

Effect of Y- Zeolite Acidity on 1,2,4 Tri Methyl Benzenes Reactions

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Abstract

Catalytic transformation of *1,2,4-trimethyl benzene* has been investigated over two different USY zeolite based catalysts in a novel riser simulator at different operating conditions. FCC-SY catalyst has low acidity and FCC-CY contains high acidity. The effect of reaction conditions on the variation of isomerization to disproportionation products ratio (I/D), distribution of trimethylbenzene (TMB) isomers (1,3,5-to-1,2,3-) and values of *p*-xylene/*o*-xylene (P/O) ratios are reported on both catalysts. Low acidity catalyst was favoring only two reactions; isomerization and disproportionation. No coke and gases were produced over low acidity catalyst. On the other hand, high acidity catalyst produces huge amount of gases and coke which are an indication for paring reaction.

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Keywords: FCC zeolite catalyst; USY; Toluene; *m*-Xylene; Disproportionation; Isomerization

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1. Introduction

The demand for xylenes as a raw material for polyester fibers and films continues to grow and drive the search to increase xylene production processes. In the year 1999, the world consumption of mixed xylene was about 24 million tons, and is expected to grow at a rate of 6.2% to 32.5 million tons by the year 2004. This indicates that xylenes are still gaining importance in the petrochemical market. Most of the currently working isomerization plants are using zeolite based catalysts.

One common way for xylene production is the conversion of the lower value toluene (C₇) and trimethylbenzene (C₉) into xylenes. Considerable research effort has been devoted for this purpose. It is well known that these hydrocarbons undergo several simultaneous chemical reactions which include; Isomerization, disproportionation, transalkylation, dealkylation, and coke formation.

Trimethyl benzene transformations have been investigated over medium-pore zeolites like ZSM-5 and large-pore zeolites such as Y, Beta, and also mordenite. Collins et al. [1] investigated the transformation (isomerization and disproportionation) of trimethylbenzenes (TMBs) over LaY catalysts. In the disproportionation reaction, the transfer of one methyl group from TMBs led to the formation of equal amount of xylene and tetramethylbenzene (TeMBs) isomers. The authors reported that disproportionation appeared to be linearly related to the total conversion over most of the conversion range studied for both 1,2,4- and 1,3,5-TMB, whereas for 1,2,3-TMB, isomerization was much more favored than disproportionation. They also observed that the pre-dried LaY catalyst was 2 to 3 times more active for disproportionation than the other catalyst calcined by rapid heating of the wet cake. The work by Matsuda et al., [2] concluded that isomerization reaction can take place only over Bronsted acid sites, whereas both Bronsted and Lewis sites are responsible for disproportionation reaction.

Roger et al. [3,4] studied the conversion of 1,2,4- Trimethylbenzene (1,2,4-TMB) over amorphous silica-alumina and HZSM5 in the gas phase and investigated the effect of pore mouth narrowing. They concluded that paring reaction played a decisive role during the conversion over HZSM5 at elevated temperature (450°C). Over both silica-alumina and HZSM5, isomerization of 1,2,4-TMB to 1,2,3- and 1,3,5-TMB isomers were found to be the most rapid reaction with about 90% selectivity at low conversion and this 1,2-methyl-shift were shown to take place on the external surface of the zeolite crystals. They also reported

that over silica-alumina, the reaction almost terminated at the disproportionation step, whereas over HZSM5, the disproportionation of 1,2,4-TMB was followed by rapid paring dealkylation of the TeMBs. The bulky intermediates (TeMBs) that reinforced the diffusional resistances by pore mouth narrowing favored the paring reaction inside the zeolite crystals.

Atias et al. [5] developed a heterogeneous kinetic model for the catalytic conversion of 1,2,4-trimethylbenzene in a CREC riser using USY zeolite catalysts under FCC operating conditions. They determined the intrinsic kinetic parameters for both isomerization and disproportionation reactions. Cejka et al. [6] studied the effect of the structure of large pore zeolites on the activity, selectivity and time-on-stream (T-O-S) in trimethyl benzene disproportionation. They used zeolites of beta, Y, L and Mordenite types which exhibited significant difference in conversion and T-O-S. They found higher conversions of TMBs and high selectivity to xylenes and TMBs at 400°C with zeolites Y and beta (which provides optimum reaction space) compared to other large pore sieves (Mordenite and zeolites L). They also measured the diffusion coefficients of 1,2,4- and 1,3,5-TMBs and 1,2,3,5-TeMBs at 25 and 100°C over zeolites Y, beta and Mordenite and the measured values followed the decreasing order of *m*-xylene \gg 1,2,4-TMB $>$ 1,3,5-TMB \approx TeMB. Recently, AL-Khattaf et al [7] investigated the catalytic transformation of three methyl benzenes (toluene, *m*-xylene, and 1,2,4-trimethyl benzene) over USY based catalyst. The sequence of reactivity of the three alkyl benzenes was found to decrease as the number of methyl group per benzene ring decreases, as follows: 1,2,4-trimethyl benzene $>$ *m*-xylene $>$ toluene.

The present study is aimed at investigating methyl benzenes transformation (1,2,4-trimethyl benzene) over low acidity catalyst (FCC-SY) and high acidity catalyst (FCC-CY) in a fluidized-bed reactor. The study will focus on the effect of catalyst acidity and reaction conditions (time, temperature, and conversion) on the variation of the ratios of disproportionation to isomerization products (D/I), distribution of trimethylbenzene (TMB) isomers (1,3,5-to-1,2,3-) and values of *p*-xylene/*o*-xylene (P/O) ratios.

2. Experimental Procedure

2.1 The Riser Simulator

All the experimental runs were carried out in the Riser Simulator. This reactor is a novel bench scale equipment with internal recycle unit invented by de Lasa [8] to overcome the technical problems of the standard micro-activity test (MAT), and it is fast becoming a

valuable experimental tool for reaction evaluation involving model compounds [9,10], and also for testing and developing new FCC in VGO cracking [11,12]. The Riser Simulator consists of two outer shells, the lower section and the upper section which allow to load or to unload the catalyst easily. The reactor was designed in such 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 towards the walls. This creates a lower pressure in the centre 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 (see Fig 1). A detailed description of various Riser Simulator components, sequence of injection and sampling can be found in Kraemer [13].

2.2 Materials

Ultrastable Y zeolite (USY) was obtained from Tosoh Company. The Na-zeolite was ion exchanged with NH_4NO_3 to replace the sodium 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 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 sol. The process of sodium removal was repeated for the pelletized catalyst. Following this, the catalyst was calcined for 2 hr at 600°C. This calcined catalyst is called FCC-CY. Finally, part of FCC-CY (fluidizable catalyst particles, 60- μm average size) were treated with 100% steam at 760°C for 5 hr. This steamed catalyst is called FCC-SY.

Analytical grade (99% purity) pure 1,2,4-trimethylbenzene was obtained from Sigma-Aldrich. The chemical was used as received as no attempt was made to further purify the sample.

