3. RESULTS AND DISCUSSION

3.1. ALKYLATION OF TOLUENE WITH METHANOL:

3.1.1. Methylation of Toluene with Methanol on Unloaded and Pt-Loaded H-ZSM-5 Catalysts:

3.1.1.1. Toluene conversion:

The methylation of toluene with methanol is traditionally accepted as an acid catalyzed reaction. Hence, in the present work, the catalytic acid sites are provided by a solid acidic zeolite, which is capable of carrying out the formation of the carbonium ions necessary for this alkylation reaction **[47-49]**. This alkylation may be capable of the formation of a mixture of C_8 aromatics (the xylenes plus ethylbenzene) and C_9 aromatics (trimethylbenzenes and ethyltoluene).

The privilege of using H-ZSM-5 zeolite over other acidic solids is their channel dimensions (~5Å) which admit preferentially the formation and diffusion of para-xylene in order to minimize the other xylenes (meta and ortho-xylenes) which possess larger molecular size. Such materials are classified as shape-selective catalysts.

Although H-ZSM-5 is considered as a typical toluene methylation acidic solid catalyst, we have previously tested promoting H-ZSM-5 and H-MOR zeolites with platinum **[39,40]**, in order to catalyze stabilization of the carbonium ion via extending its life-time on the catalytic sites. Moreover, the metal crystallites that migrate inside the zeolitic channels can also play a significant role in pore size engineering **[129]** via narrowing these channels whereby para-xylene production selectivity is enhanced.

Hence, in the present work, we have changed the platinum content of the catalysts to be 0.1, 0.2 and 0.3wt%.

Tables 1-4 and Fig. 1 show that the total conversion of toluene on H-ZSM-5 as a catalyst increases with reaction temperature from 24.2% at 300^{o}C up to 48.4% at 400^{o}C, beyond which it decreases to 34.5% at 500^{o}C. Evidently, promotion of H-ZSM-5 with 0.1wt%Pt has increased toluene conversion during the whole reaction temperature region up to 450^{o}C, beyond which the conversion of toluene has slightly decreased, but however, still significantly exceeding that obtained using the unloaded H-ZSM-5. A further increase of platinum in H-ZSM-5 to 0.2wt% gives some little increase of toluene conversion. However, increasing Pt further to 0.3wt% in the zeolite results in a significant drop of its activity at all reaction temperatures, compared to the catalysts containing lower Pt content. Furthermore, the activity of the 0.3wt% Pt/H-ZSM-5 catalyst has dropped to be even lower than that of the unloaded H-ZSM-5 zeolite during the lower reaction temperatures (350–400^{o}C). This can be attributed to some decrease of the catalyst surface area and pore volume (Table 5) and to more significant extent the decrease of acid site number and strength with increasing the Pt concentration (Table 6). Evidently, the obtained data indicate that a Pt content of 0.3wt% should have exceeded the allowable Pt concentration.

3.1.1.2. Total xylenes in products:

Tables 1-4 and Fig. 2 show that the production of total xylenes increases as a function of reaction temperature in different ways. Excluding the overlaps of the curves of the 0.1 and 0.2wt%Pt/H-ZSM-5 catalysts, total xylenes production overlaps; can be generally arranged in the order: 0.1 % Pt/H-ZSM-5 > 0.2 % Pt/H-ZSM-5 > 0.3% Pt/H-ZSM-5. Even though, the xylenes are generally lower on the unloaded catalyst than on the Pt loaded H-ZSM-5 zeolite catalysts.

However at higher temperatures, the order of activities for total xylenes production is in the order: 0.2% Pt/H-ZSM-5 > 0.1% Pt/H-ZSM-5 > 0.3% Pt/H-ZSM-5. Hence, the 0.2 wt %Pt /H-ZSM-5 catalyst can be considered as the catalyst of choice for total xylenes production. At low temperatures, the higher activity of the 0.1wt%Pt catalyst can be attributed to the larger space in the channels and cavities of this catalyst than in the two other catalysts, allowing more xylenes production. The platinum atoms dispersed in the zeolite surface, by virtue of their vacant d-orbitals (a property of transition metals), facilitates the formation of carbocations and hence enhance the rate of methylation of toluene **[39,40]** in spite of decreasing the number and strength of the acid sites in these catalysts **[130-133]**, and also decreasing the surface area with increasing the Pt content (Tables 5 and 6).

In contradistinction to what occurs on the Pt loaded catalysts, the decreasing activity of xylenes production at higher temperatures (beyond 400^{o}C) on the unloaded H-ZSM-5 catalyst is evidently attributed to the absence of the noble metal sites which are necessary for carbonium ion stabilization.

Table 5. Effect of Pt concentration on surface area and pore volume of H-ZSM-5 zeolite.

Catalyst	**BET surface area (m^2/g)**	**Total pore volume (ml/g)**
Unloaded H-ZSM-5	345.4	0.220
0.1%Pt/H-ZSM-5	341.5	0.199
0.2%Pt/H-ZSM-5	336.0	0.180
0.3%Pt/H-ZSM-5	292.4	0.153

Table 6. Ammonia desorption enthalpy (ΔH) and peak temperature for untreated and Pt loaded H-ZSM-5 catalysts.

Catalyst	Strong acid sites	
	$\Delta H_{des.}$, Jg^{-1} [a]	Peak Temp., °C [b]
Unloaded H-ZSM-5	105.1	380
0.1%Pt/H-ZSM-5	80.8	372
0.2%Pt/H-ZSM-5	78.2	368
0.3%Pt/H-ZSM-5	61.0	349

