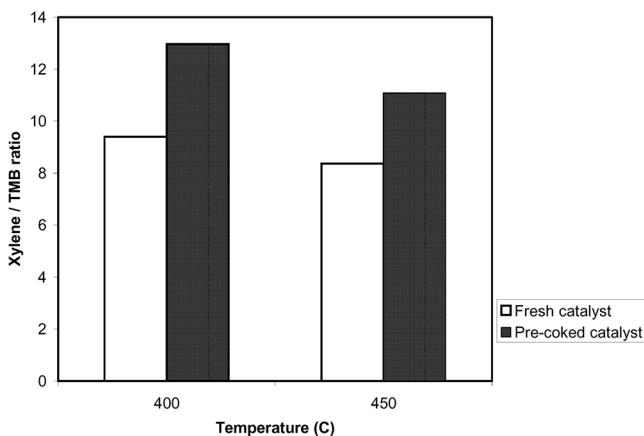

Fig. 9
Comparison of xylene/TMB ratio for fresh and pre-coked ZSM-5 based (GKF-3) catalysts at 400 and 450 °C

about 9.6 to 13.0 representing an increase of 36%. The effect of catalyst pre-coking on the ratio was less pronounced at 450 °C with its value increasing from approximately 8.4 to 11.3 representing only a 25% increase.

Furthermore as expected, catalyst pre-coking was found to have a significant positive effect on the P/O ratio due to the partial deactivation of the external active sites, which are responsible for the undesirable isomerization of *p*-xylene selectively formed in the pores of the catalyst into the other isomers. Figure 10 compares the P/O ratio for the fresh and pre-coked catalyst at 400 and 450 °C for toluene conversion of 8%. From this figure it

TABLE V
Product distribution of toluene methylation (composition of feed stock: toluene/methanol molar ratio 1:1)
(a) Product distribution of toluene methylation over fresh ZSM-5 based (GKF-3) catalyst at 450 and 400 °C

Temp. °C	Time s	Yield, %						Toluene conversion %	P/O
		Toluene	Methanol	*p*-Xylene	*o*-Xylene	*m*-Xylene	TMB		
450	5	69.46	18.44	3.61	0.873	2.51	0.84	6.38	4.13
	10	66.05	15.13	5.77	1.52	4.37	1.41	10.99	3.81
	15	61.69	13.38	6.96	2.19	6.27	1.81	16.86	3.17
400	5	70.38	18.54	3.25	0.58	1.49	0.55	5.15	5.60
	10	69.04	16.29	4.33	0.82	2.00	0.75	6.96	5.26
	15	66.82	12.61	6.10	1.11	2.86	1.04	9.95	5.51

(b) Product distribution of toluene methylation over the pre-coked ZSM-5 based (GKF-3) catalyst at 450 and 400 °C

Temp. °C	Time s	Yield, %						Toluene conversion %	P/O
		Toluene	Methanol	*p*-Xylene	*o*-Xylene	*m*-Xylene	TMB		
450	5	69.53	19.64	3.904	0.84	2.53	0.64	6.29	4.66
	10	66.40	15.74	6.38	1.22	3.70	0.98	10.53	5.22
	15	61.73	13.11	7.63	1.90	5.44	1.36	16.81	4.02
400	5	70.48	20.01	2.71	0.38	0.91	0.31	5.02	7.23
	10	69.03	15.32	4.54	0.60	1.29	0.49	6.97	7.54
	15	67.96	13.25	5.45	0.75	1.65	0.59	8.41	7.28

can be seen that at 400 °C, the P/O ratio increased from about 5.5 to approximately 7.6 representing an increase of 27%. Similarly at 450 °C, the effect of catalyst pre-coking was also clear with P/O increasing from approximately 3.8 to 4.7 representing a 24% increase.

Fɪɢ. 10
Comparison of P/O ratio for fresh and pre-coked ZSM-5 based (GKF-3) catalysts at 400 and 450 °C

Kinetic Modeling

Model Formulation. As discussed earlier, experimental runs at 375, 400, 425 and 450 °C for reaction times of 3, 5, 7, 10, 13 and 15 s were carried out over the Y zeolite based (USY-1) and the ZSM-5 based (GKF-3) catalysts. The experimental data over both catalysts were modeled using the time-on-stream model (TOS).

For the USY-1 catalyst, the experimental data was modeled according to the following reaction scheme

$$T + M \xrightarrow{k_1,\, E_1} X + W + M$$
$$\downarrow{\scriptstyle k_2,\, E_2}$$
$$TMB + W$$

which is based on the fact that all the molecules involved can be formed within the relative large pore size of the Y-based zeolite. Hence the three xylene isomers are grouped into one component denoted by X.