2.3 Procedure

Regarding the experimental procedure in the Riser Simulator, 0.81g 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. Furthermore, the reactor was heated to the desired reaction temperature. The vacuum box was also heated to

around 250°C and evacuated at around 0.5psi to prevent any condensation of hydrocarbons inside the box. The heating of the Riser Simulator was conducted under continuous flow of inert gases (argon) and the process usually takes few hours until thermal equilibrium is finally attained. Meanwhile, before the initial experimental run, the catalyst was activated for 15 minutes at 620°C in a stream of air. The temperature controller was set to the desired reaction temperature and 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 feed stock 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 on-line to the analytical equipment via a pre-heated vacuum box chamber.

2.4 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.

Experiments were carried out at catalyst/reactant ratio of 5 (weight of catalyst = 0.81g, weight of reactant injected = 0.162g); residence times of 3, 5, 7, 10, 13 and 15 s; and temperatures of 400, 450 and 500°C. During the course of the investigation, a number of runs were repeated to check for reproducibility in the conversion results, which was found to be excellent. Typical errors were in the range of $\pm 2\%$.

▲Coke deposited on spent catalysts is determined by a common combustion method. In this method, a carbon analyzer multi EA 2000 (Analytikjena) is used. Oxygen is supplied to the unit directly. A small amount of the spent catalyst (0.35 g) is used for the analysis. The coke laid out on the sample during reaction experiments is burned completely converting the carbonaceous deposit into carbon dioxide. The amount of coke formed is determined by measuring the moles of carbon dioxide. An NDIR detector (employing non-dispersive infrared gas analysis) is used to determine CO₂ content in the carrier gas.

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3. Results and Discussions

3.1 Catalyst Characterization

Zeolite catalysts for use in fluidized-bed reactors are often incorporated in amorphous matrix to achieve the desired fluidization of the catalyst particles. As a result, the determination of the crystallinity and phase purity of the zeolite samples in the presence of this matrix is important in catalytic reactions. The results of the catalyst characterization are presented in Table 1. The total acidity was determined by NH₃ adsorption (TPD). The measured BET surface areas are also summarized in the table.

3.2 1,2,4-Trimethylbenzene Transformation Reactions

3.2.1- Low acidity FCC-SY

Results of transformation reaction of 1,2,4-TMB over FCC-SY at different reaction temperatures and contact times has been presented in recent publication [7]. Fig 2 depicts that 1,2,4 TMB conversion increases with both reaction time and temperature. The experimental results (see Table 2) show that isomerization, disproportionation and transalkylation reactions are taking place. The disproportionation reaction involves the formation of xylenes and tetramethylbenzenes (TeMB) from 2 molecules of 1,2,4-TMB. Subsequently, the xylenes (one of the disproportionation product) react with the TMB to form a transalkylation product toluene. Xylene yields are shown in Fig 3 at different temperatures. It can be depicted from this figure that xylene yields increase with conversion and it is less sensitive to the increment in temperature. Toluene was also detected in the product but in little amount as shown in Table 2. For the reaction of 1,2,4 TMB over Y-zeolite, toluene is proposed to be a secondary product formed by disproportionation of xylenes. Since ethylene was not observed in the product, it can not be concluded that toluene is produced as a result of 1,2,4 TMB decomposition in to toluene and ethylene [3].

The data from the isomerization reaction show that the isomerization yield (both 1,2,3 TMB and 1,3,5 TMB) increases with both conversion and reaction temperature (see Fig 4). However, higher amounts of 1,3,5-TMB were found as compared to the 1,2,3-TMB. Regarding the second disproportionation product TeMBs, Fig 5 shows that the TeMBs yield increases also with both conversion and temperature for FCC-SY. Furthermore, three different isomers of tetra methylbenzenes (TeMBs) were detected (1,2,4,5-TeMB, 1,2,3,5-TeMB and 1,2,3,4-TeMB). Benzene and pentamethylbenzene (PeMBs) have been found to

be negligible. Only minor amount of gaseous products was formed, indicating negligible dealkylation in our reaction condition. The experiments also suggest that the distribution of the xylenes and tetra methylbenzenes (TeMB) in the disproportionation products follow closely the values reported in the literature [14,15].

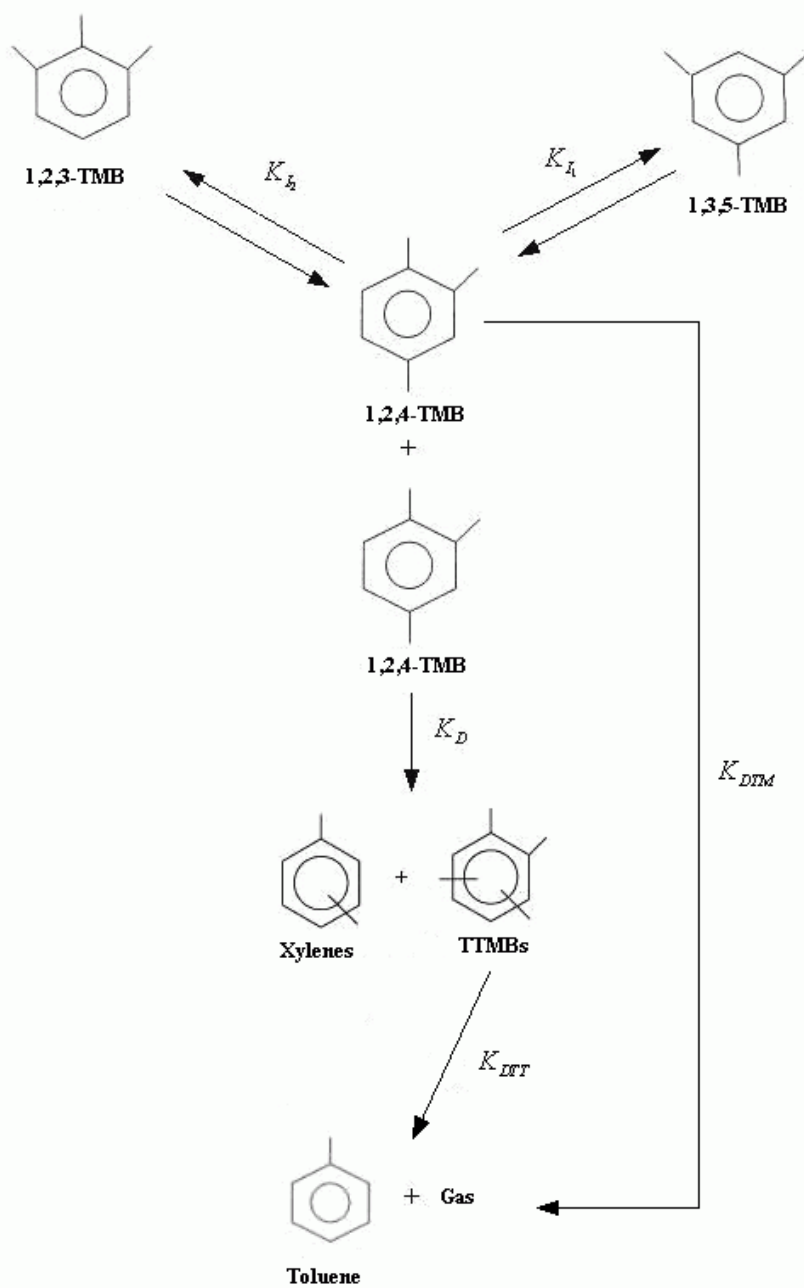
1,2,4-TMB can simultaneously undergo isomerization and disproportionation reactions. Fig 6 shows that the disproportionation to isomerization (D/I) ratio lies between 2.5 and 3.0 at all conversion levels over the FCC-SY catalyst. This indicates that 1,2,4-TMB preferentially undergoes disproportionation as compared to isomerization (approx. 3 times greater) over the FCC-SY catalyst. This result is in good agreement with Cejka et al [6] who reported D/I ratio of about 2.4 at 400°C over beta zeolite. Furthermore, Bourdillon et al [16] reported that D/I ratio over Y-zeolite are 3-4. The main reason for the higher disproportionation rate over zeolite compared to isomerization rate is that while isomerization reaction can take place only over Bronsted acid sites, disproportionation reaction can occur over both Lewis and Bronsted sites [2].