[a] proportional to acid sites number
[b] proportional to acid sites strength

3.1.1.3. Para-xylene selectivity:

The percentage of para-xylene in the xylenes mixture in product is denoted as its selectivity, i.e., para-selectivity=100[para-xylene / (ortho- + meta- + para-xylene)]. The para-xylene selectivity is of industrial importance because the para xylene isomer is an important starting material for the producting of polyester fibers, adhesives, etc. Tables 1-4 and Fig. 3 show that the activity of the 0.3%Pt/H-ZSM-5 catalyst for para-xylene selectivity exceeds that of the unloaded H-ZSM-5 catalyst at all reaction temperates. The increase of para-xylene selectivity, using the 0.3%Pt/H-ZSM-5 catalyst in the present study, is compatible with the assumption given by **Wei [71]**, based on a mathematical model, according to which it is indicated that increased diffusion limitation in the zeolite pores of a catalyst increases the opportunity for large reactant molecules to come in contact with a large number of catalytic active sites and react with higher reaction rate. Less voluminous reaction products will diffuse faster to the outside of the pore, i.e., in H-ZSM-5 zeolite, para-xylene diffuses 1000 times faster than ortho- and meta-xylene **[134,135]**, and thus para-xylene in the product may surpass the thermodynamic equilibrium values significantly. Fig. 3 shows that the position of the selectivity curve for para-xylene produced using the unloaded H-ZSM-5 zeolite is not as expected, in comparison with the Pt-promoted curves. Its higher position above the curve obtained for the 0.1 and 0.2wt%Pt/H-ZSM-5 catalysts and its position below the 0.3wt%Pt/H-ZSM-5 catalyst curve can be attributed to the preferential formation and stronger adsorption of para-xylene on the external surface of the H-ZSM-5 zeolite.

3.1.1.4. Trimethylbenzenes in product (TMBs):

Trimethylbenzenes (TMBs) are formed as byproducts during the current reaction of toluene methylation both on the unloaded and Pt loaded H-ZSM-5 catalysts. Using the unloaded H-ZSM-5 catalyst, trimethylbenzenes are 4.2% at 300^{o}C and increase to 15.7% at 400^{o}C then drop to 6.7% at 500^{o}C (Tables 1-4 and Fig.4). However, using the 0.1, 0.2 and 0.3%Pt/H-ZSM-5 catalysts, TMBs are around 4.1, 4.6 and 4.3%, respectively at 300^{o}C and increase to a maximum of 15.3, 16.1 and 11.7% at 450^{o}C then decline to 12.1, 14.7 and 10.8% at 500^{o}C. These TMBs are relatively somewhat lower on the 0.3wt%Pt/H-ZSM-5 catalyst. This decreasing of TMBs production using the 0.3wt%Pt/H-ZSM-5 catalyst, may be due to the lower surface area and acidity of this catalyst than the other used catalysts.

3.1.1.5. Gas production:

Tables 1-4 and Fig. 5 show that the gaseous hydrocarbons produced using the catalysts under study increase with increasing the reaction temperature from 300 to 500^{o}C. On the unloaded zeolite, they range between 5.0 and 6.6% at 300-500^{o}C, respectively, whereas on the Pt/H-ZSM-5 catalysts they are somewhat higher; i.e., ranging between 5.6 and 7.4% at 300^{o}C up to 8.2 and 10.1 at 500^{o}C, with some increase as Pt content increases due to some enhanced hydrogenolysis reactions.

3.1.1.6. The individual xylene isomers in the xylenes mixture relative to the corresponding equilibrium values (X/Xe):

Tables 1-4 and Fig. 6 show that the para-xylene selectivity in the mixture of xylenes in product relative to its selectivity in the thermodynamic equilibrium composition increases with increasing the platinum content in the catalyst. In all the Pt/H-ZSM-5 catalysts, this para-xylene (X/Xe) curve is curved with a meniscus at ~ 400-450°C. This meniscus occurs at X/Xe = unity on the 0.1%Pt/H-ZSM-5 catalyst and rises to 1.07 on the 0.2%Pt/H-ZSM-5 catalyst, then to X/Xe of 1.34 using the 0.3%Pt/H-ZSM-5 catalyst. At other temperatures, the X/Xe values are higher than the mentioned values.

On the contrary, the X/Xe curves for meta-xylene in product relative to equilibrium show a maximum acquiring curvature around 400-450°C and this maximum occurs at X/Xe ~ unity on the 0.1 and 0.2%Pt/H-ZSM-5 catalysts then decreases to 0.89 using the 0.3%Pt/H-ZSM-5 catalyst. These data are of industrial importance since para-xylene is of an economic commercial importance because it is a starting material for polymer synthesis.

On the other hand, meta-xylene is the cheapest isomer among the three xylenes. The reason for this behavior of the para- and meta-xylenes may be attributed to the molecular volumes of these isomers; para-xylene is of the smallest size, whereas meta-xylene is considered the largest molecule. The third isomer of these xylenes, ortho-xylene, which acquires a medium commercial value, acquires higher X/Xe values (above unity) at lower temperatures, in general, and lower values (almost decreasing values) at higher temperatures. In general, the catalyst of choice among the Pt/H-ZSM-5 is the 0.3%Pt/H-ZSM-5 one; in particular at 500°C.

Table 7: Thermodynamic equilibrium values of p-, m-, and o-xylenes at different temperatures **[136]**.

Component, %	**Reaction Temperature, oC**				
	300	**350**	**400**	**450**	**500**
p-Xylene	23.88	23.73	23.55	23.37	23.19
m-Xylene	53.65	52.98	52.42	51.94	51.56
o-Xylene	22.47	23.29	24.03	24.69	25.25

The unloaded H-ZSM-5 zeolite shows a unique feature; at most temperatures, the X/Xe values of ortho-xylene are much higher than that of para-xylene since the zeolitic channels in this unloaded zeolite should be larger than in the Pt containing catalysts, where the Pt crystallites diminish the size of these channels. Hence, the shape selectivity privilege will be less effective or even ineffective in the unloaded zeolite catalyst, compared to the Pt loaded ones. Although according to thermodynamic equilibrium data (Table 7), meta-xylene occupies almost double the quantity of either para- or ortho-xylene, Fig. 6 shows that meta-xylene gives X/Xe values of ≤ 0.81, which exhibits greater deviation from shape-selectivity than the Pt-loaded catalysts.

3.1.1.7. Kinetics of toluene alkylation with methanol using the Pt/H-ZSM-5 catalysts:

3.1.1.7a. Reaction rate constant:

The apparent reaction rate constant (k) has been calculated at different reaction temperatures according to the first order flow reactor equation 17:

$$k = \frac{F}{W}\ \ln\left(\frac{1}{1-x}\right) = \frac{WHSV}{3600}\ \ln\left(\frac{1}{1-x}\right) \ldots\ldots\ldots\ldots (eq. 17)$$

Where: F is the rate of feed injection (cm^3s^{-1}), WHSV is the weight hourly space velocity (h^{-1}), W is the catalyst weight (1 gm) and x is the wt% of total xylenes in products divided by 100. The apparent reaction rate constant (k) values are listed in Table (8).