For the relative small pore sizes of the ZSM-5 based (GKF-3) catalyst, the reaction scheme is slightly more complicated. As shown below the scheme takes account of reactions within the pores and the surface of the catalyst.

Reactions within the pores:
a) Toluene alkylation. It has been observed by IR spectroscopy[17] that all the isomers of xylene are formed through the first step of toluene methylation. Therefore we have included all the three isomers in the alkylation step as shown in Eq. (*1*).

$$
\text{T + M} \quad
\begin{array}{c}
\nearrow^{k_1} \quad \text{P–X + H}_2\text{O} \\
\xrightarrow{k_2} \quad \text{O–X + H}_2\text{O} \\
\searrow_{k_3} \quad \text{M–X + H}_2\text{O}
\end{array}
\qquad (1)
$$
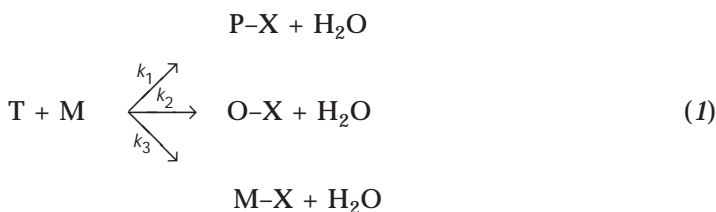
b) Internal isomerization. Because of the relative low diffusion rate of *m*- and *o*-xylene they are almost completely isomerized to *p*-xylene before leaving the pores of the catalyst. This is reasonable given the small pore size of ZSM-5 and also the crystal size used. We have represented these internal isomerizations of *m*- and *o*-xylene by Eqs (*2*) and (*3*), respectively.

$$ \text{M}_\text{X} \xrightarrow{k_4} \text{P}_\text{X} \qquad (2) $$

$$ \text{O}_\text{X} \xrightarrow{k_5} \text{P}_\text{X} \qquad (3) $$

Reactions on the external surface of the catalyst:
a) Isomerization on the catalyst surface. The undesirable isomerization of *p*-xylene into the *m*- and then to *o*-isomers occurs on the catalyst crystal surface where shape selectivity property is absent. These reactions are represented by Eq. (*4*).

$$
\text{P–X} \quad
\begin{array}{c}
\nearrow^{k_6} \quad \text{M–X} \\
\searrow_{k_7} \quad \text{O–X}
\end{array}
\qquad (4)
$$
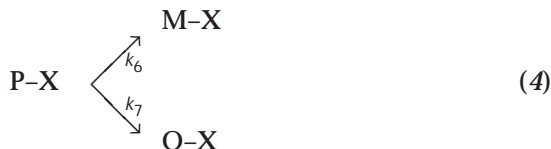
b) Xylene alkylation to produce TMB. As explained above, the formation of TMB in the pores of ZSM-5 is highly hindered. Therefore, its formation is limited to the external surface of the catalyst as a result of the reaction of produced xylene with methanol. We assume that all the xylene isomers are converted to TMB at the same rate. Therefore, we have represented this reaction with a single equation as shown in Eq. (*5*).

$$(M_X + O_X + P_X) + M \xrightarrow{\ k_8\ } TMB + H_2O \tag{5}$$

The experimental data were modeled based on the above scheme and the activation energies of the reaction steps in the scheme were determined.

Model Parameters. The experimental data were modeled for the different catalysts based on time-on-stream. Table VI shows the model parameters for the reaction over USY-1 zeolite comprising of the activation energies (E_1 and E_2) and the pre-exponential factors (A_1, A_2) for the two reaction steps. The value of the catalyst activation decay constant α is also given. Similarly Table VII shows the activation energies, (E_1–E_8) and the pre-exponential factors (A_1–A_8) for all reaction steps represented in the reaction scheme over the ZSM-5 based (GKF-3) catalyst. It can be seen from Table VII that the activation energies for the formation of the three xylene isomers follow the order *m*- > *o*- > *p*-. This is a reflection of the steric constraint of the ZSM-5 based catalyst on the formation of the three isomers. The formation of *m*-

TABLE VI
Estimated kinetic parameters of toluene methylation over the USY-1 zeolite based catalyst

	E_1 kJ/mol	E_2 kJ/mol	$A_1{}^a \times 10^3$ m^3/kg of catalysts	$A_2{}^a \times 10^3$ m^3/kg of catalysts	α
Value	43.18	41.20	0.0186	0.1037	0.0166
95% CL $\times 10^{3\ b}$	1.62	7.90	0.003	0.0304	0.0269

^{a} Pre-exponential factor unit for the second order (in m^3/kg of catalyst s). ^{b} CL, confidence limit.

xylene with the largest kinetic diameter has the highest activation energy (79.42 kJ/mol) while the formation of *p*-xylene, the smallest of the three isomers has the lowest activation energy (56.83 kJ/mol).