Furthermore, our data show that the effect of temperature and conversion on the D/I ratio is not very significant. Thus, it can be concluded that for low Y-zeolite acidity, 1,2,4 TMB undergoes only two major reactions; disproportionation and isomerization [7].

3.2.2- High acidity FCC-CY

The results of transformation reaction of 1,2,4-TMB over FCC-CY at different reaction temperatures and contact times are presented in Table 3. The experimental results show that isomerization, disproportionation and transalkylation reactions are taking place. The disproportionation reaction involves the formation of xylenes and tetramethylbenzenes (TeMBs) from 2 molecules of 1,2,4-TMB. Subsequently, the TeMBs isomers (one of the disproportionation product) transform via paring reactions to form more toluene and gas [17] as illustrated in scheme 1. Analyzing the gas composition shows that it mainly includes C3, C4 and little amount of C2. C2 gas is coming from 1,2,4 TMB transformation via paring reaction into C2 and toluene (as shown in scheme 1). Xylenes yields are shown in Fig 7 at different temperatures. The figure indicates that xylene yields increase with conversion. It can be seen, however, that at high temperature (500°C) xylene yield decreases. This decrease can be attributed to the xylene transalkylation with TeMBs isomers and TMB isomers forming more toluene and PeMBs (Pentamethylbenzene) and TeMBS. These two

molecules (PeMBs and TeMBs) are



Scheme 1

subsequently transformed via paring into C4 and C3 gases respectively in addition to toluene which explains the high toluene yield especially at high temperatures. It has to be clear that for each mole of xylene formed one mole of tetramethylbenzene (TeMBs) should also be formed. However, the xylenes/TeMBs is far from unity (section 4.2.3). Fig 4 shows that isomerization reaction always increases with conversion (contact time). This result is true for both catalysts. However, reaction temperature has a negative impact on isomerization yield. This can be easily explained through the dealkylation reaction (via paring mechanism). For high acidity catalyst, increasing the temperature has led to an increase in dealkylation reaction which consumes TMB isomers and forms more xylene, toluene and gases. Fig 4 also shows that since the role of dealkylation reaction is not significant in FCC-SY, temperature has no influence on isomerization yield for this catalyst. Furthermore, due to the high dealkylation reaction rate for FCC-CY, isomerization selectivity for this catalyst is always less than that of FCC-SY.

Regarding the disproportionation selectivity, the yield of TeMBs is taken as a reference for this reaction. A relatively low temperature (400°C) has been chosen since dealkylation reaction rate increases with temperature. Fig 5 shows that disproportionation reaction increases with conversion for both catalysts. But the disproportionation rate for FCC-SY is much higher than that for FCC-CY. Hence for both isomerization and disproportionation reactions, FCC-SY has higher selectivities than FCC-CY catalyst. Thus it is clear from the above analysis that the role of the two prominent reactions in 1,2,4 TMB (isomerization and disproportionation) has decreased due to the rise of dealkylation reaction as catalyst acidity increases.

Table 4 shows that catalyst FCC-CY has generated huge amount of coke compared to catalyst FCC-SY. As an average, the coke amount made by FCC-CY is in a range of 2.2 wt% while that made by FCC-SY is in a range of 0.16 wt%. Thus, coke yield for FCC-CY is 14 times higher than FCC-SY. Table 1 shows that the acidity of FCC-CY is higher than that of FCC-SY by around 16 times. Consequently, the relation between catalyst coking ability and its acidity is a direct relation.

While FCC-SY produces negligible gas, FCC-CY gas yield is substantial. **Fig 8** depicts clearly the gases behavior for catalyst FCC-CY. It can be seen from this figure that gas yield increases with both conversion and reaction temperature. Analysis of the produced gas shows that propane is the major component followed by C4 paraffins. Since benzene is not a major product as shown in Table 3, it can be concluded that 1,2,4 TMB dealkylation is

not a simple reaction. But rather, it is a complicated reaction which produces toluene and C2-C4 gases. A simple dealkylation reaction requires hydrogen and produces methane which was negligible in the products. However, aromatics with 4 and more methyl groups can undergo paring reaction forming C2-C4 gases and toluene [4]. Consequently, it can be understood that paring reaction depends on the transalkylation and disproportionation reactions forming aromatics with higher methyl group number.

It can be inferred that, increasing catalyst acidity changes the path of the 1,2,4 TMB reactions. Also, it decreases both isomerization and disproportionation and increases both paring dealkylation and coking reactions.

3.2.3 Xylene to tetramethylbenzene (TeMBs) ratio

In the absence of secondary transalkylation or dealkylation, the molar ratio of xylene-to-tetramethylbenzene (X/TeMB) should be unity. Fig 9 shows xylene-to-tetramethylbenzene (Xylenes/TeMBs) ratio at various conversion levels over both FCC-SY and FCC-CY catalysts. For FCC-SY, it can be seen in this Figure that Xylenes/TeMBs ratio is higher than the stoichiometric ratio of 1.0. This is in agreement with the results of Atias et al. [5] who found increased amounts of xylenes over TeMBs. Roger et al [3] found that the initial rate of formation of xylenes is 2.6 higher than that of TeMBs over ZSM-5 zeolite. The higher ratio of Xylenes/TeMBs indicates that either secondary transalkylation or dealkylation reactions are taking place. Dealkylation reaction was found to be inconsequential due to the very small amount of gases observed. TeMBs may then have been trapped in micropores as coke precursors to account for the excess xylenes in relation to TeMBs. This behavior is similar to toluene/TMBs ratio in *m*-xylene conversion. And it can also be attributed to the higher desorption rates of xylenes as compared to tetramethylbenzenes.