Table 8: Apparent reaction rate constant, k (h^{-1}), for the alkylation of toluene with methanol reaction using the current Pt/H-ZSM-5 catalysts.

Catalyst	Reaction temperature, °C			
	300	350	400	450
Unloaded H-ZSM-5	$1.54x10^{-4}$	$2.08x10^{-4}$	$2.37x10^{-4}$	$2.49x10^{-4}$
0.1%Pt/ H-ZSM-5	$1.68x10^{-4}$	$2.55x10^{-4}$	$3.22x10^{-4}$	$3.51x10^{-4}$
0.2%Pt/ H-ZSM-5	$1.73x10^{-4}$	$2.24x10^{-4}$	$2.98x10^{-4}$	$3.68x10^{-4}$
0.3%Pt/ H-ZSM-5	$1.51x10^{-4}$	$1.87x10^{-4}$	$2.79x10^{-4}$	$3.35x10^{-4}$

3.1.1.7b. Activation energy:

The activation energy (E_a) for the alkylation reaction using the current catalysts has been calculated using the traditionally accepted Arrhenius equation (18) and the plot given in Fig. 7. A plot of lnk against 1/T is a straight line with a slope of $-E_a/R$. Then, E_a values can be calculated from the slope of the line.

$$k = A \,.\, e^{-E_a/RT} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots. (eq. 18)$$

$$lnk = lnA - E_a/RT \ldots\ldots\ldots.\ldots\ldots\ldots. (eq. 19)$$

Where: R is the universal gas constant=8.3143 J/mol K, T is the absolute reaction temperature (K), A is the pre-exponential factor and E_a is the energy of activation of the reaction.

The apparent activation energy values obtained for the reaction of toluene conversion during its alkylation with methanol are almost indifferent or at least exhibit slightly different values. The E_a values obtained using 0.1 and 0.2%Pt containing catalysts are almost equal, whereas that using the 0.3%Pt one is slightly higher. All the E_a values in Table 9 are relatively low showing that diffusion restrictions may play a significant role during this reaction on all current catalysts.

Table 9: Activation parameters for the alkylation of toluene with methanol reaction using the current Pt/H-ZSM-5 catalysts.

Catalyst	**Activation Energy (E_a), kJ.mol^{-1}**
Unloaded H-ZSM-5	11.0
0.1%Pt/ H-ZSM-5	16.8
0.2%Pt/ H-ZSM-5	17.1
0.3%Pt/ H-ZSM-5	18.8

3.1.1.8. Diffusion effects resulting via platinum inclusion in the catalysts:

Many variables affect reaction rates, i.e., pressure, temperature and composition of the catalyst, but diffusion along the pores of a catalyst may mask the effects of all such variables. A good catalyst may be ineffective if the reactants can not get to the active surface and the products removed. A detailed diffusion study appears very important for understanding the behavior of the variety of the catalysts used in this study.

Since porous solid catalysts possess surfaces being extended to as much as several hundred square meters per gram of solid, reactants must diffuse through the pores, and product back out. Pore diffusion may occur by one or more of three mechanisms: Ordinary diffusion, Knudsen diffusion and surface diffusion. If the pores are large and the gases relatively dense, the process is ordinary diffusion. The channels through which diffusion occurs are of irregular shape and varying cross section; constrains offer resistances which are not offset by the enlargement, so that the flux tends to be less than would be possible in a uniform pore of the same length and mean radius.

For ordinary diffusion in porous solid, an effective binary diffusion coefficient, $D_{12,eff}$, may be used to relate the flux to the total cross section of the porous solid, where:

$$D_{12,eff} = \frac{D_{12}\,\theta}{\tau} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (eq.\,20)$$

Here, D_{12} is the ordinary diffusion coefficient, θ is the void fraction with porous mass and τ is a factor to allow for both tortuosity and varying pore cross section.

If the gas density is low, or if the pores are quite small, or both, the reactant molecules colloid with the pore wall much more frequently than with each other. This is known as the Knudsen diffusion ($D_{K,eff}$), which can be calculated according to the following equation:

$$D_{K,eff} = 19400 \frac{\theta^2}{\tau S_g \rho_p} \sqrt{\frac{T}{M}} \dots\dots\dots\dots\dots\dots .. (eq.\,21)$$

Where: S_g is the total surface area of porous solid (gm/cm^2) ,as measured by B.E.T. method, ρ_p particle density of the catalyst (gm/cm^3), T is the reaction temperature (K) and M is the molecular weight of the feed.

To correlate quantitatively the difference in diffusion resistance in a series of catalysts, the dimensionless parameter Thiele modulus (Φ_L) can be considered the most appropriate approach. This modulus is calculated by iteration on the reaction rate constant (k_v) applying equations 22 and 23.

$$\Phi_L = L(k_v C_s^{m-1}/D_{eff})^{1/2} \ldots\ldots\ldots\ldots\ldots (eq.22)$$

Where: Φ_L is the Thiele diffusion modulus for general case (dimensionless), L is the volume of a catalyst/external surface area of particle (cm), k_v is the intrinsic first order reaction rate constant (sec^{-1}). C_s is the surface concentration (gm mol/cm^3), D_{eff} is the effective diffusion coefficient ($cm^2\ s^{-1}$) and m is the order of the reaction.

Detailed calculation of the Thiele modulus is given by **Satterfield and Sherwood [137]**. The effective binary diffusivity ($D_{12,eff}$) for methanol and toluene, the Knudsen diffusivity ($D_{k,eff}$) and the effective diffusivity (D_{eff}) are correlated together according to:

$$1/D_{eff} = 1/D_{12,eff} + 1/D_{k,eff} \ldots\ldots\ldots\ldots\ldots (eq.23)$$

Hence, the Thiele modulus for the current reaction using Pt- loaded H-ZSM-5 catalysts containing 0.1, 0.2 and 0.3wt%Pt has been calculated and listed in Table 10.

Table 10: Thiele modulus values (Φ_L) for the alkylation of toluene with methanol reaction using the current Pt/H-ZSM-5 catalysts.