TABLE VII
Estimated model parameters of toluene methylation over ZSM-5 based (GKF-3) catalyst

Parameters	Values	95% Confidence limit
Activation energy, E kJ/mol		
E_1	56.83	4.83
E_2	67.11	5.34
E_3	79.42	6.31
E_4	31.50	3.88
E_5	32.00	2.95
E_6	25.16	3.57
E_7	25.24	5.11
E_8	24.49	4.86
Pre-exponential factor, A m^3/kg of catalysts $\times 10^4$		
A_1	0.1435	0.0003
A_2	0.0298	0.0001
A_3	0.0880	0.0033
A_4	0.3590	0.0044
A_5	0.6975	0.0106
A_6	0.0070	0.0034
A_7	0.0086	0.0045
A_8	8.8721	1.2990
Catalyst deactivation constant, α		
	0.0010	0.0005

m-Xylene Isomerization

m-Xylene isomerization (Scheme 3) was effected using the calcined Y-based catalyst (H-Y), and the other catalyst samples prepared by steaming H-Y at different conditions. The physiochemical properties of H-Y and the

steamed catalyst USY-1, USY-2, USY-3 and USY-4 have already been given in Table Ia. The reaction was carried at 400, 450 and 500 °C for reaction times 3, 7, 10 and 15 s. Table VIII compares *m*-xylene conversion and the amount of coke deposited for the most and least acidic catalyst samples, i.e., H-Y and USY-1, respectively.
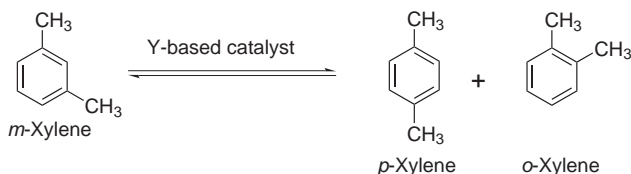
SCHEME 3

Effect of Catalyst Acidity on m-Xylene Conversion

As may be observed in Fig. 11, an initial increase in catalyst acidity resulted in higher *m*-xylene conversion. However, beyond acidity of about 0.1 mmol/g, any further increase in the acidity led to a slight decrease in *m*-xylene conversion. The initial increase in conversion with acidity can be explained easily, since transformation of *m*-xylene over Y zeolite is enhanced by total acidity[18,19]. However, the subsequent decrease in conversion at higher acidity (>0.1 mmol/g) was probably due to the rapid deactivation of the catalyst
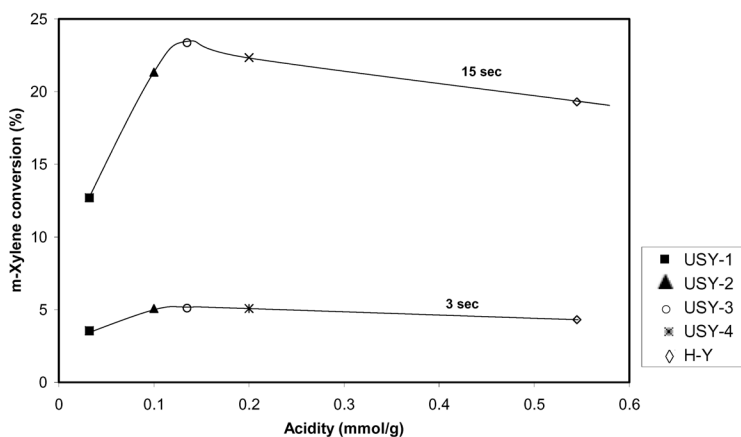

FIG. 11
m-Xylene conversion over the different catalysts versus total acidity at various reaction times at 450 °C

through coking. Highly acidic Y-based zeolites have abundant 1,2,3,4-NNN sites ("next nearest neighbors"), which have been reported to have high coke-making and less cracking and isomerization tendency[20]. The latter statement is corroborated by the data shown in Table VIII where the amount of coke deposited on the H-Y is several times higher than that deposited on the USY-1. The relative high conversion achieved with USY-2 and USY-3 can be due to the high number of 0-NNN sites (isolated framework aluminum atoms) in these two catalyst samples.