Regarding Xylenes/TeMBs ratio for FCC-CY catalyst, Table 3 reports ratios between 4 and 10 and the ratio was found to increase with temperature. The large ratio of Xylenes/TeMBs hints to the direct consumption of TeMBs via paring reactions. Furthermore, Fig 9 shows that this ratio is not a significant function of contact time or conversion at 400C. However, at 450 and 500C reaction temperatures, this ratio goes through maximum (at 10 sec contact time or 30 % conversion) then starts to decrease with conversion. This behavior can be due to the increased secondary transformation of the

produced xylenes (at high contact time and temperature) through transalkylation followed by pairing dealkylation.

3.2.4 *p*-Xylene to *o*-Xylene (P/O) ratio

The *p*-Xylene to *o*-Xylene (P/O) ratio provides very good insights as well into the zeolite pore size. Larger values of the P/O ratio point to small pores while lower values tend to show existence of large pores. Generally, P/O ratio increases with both temperature and conversion. This behavior might be due to the increased coke deposition as temperature increases leading to the narrowing of the zeolite channel thereby giving *p*-xylene (kinetic diameter, $d_k = 0.58\text{nm}$) advantage over *o*-xylene ($d_k = 0.68\text{nm}$).

The ratios of *para*- to *ortho*-xylene (P/O) in the product mixture are presented in Fig 10 for both catalysts. The P/O ratio for FCC-SY is bounded between 0.7 and 0.8 over the whole conversion range and temperatures. Similar ratios were obtained by Park et al. [15] over HCM-22 at 350°C. These P/O ratios (over the FCC-SY) are well below the equilibrium value of 1.0. Thus, FCC-SY does not show *para*-selectivity during the 1,2,4 TMB transformation. It is believed that during 1,2,4 TMB disproportionation, *o*-xylene is preferentially produced among the xylene isomers and subsequently isomerized into the other isomers [14,18]. The mechanism based on biphenyl-methane carbonium ion intermediates [19] where the intermediate that produces *o*-xylene and 1,2,4,5 TeMB is the most linear one which has least diffusion limitations [1].

Similarly, Fig 10 shows P/O ratio for FCC-CY having equilibrium value of 1.0 for all conversions and temperatures. To analyze this result, it is significant to study *p*-xylene and *o*-xylene yields for both catalysts at same conditions. For example at 450C and 36% conversion (Table 2) FCC-SY produces 2.5 and 3.4 wt% *p*-xylene and *o*-xylene respectively. Table 3 shows that FCC-CY for the same conditions makes 3 and 3 wt% for *p*-xylene and *o*-xylene. It is clear that while *p*-xylene yield decreases, *o*-xylene yield increases. Thus the proposed mechanism which was claimed to be selective for *o*-xylene [19] is not applicable in the case of FCC-CY where pairing dealkylation is a very significant reaction.

3.2.5 *1,3,5*-TMB to *1,2,3*-TMB ratio

Experimental results for isomerization reaction over FCC-SY (Fig 11) show that higher amounts of 1,3,5-TMB were found as compared to the 1,2,3-TMB even though the 1,2,3-isomer has a smaller molecular size than 1,3,5-TMB [16,19]. However, 1,3,5-TMB is thermodynamically favored over the 1,2,3-isomer [20]. The ratio of 1,3,5- to-1,2,3-isomer

over the FCC-SY is about 2.0 and is invariant with conversion but decreases slightly with temperature. Wang et al. [14] reported a value of 2.7 for the 1,3,5-/1,2,3-trimethylbenzene ratio at 348°C over USY zeolite. While Park and Rhee [15] reported the ratio 1,3,5-/1,2,3-TMB as 1.99 over HNU-87 (a zeolite with catalytic properties falling between those of medium and large pore zeolites). It should be noted that the equilibrium ratios are 3.5 [14] and 3.16 [21] at 350 and 400°C respectively. Thus, our ratio of 2.0 is below the equilibrium value. For the *m*-xylene transformation reaction, the FCC-SY gave a ratio of about 3.3 at 400°C and 2.4 at 500°C [9,10]. While the 1,3,5-TMB/1,2,3-TMB ratio of about 2.0 was obtained for the 1,2,4-TMB transformation under the same experimental conditions. Thus it seems this ratio is affected by the reaction path. In our experimental conditions, it is higher for disproportionation reaction (*m*-xylene conversion) than for isomerization reaction (1,2,4-TMB conversion).

Fig 11 also depicts the relationship between the 1,3,5-TMB/1,2,3-TMB ratio and conversion for FCC-CY at several temperatures. Table 3 shows that this ratio is a function of temperature for this catalyst. For example, at 37 % conversion this ratio is 2.6 and 2.3 for reaction temperature of 400°C and 500°C respectively. Furthermore, this ratio seems to slightly increase with conversion. For example, at 500°C, this is 2.11 and 2.3 for 14% and 37% conversion respectively. Thus the 1,3,5 TMB can be formed from secondary reactions and it is more consumed than 1,2,3 TMB when the temperature is raised (probably through paring reactions).

4. Conclusions

The following conclusions can be drawn from the catalytic transformation of 1,2,4-trimethyl benzene over high and low acidity catalysts.

1. The reactivity of *1,2,4-trimethyl benzene* over Y-zeolite was found to be extremely affected by zeolite acidity.
2. The results show that *1,2,4-trimethyl benzene* transforms mainly through two reactions; isomerization and disproportionation over low acidity catalyst. The transformation of *1,2,4-trimethyl benzene* over high acidity catalyst is far more complicated and paring reaction plays a vital role.
3. Xylene yields are substantial function of catalyst acidity and reaction temperature. Both catalysts produce a negligible amount of benzene.

4- Tetramethylbenzenes (TeMBs) were found as major products, for low acidity catalyst, while toluene was found a major product for high acidity catalyst.

5- Gases produced are mainly C3 and C4 which are strong indication for paring reactions. This is further substantiating that single dealkylation reaction of the methyl group does not take place in our reaction conditions.

6. High acidity catalyst produces high amount of toluene, gases, coke and low amount of TeMBs which indicates the transformation of TeMBs in to these compounds via paring dealkylation.