Catalyst	**Φ_L**			
	300	**350**	**400**	**450**
Unloaded H-ZSM-5	6.64	7.54	7.88	7.91
0.1%Pt/ H-ZSM-5	7.61	9.14	9.87	10.31
0.2%Pt/ H-ZSM-5	9.23	10.26	11.55	12.59
0.3%Pt/ H-ZSM-5	9.69	10.53	12.62	13.44

Weisz [138] has indicated that the concentration gradient due to diffusion limitation is negligible when Φ_L is less than unity for first order reactions. Accordingly, the data depicted in Fig. 8 and Table 10 for the current unloaded and Pt loaded catalysts show that all of these catalysts encounter significant diffusion limitation since at all current reaction temperatures, the Φ_L values are higher than 6 (Table 10), which assumes that the H-ZSM-5 zeolite by itself encounters the lowest diffusion restriction (lowest Φ_L values, i.e. 6.64-7.91) at all reaction temperatures (300-450^{o}C), whereas, the Pt containing catalysts encounter more significant diffusion restriction. This restriction increases as a function of increasing the Pt content in the catalyst and reaction temperature. Using the catalysts containing 0.1, 0.2 and 0.3wt%Pt, the Φ_L values are 7.61-10.31, 9.23-12.59 and 9.69-13.44, respectively at the same temperatures range. This indicates that H_2PtCl_6 in its solution has penetrated the zeolitic pores during the impregnation process, and deposited in the zeolitic channels causing more restriction of diffusion of the reaction hydrocarbon mixture. Logically, the penetrating platinum increases as the Pt concentration in the solution increases. Accordingly, we observe that the diffusion resistance increases more significantly via loading with 0.3%Pt in the pores of the zeolite than through increasing the Pt loading to 0.2%Pt, etc.

3.1.2. Alkylation of Toluene with Methanol Using Pd Loaded H-ZSM-5 Catalysts

3.1.2.1. Toluene conversion:

Tables 1, 11-13 and Fig. 9 show that toluene conversion during its alkylation with methanol using 0.1, 0.2 and 0.3%Pd/H-ZSM-5 catalysts increase with increasing reaction temperature from 300 up to 450°C. This can be explained based on the fact that the reactants and products need high temperature to go into and out from the narrow pore of the H-ZSM-5 zeolite **[139]**.

The superiority of loading H-ZSM-5 with Pd metal over the unloaded H-ZSM-5 in catalyzing the alkylation of toluene with methanol is evident in Fig. 9, which shows that the toluene conversion is highest on the 0.2%Pd/H-ZSM-5 catalyst but lowest on the 0.3%Pd/H-ZSM-5 catalyst. This minority of the 0.3%Pd/H-ZSM-5 catalyst may be due to decreasing the acidity with increasing the Pd concentration (Table 14).

Using all Pd/H-ZSM-5 catalysts, toluene conversion increases via increasing reaction temperature from 300 to 450°C, where a maximum conversion occurs, beyond which the conversion declines with a further increase of temperature. However, Using the unloaded H-ZSM-5 catalyst, the toluene conversion increases with increasing the reaction temperature to reach a maximum value of 48.4% at 400°C, beyond which, the conversion decreases to 34.5% at 500°C. This higher increase of the temperature maximum on the Pd loaded H-ZS-5 catalysts relative to the unloaded one is indication of the stabilization of the carbonium ion formed to carry out the alkylation of toluene.

Table 14. Ammonia desorption enthalpy (ΔH) and peak temperature for unloaded and Pd/H-ZSM-5 catalysts.

Catalysts	**TPD of Ammonia**	
	ΔH_{des} (Jg^{-1})[a]	**Peak Temperature (°C)[b]**
Unloaded H-ZSM-5	105.1	380
0.1%Pd/H-ZSM-5	91.2	374
0.2%Pd/H-ZSM-5	89.0	370
0.3%Pd/H-ZSM-5	86.3	363

[a] proportional to acid sites number

[b] proportional to acid sites strength

3.1.2.2. Total xylenes in product:

Xylenes production on the current catalysts (Tables 1, 11-13 and Fig. 10) is almost similar to that of the conversion of toluene (Fig. 9) with only some difference between the activities of the 0.3%Pd/H-ZSM-5 and the unloaded catalysts. At 450°C, where the maximum production of xylenes takes place on the Pd-loaded H-ZSM-5 catalysts, a maximum formation of xylenes is reached via increasing the Pd content of the catalyst to 0.2wt%Pd then declines at 0.3wt%Pd. This may be due to masking a portion of the strong acid sites on the zeolite surface (Table 14).

3.1.2.3. Para-xylene selectivity:

Although the 0.3%Pd/H-ZSM-5 catalyst is the least active metal-loaded one, it acquires the highest para-xylene selectivity among all current catalysts (Tables 1, 11-13 and Fig. 11). This can be attributed to decreasing of the pore diameter of H-ZSM-5 zeolite by a portion of Pd atoms incorporated in the zeolitic channels and cavities of the support. This decreasing of the pore diameter causes higher diffusion of para-xylene than ortho- and meta-xylenes outside the zeolitic channels **[70,71].**

3.1.2.4. Trimethylbenzenes in product (TMBs):

At 400°C, where TMBs are still increasing almost in parallel, magnitude of TMBs formation is in the order: unloaded H-ZSM-5 > 0.1%Pd/H-ZSM-5 > 0.2%Pd/H-ZSM-5 > 0.3%Pd/H-ZSM-5. It can be assumed that these TMBs with their relatively larger molecular volumes decrease as a function of increasing the Pd content in the catalysts. Larger nucleuses of Pd atoms are incorporated in the zeolitic pore and narrow these pores, hence, producing lower percentage of TMBs. At 450°C, the higher activities of the 0.1 and 0.2%Pd/H-ZSM-5 catalysts than the unloaded H-ZSM-5 can be attributed to stabilizing the carbonium ion, necessary for the alkylation reaction, particularly at higher reaction temperatures. Higher temperatures (450-500°C) are assumed to reverse the reaction from alkylation to dealkylation. Anyhow, the 0.3%Pd/H-ZSM-5 catalyst seems to have a relatively excessive Pd in the pores of the catalyst which gives an inhibiting effect.

3.1.2.5. Gas production:

The production of gases during the alkylation of toluene can be result of hydrocracking of C-C bonds in toluene molecules or terminal C-C bonds via hydrogenolysis. The former reaction can be achieved on acid sites, whereas the latter reaction can take place on metal sites. Fig. 13 shows that gaseous products increase with increasing the Pd content in the following order: 0.3%Pd/H-ZSM-5 > 0.2%Pd/H-ZSM-5 > 0.1%Pd/H-ZSM-5 > unloaded H-ZSM-5. It can be safely assumed that these gases are formed via hydrogenolysis reaction.