TABLE VIII
Comparison of *m*-xylene conversion and amount of coke deposit on H-Y and USY-1

Temperature, °C	Conversion, %		Total coke deposited, wt.%	
	USY-1	H-Y	USY-1	H-Y
400	2.2	4.0	0.044	1.63
	4.6	9.8	0.035	1.00
	5.1	13.1	0.039	1.30
	8.5	19.7	0.059	1.66
450	3.9	6.4	0.065	0.67
	9.1	11.1	0.051	1.17
	11.2	14.8	0.050	1.44
	13.3	20.9	0.041	1.72
500	8.2	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

Product Distribution

The product distribution of *m*-xylene isomerization was found to vary from one catalyst sample to the other. At 10% *m*-xylene conversion, it was found that toluene has the highest yield over all 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 this level of conversion. Furthermore, the yields of *p*- and *o*-xylene were closely identi-

cal 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 C_2–C_4 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 C_2–C_4 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. 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 C_2–C_4 gases indicates that they are probably the products of such secondary reactions.

The secondary formation of benzene suggests that in addition to the well-known reaction pathways of *m*-xylene transformation (i.e. isomerizaion and disproportionation) an alternative reaction pathway exist during the *m*-xylene transformation over the highly acidic H-Y catalyst. This reaction pathway commonly referred to as pairing reaction is believed to initiate the paring of the produced trimethylbenzene leading to the formation of benzene and gaseous hydrocarbons. A similar conclusion regarding the formation of benzene via paring reaction was reported by Roger et al.[21] in their study of 1,2,4-trimethylbenzene conversion over a H-ZSM5 based catalyst. TMB is formed via disproportionation reaction of the three xylene isomers, which suggests that all of them undergo a similar pairing reaction pathway. 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. This might further lead to the formation of gases and benzene via dealkylation.

Selectivity to Different Reaction Pathways

Generally, during the *m*-xylene isomerization, two main reaction pathways are involved namely, isomerization and disproportionation. However, over a highly acidic zeolite catalyst an additional pathway known as the paring reaction (see above) has been proposed to explain the product distribution[22]. Therefore, 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[23]. Thus, the selectivity of *m*-xylene

transformation towards isomerization, disproportionation and paring pathways are plotted in Figs 12, 13 and 14, respectively, at 450 °C, as a function of *m*-xylene conversion for the four Y zeolite based catalysts used.

It is clear from Fig. 12 that the highly dealuminated (USY-1) catalyst showed the highest isomerization selectivity, which is around 50% higher than that of the H-Y catalyst. This result suggests that the low concentration of acid centers in the USY-1 catalyzes above all the isomerization reac-
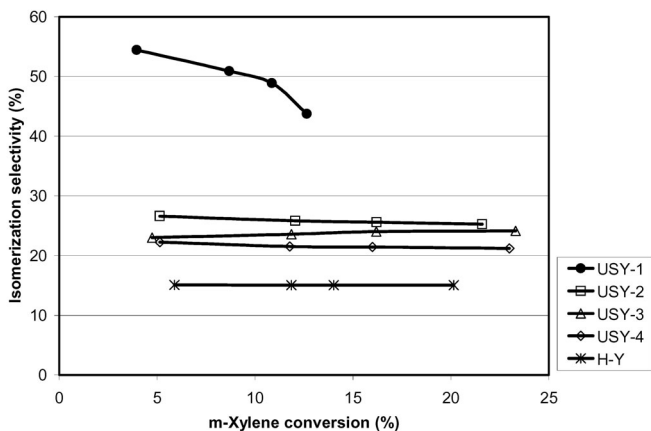

F<small>IG</small>. 12
Isomerization selectivity as a function of *m*-xylene conversion at 450 °C
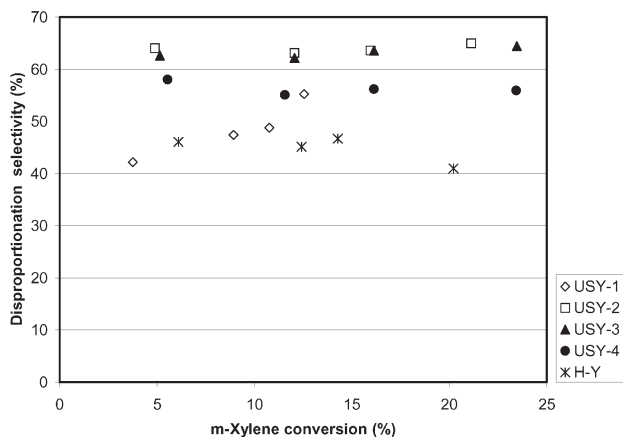

F<small>IG</small>. 13
Disproportionation selectivity as a function of *m*-xylene conversion at 450 °C

tion. This is in agreement with the well-established fact that isomerization being a monomolecular reaction requires lower acid site density than bimolecular reactions.