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Table 1: Characterization of used Catalyst

Catalyst	Acidity (mmol/g)	Surface Area (m ² /g)	Crystallite size (μm)	Unit cell size (Å)	SiO ₂ /Al ₂ O ₃ (mol/mol)	Na ₂ O wt %
FCC-SY	0.033	197	0.9	24.27	5.7	Negligible
FCC-CY	0.55	240	0.9	24.5	5.7	Negligible

Table 2: Product distribution (wt %) at various reaction conditions for *1,2,4-Trimethylbenzene* transformation over FCC-SY

Temp (°C)/ time (s)	Conv. (%)	<i>1,3,5</i> - TMB	<i>1,2,3</i> - TMB	TI*	<i>p</i> - xylene	<i>m</i> - xylene	<i>o</i> - xylene	Toluen e	TTMB's (<i>1,2,3,4</i> - , <i>1,2,3,5</i> -, & <i>1,2,4,5</i>)	TD**
400										
3	8.12	1.33	0.65	1.99	0.55	1.31	0.82	0.30	2.09	5.07
5	12.64	2.04	0.99	3.03	0.89	2.10	1.30	0.47	3.73	8.49
7	17.40	2.76	1.34	4.10	1.23	2.89	1.78	0.64	5.48	12.02
10	23.00	3.80	1.84	5.64	1.68	3.98	2.47	0.84	7.99	16.96
13	27.80	4.72	2.27	6.99	2.08	4.92	3.03	1.03	10.22	21.28
15	31.25	5.22	2.5	7.72	2.32	5.48	3.37	1.15	11.55	23.87
450										
3	9.90	1.67	0.82	2.49	0.67	1.54	0.94	0.38	2.75	6.28
5	15.64	2.60	1.26	3.86	1.07	2.48	1.49	0.60	4.80	10.44
7	20.00	3.31	1.60	4.91	1.38	3.19	1.90	0.77	6.42	13.66
10	26.88	4.44	2.12	6.56	1.88	4.33	2.55	1.04	8.97	18.77
13	31.40	5.31	2.53	7.84	2.25	5.21	3.06	1.23	11.01	22.76
15	36.0	6	2.80	8.8	2.46	5.8	3.37	1.35	12.20	25.09
500										
3	11.48	1.96	0.97	2.93	0.78	1.76	1.02	0.49	3.25	7.30
5	16.22	2.74	1.34	4.08	1.13	2.55	1.46	0.71	4.90	10.75
7	21.44	3.61	1.76	5.37	1.50	3.39	1.94	0.92	6.72	14.47
10	28.20	4.73	2.29	7.02	1.98	4.50	2.56	1.23	9.06	19.33
13	34.5	5.8	2.7	8.5	2.4	5.6	3.2	1.45	10.80	22.49
15	38.0	6.2	2.9	9.1	2.7	6.3	3.5	1.7	11.8	24.70

*TI – Total isomerization
**TD – Total Disproportionation

Table 3: Product distribution (wt %) at various reaction conditions for *1,2,4-Trimethylbenzene* transformation over FCC-CY

Temp (°C)/ time (s)	Conv. (%)	Gas	Benzene	<i>1,3,5</i> - TMB	<i>1,2,3</i> - TMB	TI*	<i>p</i> - xylene	<i>m</i> - xylene	<i>o</i> - xylene	Toluene	TeMB's (<i>1,2,3,4</i> - , <i>1,2,3,5</i> - , & <i>1,2,4,5</i>)
350											
3	7	0.8	0	0.85	0.37	1.22	0.41	0.91	0.42	0.45	0.8
5	11.1	1.9	0.1	1.4	0.55	2	0.82	1.83	0.83	1	1.7
7	17.7	3.3	0.17	2	0.8	2.8	1.4	3.1	1.4	1.74	2.7
10	24.	4.5	0.24	2.8	1.1	3.9	2	4.5	2	2.5	3.6
13	31	6.1	0.32	3.6	1.4	5	2.7	6.1	2.7	3.4	4.7
15	35	7	0.4	3.9	1.5	5.4	3	6.7	3	3.9	5
400											
3	8.7	1.7-	0.04-	1	0.41	1.41	0.61	1.35	0.61	0.9	0.9
5	15	3.3	0.23	1.5	0.6	2.1	1.2	2.62	1.20	1.9	1.4
7	21.1	4.3	0.3	2.2	0.85	3.1	1.8	3.9	1.74	2.6	2.3
10	27	6.3	0.5	2.4	1	3.4	2.2	4.8	2.2	3.6	2.8
13	33	7.2	0.6	3	1.3	4.3	2.8	6.1	2.8	4.4	3.7
15	37	8	0.6	3.9	1.5	5.4	3.2	7.2	3.3	4.8	4
450											
3	12.4	2.9	0.24	1.1	0.5	1.6	0.92	2	0.92	1.7	1.3
5	17.3	4.4	0.44	1.3	0.57	1.9	1.3	2.9	1.3	2.8	1.3
7	22	5.7	0.61	1.6	0.7	2.3	1.7	3.8	1.75	3.8	1.4
10	29.8	6.9	0.7	2.3	1	3.3	2.5	5.5	2.5	4.8	2
13	36.6	9	1	2.7	1.2	3.9	2.95	6.5	3	5.9	2.9
15	40	9.2	0.8	3.4	1.4	4.8	3.5	7.7	3.5	6.2	3.5
500											
3	14.1	3.7	0.5	0.93	0.44	1.4	1	2.1	1.	2.6	0.75
5	18.6	5	0.7	1.2	0.55	1.75	1.4	3	1.4	3.5	.9
7	24.2	6.4	0.81	1.5	0.7	2.2	1.9	4.1	1.9	4.5	1
10	31.3	8.2	1.1	1.9	0.9	2.8	2.5	5.4	2.5	5.9	1.6
13	37	10	1.4	2.3	1.1	3.1	2.8	6.1	3	6.6	2
15	42.5	11.4	1.6	2.4	1.1	3.5	3.1	6.7	3.2	8.5	2.1

*TI – Total isomerization

**TD – Total Disproportionation

Table 4: coke wt % over both catalysts at various reaction conditions for *1,2,4-Trimethylbenzene* transformation.

Temperature	Contact Time (sec)	Coke wt % FCC-SY	Coke wt % FCC-CY
350C	5	0.14	1.3
	10	0.16	2.0
	15	0.16	2.4
400C	5	0.15	1.4
	10	0.17	2.1
	15	0.17	2.5
500C	5	0.15	1.5
	10	0.14	2.4
	15	0.17	2.8