3.1.2.6. The individual xylene isomers in the xylenes mixture relative to the corresponding equilibrium values (X/Xe):

The para-xylene selectivity is greatly higher in the presence of Pd/H-ZSM-5 catalysts (Tables 11-13 and Fig. 14) than in presence of the corresponding Pt/H-ZSM-5 versions (Fig. 6). However, similarly, the para-xylene selectivity increases with increasing the Pd content. In comparison, the smaller atom of Pd (106.40) compared to that of Pt (195.09) should speculate that the fraction of Pd entering and diffusing in the pores of H-ZSM-5 should be larger than the fraction of Pt at the same metal concentration. This will result in larger narrowing of the Pd/H-ZSM-5 pores than narrowing the Pt/H-ZSM-5 pores and hence the shape selectivity in the Pd containing catalysts will be higher than in the corresponding Pt/H-ZSM-5 catalysts. The decrease of the o-xylene selectivity, particularly at the higher temperatures, with increasing the Pd content from 0.1 to 0.3 is compatible with the belief that ortho-xylene can be considered to attain the largest molecular size among the three xylene isomers.

3.1.2.7. Kinetics of toluene alkylation with methanol using the Pd/H-ZSM-5 catalysts:

3.1.2.7a. Reaction rate constant:

The apparent reaction rate constant (k) has been calculated at different reaction temperatures according to the first order flow reactor equation 17. The apparent reaction rate constant (k) values are listed in Table 15.

Table 15: Apparent reaction rate constant, k (h^{-1}), for alkylation of toluene with methanol using the Pd/H-ZSM-5 catalysts.

Catalyst	**Reaction temperature, °C**			
	300	**350**	**400**	**450**
Unloaded H-ZSM-5	1.54×10^{-4}	2.08×10^{-4}	2.37×10^{-4}	2.49×10^{-4}
0.1%Pd/ H-ZSM-5	1.69×10^{-4}	2.41×10^{-4}	3.57×10^{-4}	4.07×10^{-4}
0.2%Pd/ H-ZSM-5	1.78×10^{-4}	2.74×10^{-4}	3.90×10^{-4}	4.99×10^{-4}
0.3%Pd/ H-ZSM-5	1.58×10^{-4}	2.29×10^{-4}	3.01×10^{-4}	3.14×10^{-4}

3.1.2.7b. Activation energy:

The activation energy (E_a) for the alkylation reaction using the current catalysts has been calculated using the traditionally accepted Arrhenius equation (18) and the plot given in Fig. 15. The Pd/H-ZSM-5 catalysts exhibit a behavior of E_a values (Table 16) significantly different from those using the Pt/H-ZSM-5 catalysts (Table.9).

Table 16: Activation parameters for the alkylation of toluene with methanol reaction using the Pd/H-ZSM-5 catalysts.

Catalyst	**Activation Energy (E_a), kJ/mol**
Unloaded H-ZSM-5	11.0
0.1%Pd/ H-ZSM-5	20.4
0.2%Pd/ H-ZSM-5	23.3
0.3%Pd/ H-ZSM-5	16.0

The data in Table 16 show that the E_a values decrease in the following order: 0.2%Pd/H-ZSM-5 > 0.1%Pd/H-ZSM-5 > 0.3%Pd/H-ZSM-5 > unloaded H-ZSM-5. The activation energy is found to increase with increasing the Pd content in the catalyst to reach a maximum of 23.3 kJ/mol using the catalyst containing 0.2%Pd, beyond which, E_a decreases rabidly to 16 kJ/mol. These E_a values are compatible with catalytic activity levels of these catalysts.

3.1.3. Alkylation of Toluene with Methanol on Hydro-fluorinated H-ZSM-5 Catalysts

3.1.3.1. Toluene conversion:

One result of the fluorination is the zeolite dealumination **[140,141]**. It has been reported that dealumination may increase the catalytic activity in the reactions catalyzed by acid sites **[142-145]**. In the zeolite catalysts, Brönsted acidic sites have been suggested as responsible for the alkylation of the benzene ring **[6-8,60,146]**. Tables 1, 17-20 and Fig. 16 show that toluene conversion, using the fluorinated H-ZSM-5 catalysts doped with 1, 2, 3, and 4%HF is higher than that using the untreated HZSM-5 catalyst at reaction temperatures of 300-500°C. This higher activity may be attributed to enhancing of the surface acidity of the H-ZSM-5 zeolite (Table 21) by incorporation of fluoride ions in relatively low concentration. Doping of the untreated H-ZSM-5 zeolite (ΔH_{des} = 105.1 Jg^{-1}) with 1.0 then with 2.0%HF increases the ΔH_{des} to 106.0 and 107.5 Jg^{-1} , respectively; however, a further increase of doping the zeolite with HF to 3.0 and 4.0%, the ΔH_{des} values decrease to 101.9 and 98.3 Jg^{-1}, respectively. Since these ammonia desorption values are related to or rather correspond to the number of acid sites, this reflects that the number of acid strong sites increase slowly to reach a maximum via doping with 2.0%HF; beyond which the number decreases. However, the strength of these acid sites increase gradually as evident through correlating the desorption peak values, such that the lowest acid strength is acquired by the untreated zeolite, whereas the highest strength is acquired by the H-ZSM-5(4%HF) catalyst. H-ZSM-5 zeolite, when doped with fluorine species, shows enhance of surface acidity because of: (i) the formation of new Brönsted acid sites; (ii) and the strengthening of some acid sites of the parent zeolite **[147,148]**. It is evident that doping 2%HF in the H-ZSM-5 zeolite gives the highest activation for toluene conversion at temperature above 350°C (Fig. 16).

Scherzer [149] assumed that the amorphous alumino-debris formed via acid treatments may decrease the effective diffusivity in the zeolitic channels. This factor seems to be the reason for the lower activities of the 3 and 4%HF containing catalysts for toluene conversion than that of the H-ZSM-5(2%HF) catalyst, at reaction temperature above 350°C (Fig. 16). Using all the catalysts under study, except for the 4% HF doped catalyst, the conversion of toluene behaves in a regime of passing to a maximum followed by a decline of conversion with a further increase of temperature. Only using the 4%HF doped catalyst, the activity of the catalyst increases continually as a function of reaction temperature. Even though, the activity (toluene conversion) exceeds those of other catalysts only during the low temperatures (300 - 350°C).