On the other hand, since disproportionation is a bimolecular reaction, it requires higher amount of acid sites[21]. Based on this, the H-Y catalyst should give the highest disproportionation selectivity, since it has the highest concentration of Brønsted acid sites. However, Fig. 13 shows that the moderately dealuminated catalysts (USY-2 and USY-3) appeared to be the most active ones for *m*-xylene disproportionation, with selectivity values being about 1.45 times higher than parent H-Y catalysts at 12% *m*-xylene conversion. Apparently low selectivity of disproportionation over the H-Y catalyst is probably due to secondary transformation of TMBs, a major disproportionation product to coke precursors and paring reaction products. This can be inferred from the relatively higher amount of both coke deposit and 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.

It can be noticed that the selectivity to paring reaction differed significantly depending on the type of catalyst, as shown in Fig. 14. 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 resulted in
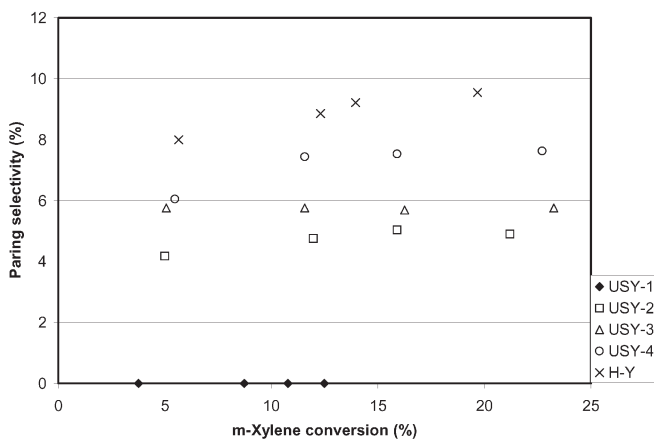

FIG. 14
Paring selectivity as a function of *m*-xylene conversion at 450 °C

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.

CONCLUSIONS

Toluene disproportionation, toluene methylation and *m*-xylene isomerization have been successfully studied over a ZSM-5 based catalyst with medium acidity of 0.23 mmol/g and a series of Y zeolite based catalysts labeled USY-1, USY-2, USY-3, USY-4 and H-Y having acidities of 0.033, 0.1, 0.14, 0.2 and 0.55 mmol/g, respectively. The following summarizes our major findings:

1) (a) No appreciable toluene disproportionation was observed in the riser simulator when the ZSM-5 based catalyst and the weakly acidic (USY-1) catalyst were used. This observation was attributed to the low acidity of the catalyst as well as the low operating pressure of the riser simulator.

(b) Toluene conversion was observed to increase with both temperature and acidity of the catalyst reaching a maximum value of 27.1 at 550 °C over the highly acidic H-Y catalyst. However, xylene yield was low owing to the dominance of pairing reaction and coking leading to a high yield of gases and rapid catalyst deactivation.

2) (a) Unlike toluene disproportionation, toluene methylation produced high levels of toluene conversions over both the ZSM-5 based catalyst and the weakly acidic (USY-1) catalyst. Within the investigated temperature range (375–450 °C), toluene conversion was found to increase with temperature reaching a maximum of 12.16 and 16.81% over the USY-1 catalyst and the ZSM-5 based catalyst, respectively.

(b) A non-equilibrium composition of xylene was obtained in the reaction product with P/O ratios higher than the equilibrium value achieved. This is directly related to short reaction time which suppresses further *p*-xylene isomerization. Furthermore, catalyst pre-coking was found to further enhance the P/O ratio.

3) (a) *m*-Xylene conversion was found to be greatly affected by catalyst acidity. Initially when acidity was increased, *m*-xylene conversion also increased. However increasing the acidity beyond 0.1 mmol/g resulted in a decrease in conversion. This observation was explained in terms of the next nearest neighbor (NNN) theory.

(b) Three reaction pathways; isomerization, disproportionation and paring reaction were observed during *m*-xylene transformation. The weakly acidic (USY-1) showed more selectivity to isomerization while the medium acidic samples USY-2, USY-3 and USY-4 showed more selectivity to disproportionation. The highly acid H–Y showed the highest selectivity to pairing reaction.

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