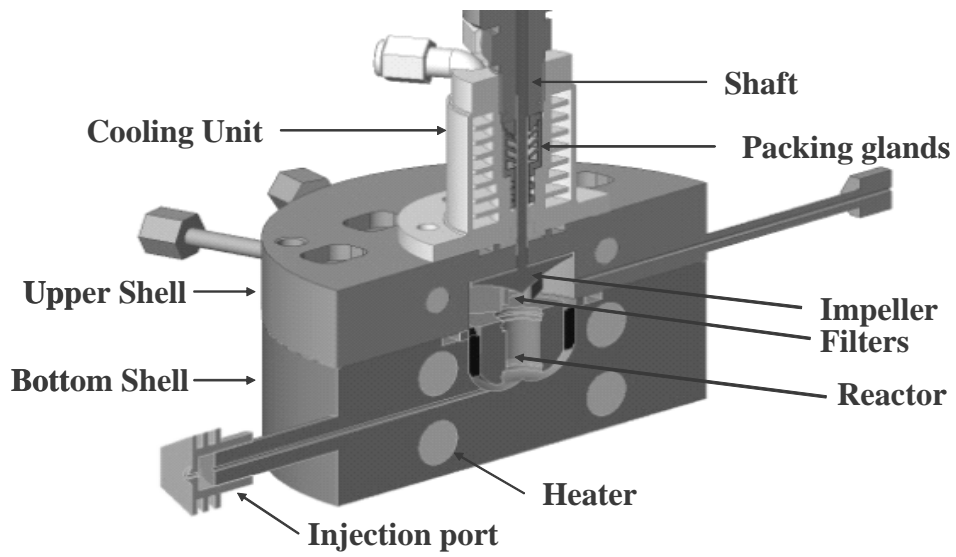


Fig. 1. Schematic diagram of the riser simulator

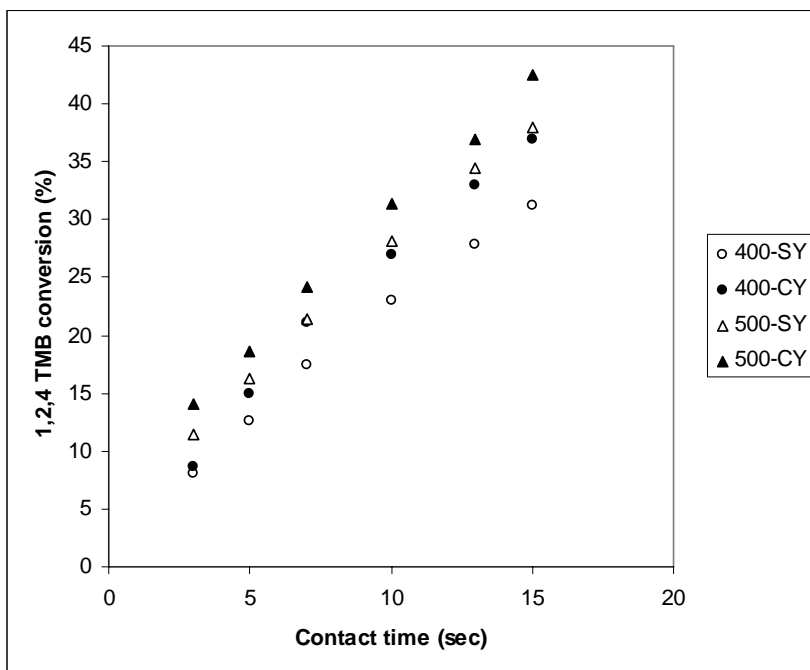


Figure 2: 1,2,4 TMB conversion using two catalysts at two temperatures.

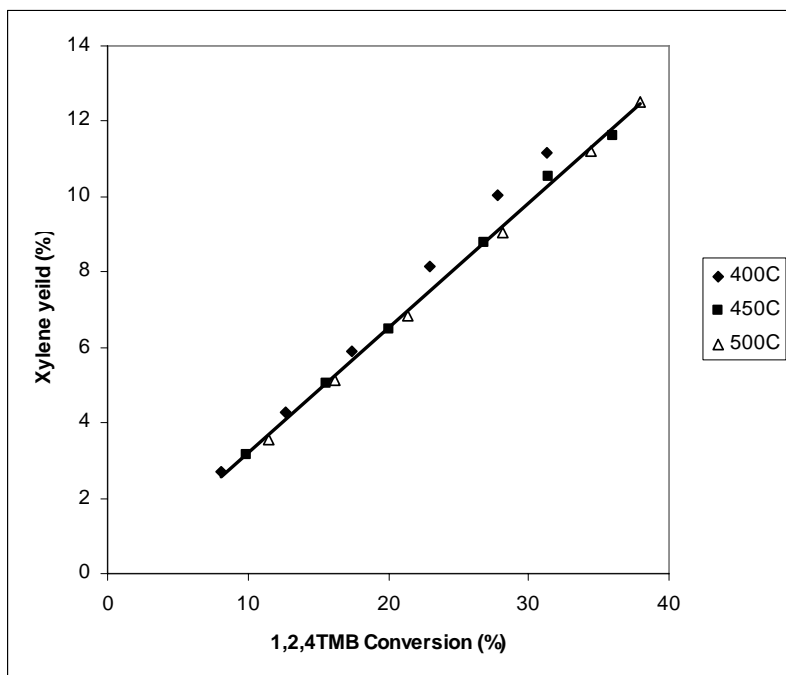


Figure 3: Xylene yields versus 1,2,4 TMB conversion using FCC-SY catalyst.

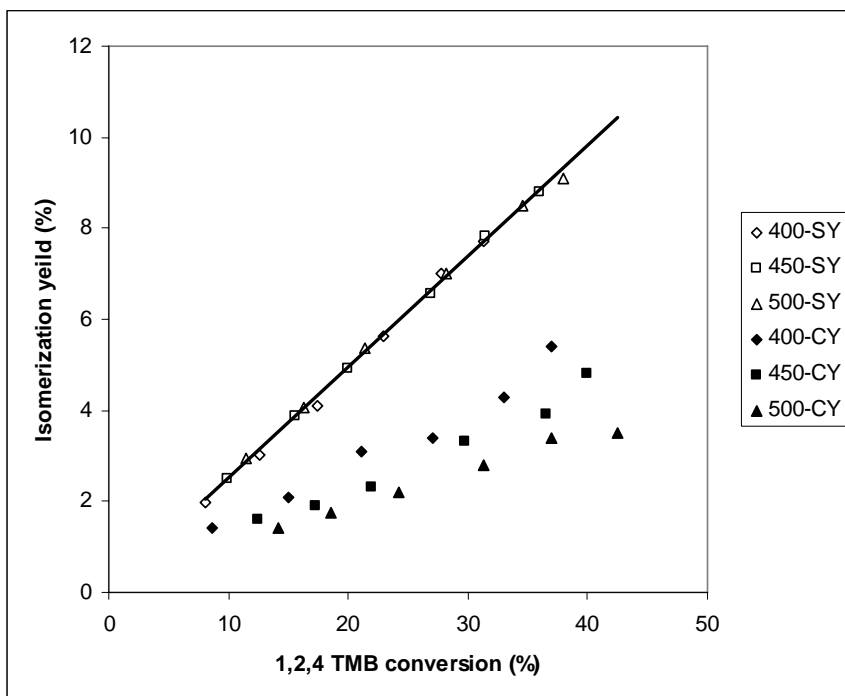


Figure 4: Isomerization yield versus conversion at several temperatures for both catalysts.