Table 21. Ammonia desorption enthalpy (ΔH_{des}) and peak temperature for untreated and hydrofluorinated H-ZSM-5 catalysts.

Catalysts	**TPD of Ammonia**	
	ΔH_{des} (Jg^{-1}) [a]	**Peak Temperature (°C) [b]**
Untreated H-ZSM-5	105.1	380
H-ZSM-5(1%HF)	106.0	382
H-ZSM-5(2%HF)	107.5	385
H-ZSM-5(3%HF)	101.9	387
H-ZSM-5(4%HF)	98.3	388

[a] proportional to acid sites number

[b] proportional to acid sites strength

3.1.3.2. Total xylenes in product:

Tables 1, 17-20 and Fig. 17 show the total xylenes production on the fluorinated H-ZSM-5 catalysts doped with 1, 2, 3 and 4%HF as a function of reaction temperature. In the lower temperature range (300-350°C), the yield of total xylenes is highest on the 4%HF doped catalyst, whereas at temperatures between 400 - 450°C, the 1%HF doped catalyst exhibits highest activity. However, beyond 450°C, the activity of this catalyst drops to be the lowest among of the HF treated catalysts at 500°C. At temperatures between 400 and 450°C, the production of xylenes is in the order: H-ZSM-5(1%HF) > H-ZSM-5(2%HF) > H-ZSM-5(3%HF). This decreasing of total xylenes can be attributed to increasing of diffusion limitation with increasing of HF concentration (see Fig. 23 and Table 25). However, the continually increasing behavior of the xylenes production on the H-ZSM-5(4%HF) catalyst can be attributed to the presence of relatively larger amount of pores falling in the mesoporous range due to more efficient leaching of Al and Si from the framework of the zeolite. The produced larger pores by 4%HF treatment facilitate diffusion of the relatively large molecules of the xylenes.

3.1.3.3. Para-xylene selectivity:

The treatment of H-ZSM-5 zeolite with HF solution via the doping technique used in the present work, has removed some aluminum species in the zeolitic channels and deposited them as amorphous extra-framework alumino-species (non-framework aluminum) in the zeolitic channels **[150,151]**. Since the production of para-xylene is the principal target of the present work, the comparison given in Tables 1, 17-20 and Fig.18 should be of prime importance. The data in Fig. 18 show that using all the catalysts under study, the para-xylene selectivity decreases with increasing the reaction temperatures from 300-500°C. This may be attributed to increasing of a secondary isomerization with increasing the reaction temperatures **[152]**. Obviously, the 3%HF doped H-ZSM-5 catalyst is the catalyst of choice by virtue of its superiority in producing para-xylene at all reaction temperatures. Using this catalyst, para-xylene comprises 40.8% at

300^{o}C then decreases continually with increasing reaction temperature to reach 34.4% at 500^{o}C. All these values exceed the thermodynamic equilibrium values which are around 23.0% at the operating temperatures in this study **[136]**. These findings prove that the H-ZSM-5(3%HF) catalyst acquires the optimum para-selectivity among the current catalysts.

The arrangement of the selectivities of the catalysts under study for para-xylene production at the whole range of temperature investigated (300-500^{o}C) is shown in Fig. 18 to be in the following order: H-ZSM-5(3%HF) > H-ZSM-5(2%HF) > H-ZSM-5(1%HF) > untreated H-ZSM-5. The enhancement of para-xylene selectivity, using the fluorinated catalysts containing 1, 2 and 3%HF can be attributed to the formation of fluoro-aluminum debris that deposited inside the pore of the H-ZSM-5 zeolite and then increases the diffusion constraints of the bulkier isomers (ortho- and meta-xylenes) **[153-155]**.

However, the H-ZSM5 (4%HF) catalyst does not behave as normally parallel to the selectivities of the other catalysts. It shows a relatively higher para-selectivity during the lower temperature range and a relatively lower selectivity during the higher temperature range. This behavior of 4%HF treated catalyst can be attributed to (1) a higher acidity which is effective in the lower temperature range, and (2) larger amorphous debris deposited in the channels which is effective in the higher temperature range. The production of para-xylene increases with the quantity of HF doped on the zeolite up to 3%HF, beyond which the para-xylene selectivity declines.

The increase of surface area and total pore volume during the 1% and 2%HF treatments (Table 22) can be attributed to dissolution of the originally present hydroxyl-alumino-debris on the surface and pores of the zeolite which was formed during the synthesis of the zeolite **[156-158]**. The treatment with 3%HF seems to have adjusted the surface properties to attain the optimum surface and pore structure that provides the optimum selectivity for para-xylene production. This finding may indicate that it is not the magnitude of surface area or pore volume of the zeolite that controls the para-selectivity but it can be said that it is the position of the debris formed during the HF treatment in the host zeolite that controls the catalytic behavior.

Table 22. Effect of HF concentration on surface area and pore volume of H-ZSM-5 zeolite.

Catalyst	BET surface area, m^2/g	Total pore volume, ml/g
Untreated H-ZSM-5	345.4	0.220
H-ZSM-5(1%HF)	370.1	0.250
H-ZSM-5(2%HF)	371.0	0.231
H-ZSM-5(3%HF)	324.3	0.203
H-ZSM-5(4%HF)	311.6	0.197

3.1.3.4. Trimethylbenzenes in product (TMBs):

Tables 1, 17-20 and Fig. 19 show that the untreated H-ZSM-5 zeolite catalyst exhibits maximum production of TMBs between 400 and 450°C. Using the 1% and 2%HF containing catalysts, TMBs are almost the same from the beginning at 300°C till at 450°C, then deviate with increasing temperature to 500°C, such that on the 1%HF catalyst, TMBs comprise 10.3% while they comprise 19.1% on the 2%HF treated catalyst. Evidently, HF concentration higher than 2% is inhibiting TMBs production. Fig. 19 shows that the H-ZSM-5(3%HF) and H-ZSM-5(4%HF) catalysts give lower TMBs. This effect can be attributed to decreasing the surface area as a function of increasing the acid concentration. Using the 1, 2, 3 and 4%HF treated zeolite catalysts, the surface areas are 370.1, 371.0, 324.3 and 311.6 m^2g^{-1}, respectively, whereas, the untreated zeolite acquires an area of 345.4 m^2g^{-1} (Table 22), These values appear in accordance with the production of TMBs.