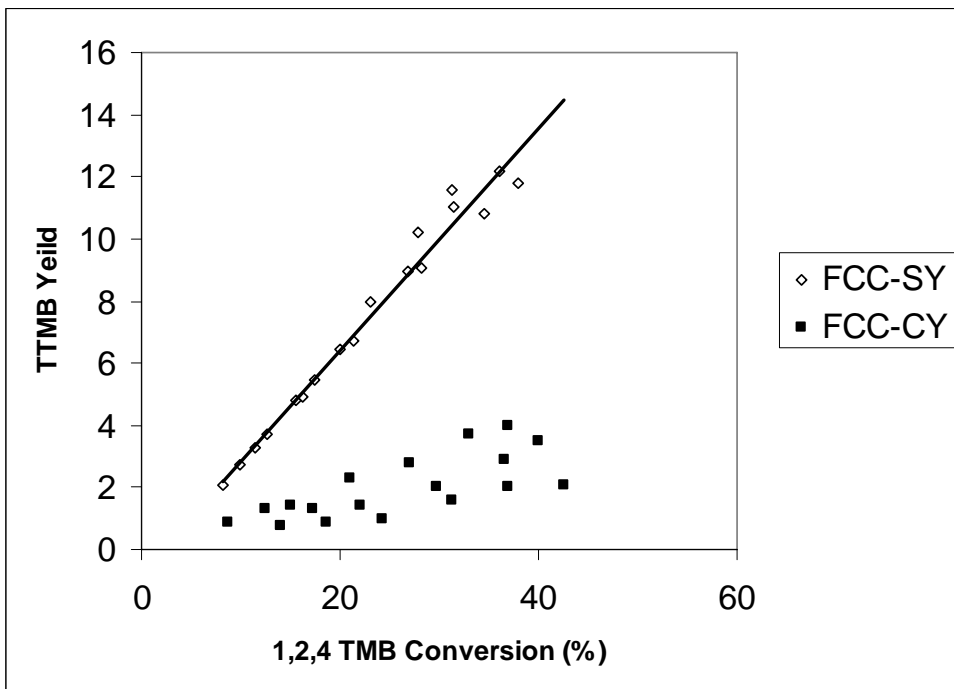


Figure 5: TeMBs yield versus conversion for both catalysts.

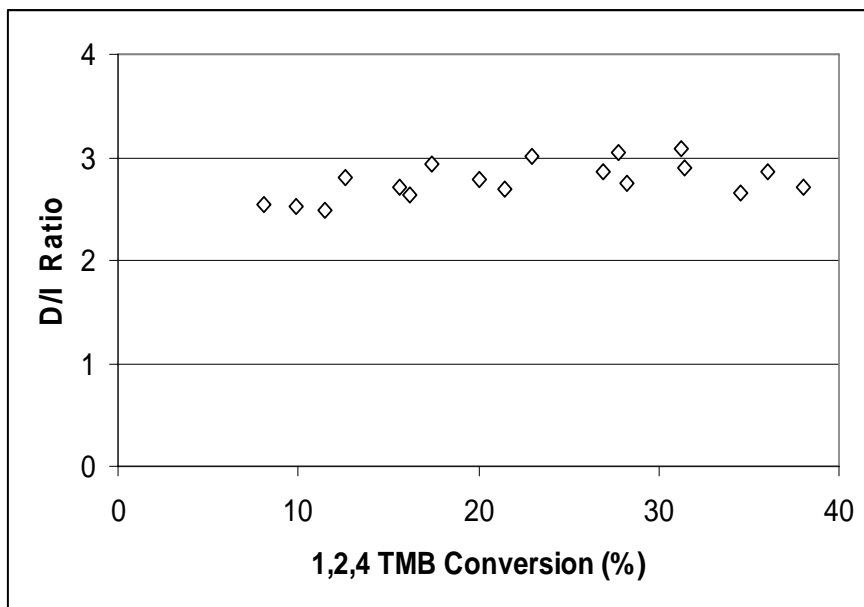


Figure 6: D/I ratio versus 1,2,4 TMB conversion using FCC-SY.

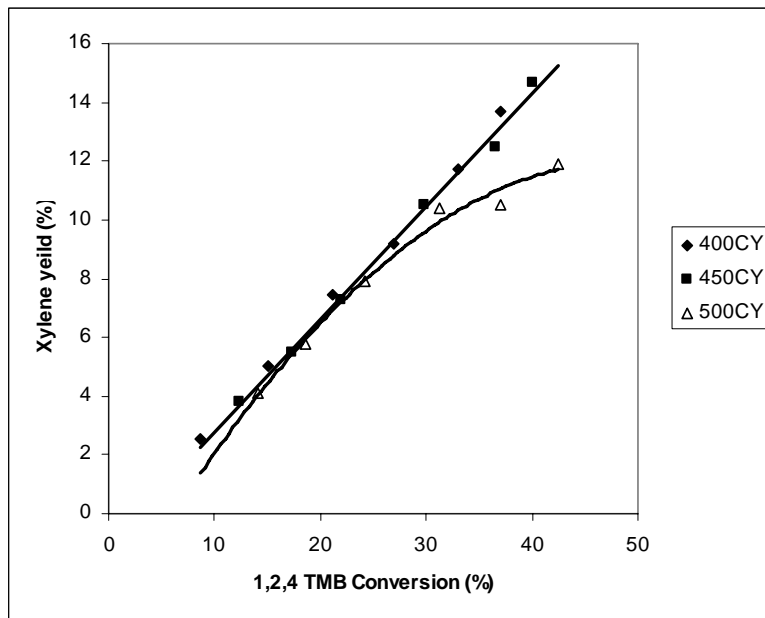


Figure 7: Xylene yields versus 1,2,4 TMB conversion using FCC-CY.

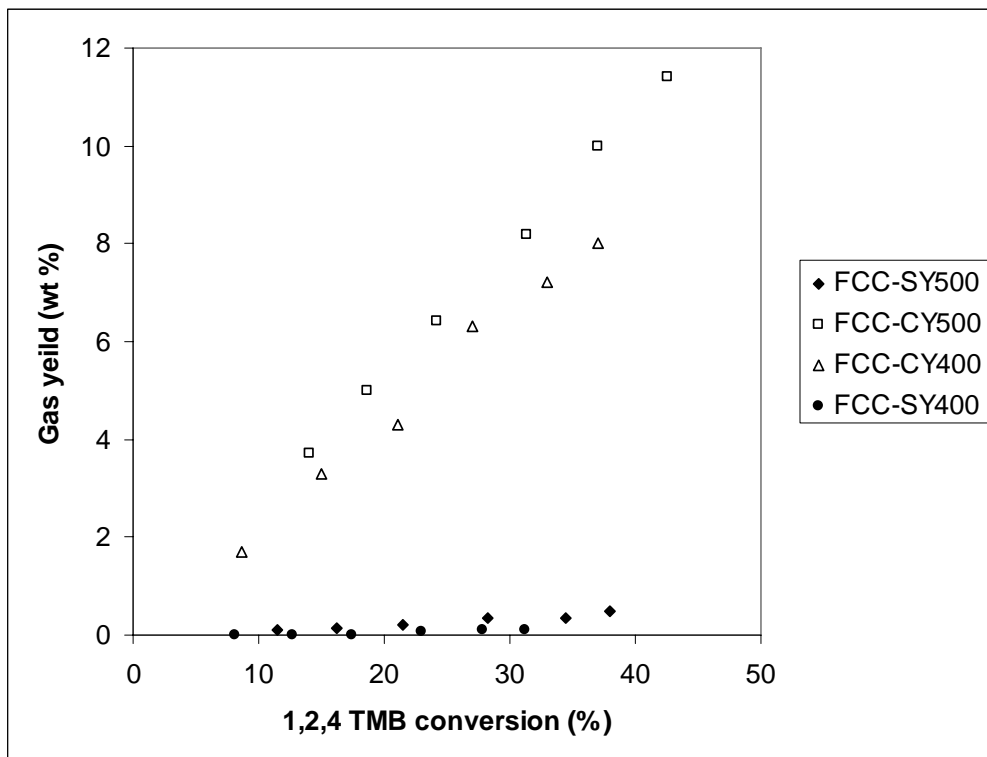


Fig 8. Gases yield versus 1,2,4 TMB conversion.