3.1.3.5. Gas production:

The production of gases via hydrocracking normally increases as a function of reaction temperature. It is evident that these gases increase significantly with the first treatment using 1%HF and continues increasing with 2%HF treatment. Increasing the concentration of HF to 3%, results in significant drop of the hydrocracked gases at all temperatures, then gets some more decrease with a further increase of HF concentration to 4%. Correlation of the production of gases (Fig. 20) with the surface area and pore volume (Table 22) indicates their mutual dependence.

3.1.3.6. The individual xylene isomers in the xylenes mixture relative to the corresponding equilibrium values (X/Xe):

The smallest molecule dimensions in the three directions, among the three-xylene isomers is para-xylene (7.8,5.3,2.8Å). However, the other dimensions of meta- and ortho-xylenes are (7.5,6.0,2.8 Å) and (6.9,6.6,2.8 Å), respectively **[159]**. The action of HF on the H-ZSM-5 zeolite can be principally directed to leaching a part of the Al atoms and a part of Si atoms. Since some amorphous Al hydroxide phase may be left in the zeolitic channels after synthesis, HF can be effective of leaching this amorphous $Al(OH)_x$ phase faster than leaching the framework Al (and Si) and instead of being deposited outside the channel system they (or some of them) become deposited along the channels and cause their narrowing, and hence improves the shape selectivity towards forming the smallest molecular dimensions para-xylene in higher percentage as a function of increasing the HF concentration from 1 up to 3% (Fig. 21).

3.1.3.7. Kinetics of toluene alkylation with methanol using the hydrofluorinated H-ZSM-5 catalysts:

3.1.3.7a. Reaction rate constant:

From the reaction data of total xylenes in Tables 1, 17-20 and Fig. 17, the apparent reaction rate constant (k) has been calculated according to equation 17. The k values are listed in Table (23).

Table 23: Apparent reaction rate constant, k (h^{-1}), for alkylation of toluene with methanol reaction using the untreated and hydrofluorinated H-ZSM-5 catalysts.

Catalyst	**Reaction temperature, ^oC**			
	300	**350**	**400**	**450**
Untreated H-ZSM-5	$1.54x10^{-4}$	$2.08x10^{-4}$	$2.37x10^{-4}$	$2.49x10^{-4}$
H-ZSM-5(1%HF)	$1.44x10^{-4}$	$2.20x10^{-4}$	$3.90x10^{-4}$	$4.50x10^{-4}$
H-ZSM-5(2%HF)	$1.52x10^{-4}$	$2.31x10^{-4}$	$3.52x10^{-4}$	$4.24x10^{-4}$
H-ZSM-5(3%HF)	$1.58x10^{-4}$	$2.39x10^{-4}$	$3.49x10^{-4}$	$3.65x10^{-4}$
H-ZSM-5(4%HF)	$2.14x10^{-4}$	$2.57x10^{-4}$	$3.27x10^{-4}$	$4.03x10^{-4}$

3.1.3.7b. Activation energy:

The activation energy (E_a) for the alkylation reaction using the current catalysts has been calculated using the traditionally accepted Arrhenius equation and k values obtained according to equation 17.

The apparent activation energy, E_a, is calculated via applying the Arrhenius plot (Fig. 22) of lnk vs. 1/T, where k is the reaction rate constant and T is the absolute reaction temperature. The E_a values calculated accordingly are tabulated in Table 24.

Table 24: Activation energy values for the alkylation of toluene with methanol reaction using the untreated and hydrofluorinated H-ZSM-5 catalysts.

Catalyst	Activation Energy (E_a), kJ.mol^{-1}
Untreated H-ZSM-5	11.0
H-ZSM-5(1%HF)	27.1
H-ZSM-5(2%HF)	23.9
H-ZSM-5(3%HF)	19.8
H-ZSM-5(4%HF)	14.8

Indeed, the values in Table 24 are relatively low, indicating that the effect of temperature in accelerating the current reaction is of a modest concern. However, evidently, the highest E_a value is obtained using the H-ZSM-5(1%HF) catalyst, indicating that such low concentration of HF results in the highest activation with temperature during the low temperature range (300-400^{o}C). The H-ZSM-5(2%HF) catalyst shows slight lowering of E_a and such decrease with increasing HF concentration continues also using the H-ZSM-5(3%HF) catalyst. The difference between the catalytic response of these three catalysts towards HF doping is very slight but exhibiting a decreasing trend. This indicates that the increase of amorphous debris formed via leaching Al and Si in the zeolite structure is slightly effective on the physical structure of the porous system of these catalysts. On the other hand, the H-ZSM-5(3%HF) catalyst exhibits a more significant physical change of the pores and cavities of the supporting H-ZSM-5 zeolite, i.e., due to significant formation and deposition of the amorphous debris on the catalytic surface.

3.1.3.8. Diffusion effects resulting via hydrofluorination of H-ZSM-5 catalysts:

The effect of hydrofluorination on H-ZSM-5 zeolite as a catalyst has been investigated via inclusion of HF acid in increasing dosage from 1% up to 4% in zeolite. The magnitude of diffusion restriction in these catalysts is expressed in a term abbreviated as Φ_L, which calculated and tabulated in Table 25.

Table 25: Thiele modulus values (Φ_L) for the alkylation of toluene with methanol reaction using the untreated and hydrofluorinated H-ZSM-5 catalysts.

Catalyst	**Φ_L**			
	300	**350**	**400**	**450**
Untreated H-ZSM-5	6.64	7.54	7.88	7.91
H-ZSM-5(1%HF)	8.98	10.92	14.09	14.85
H-ZSM-5(2%HF)	10.92	13.12	15.9	17.08
H-ZSM-5(3%HF)	12.76	15.32	18.13	18.19
H-ZSM-5(4%HF)	16.11	17.13	19.04	20.74

To correlate quantitatively the difference in diffusion resistance in a series of catalysts, the dimensionless parameter Thiele modulus (Φ_L) can be considered the most appropriate approach. This modulus is calculated by iteration on the reaction rate constant (k_v) applying equations 22 and 23. Detailed calculation of the Thiele modulus is given by Satterfield and Sherwood **[137]**.