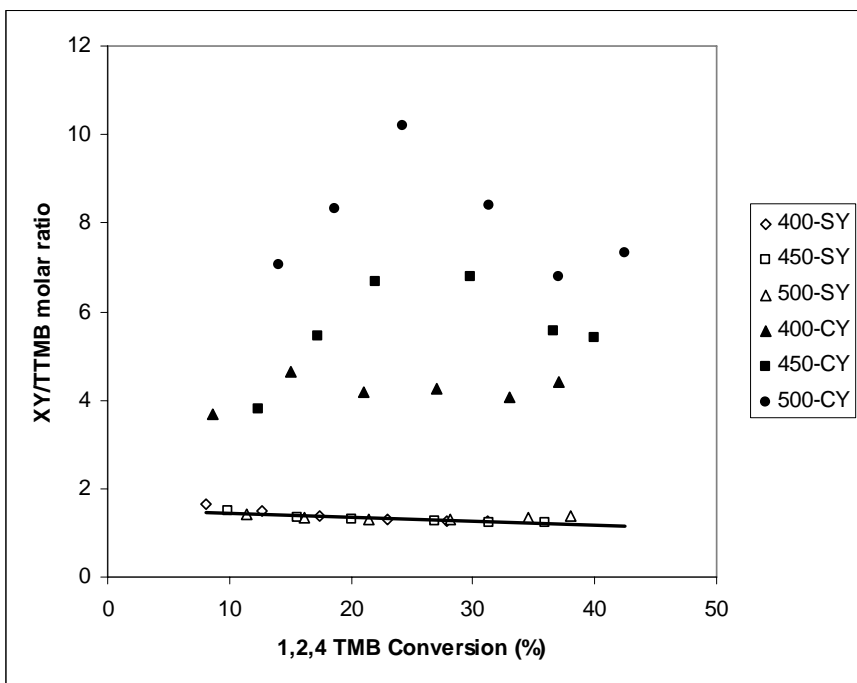


Figure 9: Xylenes/ TeMBs molar ratio versus conversion at several temperatures for both catalysts.

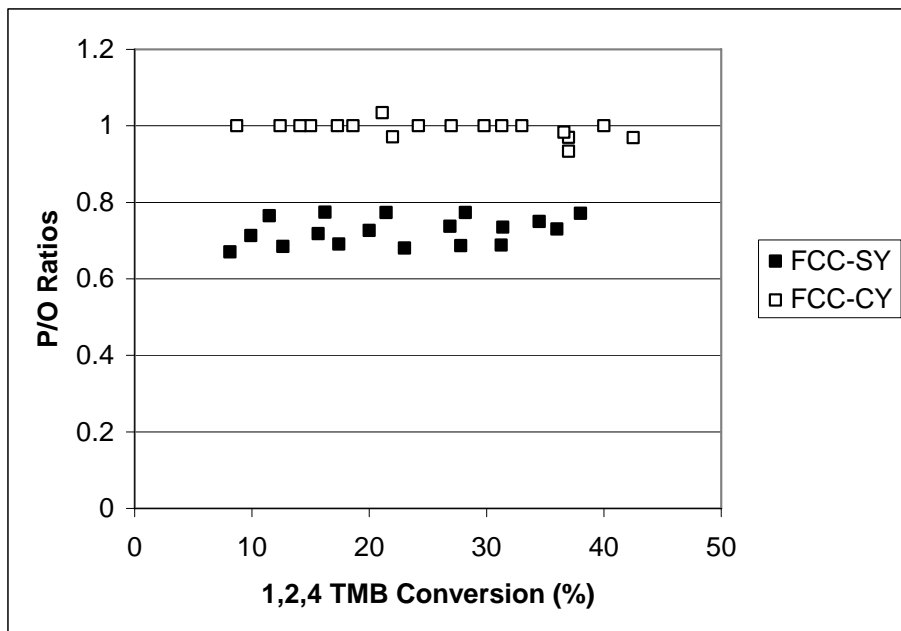


Fig 10 P/O ratio vs conversion for the two catalysts.

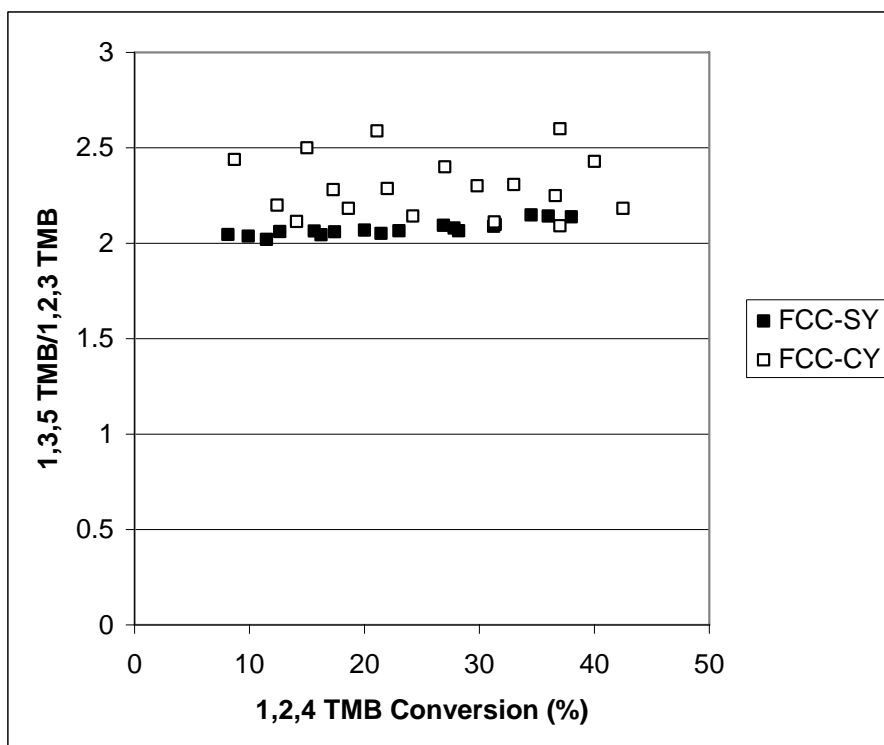


Fig 11 1,3,5 TMB/1,2,3 TMB ratio vs conversion for the two catalysts.