Fig. 23 shows that Φ_L increases consecutively with increasing the fluoride content in the H-ZSM-5 zeolite under study. The Φ_L values calculated for the untreated zeolite is also included for comparison. It is evident that 1%HF inclusion in H-ZSM-5 increases the Φ_L value from 8.98 at 300^{o}C to 14.85 at 450^{o}C. This Φ_L variation as a function of temperature is relatively high compared to the extent of Φ_L variation resulting on the untreated H-ZSM-5 catalyst. An increase of HF incorporation to 2% increases the Φ_L to 10.92 at 300^{o}C and 17.08 at 450^{o}C. Also, an increase of HF up to 3% raises Φ_L to 12.76 at 300^{o}C and 18.19 at 450^{o}C. Finally, the increase of HF to 4% increases Φ_L to 16.11 at 300^{o}C and to 20.74 at 450^{o}C.

The Φ_L increase as a function of HF incorporation can be attributed to the leaching of aluminum and silicon from the framework of the H-ZSM-5 zeolite followed by its deposition in the zeolitic channels along which diffusion takes place.

A plot of the activation energy (Fig. 24), E_a, and Φ_L values shows an inversely proportional relationship; i.e. E_a continually decreases with increasing the Φ_L (and increase of HF), which is theoretically feasible, since diffusion limitation normally decreases the activation energy of the chemical reaction.

3.1.4. Alkylation of Toluene with Methanol Using Pt-Loaded Hydrofluorinated H-ZSM-5 Catalysts

3.1.4.1. Effect of the hydrofluorination degree on 0.1%Pt/H ZSM-5 catalyst:

3.1.4.1.1. Toluene conversion:

The effect of reaction temperature on toluene conversion during its alkylation with methanol using hydrofluorinated 0.1%Pt/H-ZSM-5 catalysts doped with 1, 2, 3 and 4%HF is shown in Tables 2, 26-29 and Fig. 25. It is evident that toluene conversion increases with increasing the reaction temperature from 300°C to 500°C on all the catalysts containing 0.1% Pt and doped with 1-4%HF, whereas on the unfluorinated catalyst (0.1%Pt/H-ZSM-5), the conversion of toluene increases up to 450°C beyond which it declines at 500°C. The 0.1%Pt/H-ZSM-5(2%HF) catalyst is the most active for toluene conversion. This higher activity of the 2%HF treated catalyst may be attributed to its higher acidity caused principally by the formation of new Brönsted acid sites, and strengthening some acid sites of the parent zeolite with fluorine species in relatively low concentration as assumed by **Le Van Mao et al. [147]**.

3.1.4.1.2. Total xylenes in product:

Total xylenes production is also the highest on the 2%HF doped catalyst (Tables 2, 26-29 and Fig. 26). Lower and higher HF concentrations give lower activities for the xylenes production. The effect of the lower acidity of the unfluorinated catalyst is significant at the 400-500°C range, where the rate of xylenes formation becomes the lowest among all catalysts.

3.1.4.1.3. Para-xylene selectivity:

The para-xylene selectivities of the catalysts under study show different trends via treatments with different concentrations of HF (Tables 2, 26-29 and Fig. 27). In general, the trend of para-xylene selectivity either decreases with temperature or decreases to a minimum then increases with a further increase of temperature. The former behavior is observed on using the 2, 3 and 4%HF doped catalysts, whereas the latter behavior is observed with the untreated and the 1%HF doped catalysts. At the medium temperature range (400-450^{o}C), the unfluorinated catalyst exhibits the lowest para-xylene selectivity among all catalysts under study.

3.1.4.1.4. Trimethylbenzenes in product (TMBs):

Tables 2, 26-29 and Fig. 28 show that TMBs production is generally the highest on the unhydrofluorinated catalyst and the lowest on the 4%HF doped catalyst. Since all catalysts contain the same Pt content (0.1wt%), this difference in catalytic activity should be attributed to the HF doping, which causes Al (under mild conditions) and Si (under more severe conditions) to be leached from the zeolite structure and then the formation of fluoro-aluminum and fluoro-silicon debris in higher amounts with increased HF concentration.**[158]**. Evidently, this debris has a beneficial effect, i.e., that causes narrowing of the pores such that the formation of the larger TMBs molecules is more restricted as the HF concentration increases.

3.1.4.1.5. Gas production:

Tables 2, 26-29 and Fig. 29 show that the highest gaseous product obtained during toluene alkylation with methanol is obtained on the 2%HF doped catalyst, whereas the lowest gaseous production is obtained at the highest HF concentration (4%HF). For instance, at 300°C, the gaseous product amounts to 6.0, 6.5, 6.3 and 5.9% using the hydrofluorinated catalysts doped with 1, 2, 3 and 4%HF, respectively, and increases to 8.5, 8.7, 8.4 and 7.7% at 500°C, using the same catalysts, respectively. Two competing factors seem to affect this behavior of the gas production. First, is the acid sites number and strength, and the second is the debris formed via leaching Al and Si from the zeolite by the HF acid. Higher acidity strength enhances gas production, whereas higher quantities of the debris formed suppress gas formation via diffusion restriction enhancement.

3.1.4.1.6. The individual xylene isomers in the xylenes mixture relative to the corresponding equilibrium values (X/Xe):

Tables 26-29 and Fig. 30 show that at the lower temperature, particularly at 300°C, the X/Xe values for para-xylene increase gradually as a function of HF concentration. Para-xylene X/Xe values are always higher than unity at all reaction temperatures from 300 to 500°C using all HF concentrations (1-4%). o-Xylene X/Xe values decrease continually with temperature, whereas meta-xylene X/Xe values continually increase in the temperature ranges from 300 to 450°C, using the hydrofluorinated 0.1%Pt/H-ZSM-5 catalysts doped with 2, 3 and 4%HF concentrations. Fortunately, meta-xylene is always the lowest xylene isomer, particularly at the lower temperatures.

3.1.4.1.7. Kinetics of toluene alkylation with methanol using the hydrofluorinated 0.1%Pt/H-ZSM-5 catalysts:

3.1.4.1.7a. Reaction rate constant:

From the reaction data of total xylenes in Fig. 26 and Tables 26-29, the reaction rate constant (k) has been calculated according to the first order equation (17). These k values are listed in Table 30.

Table 30: Apparent reaction rate constant, k (h^{-1}), for alkylation of toluene with methanol reaction using the untreated and hydrofluorinated 0.1%Pt/ H-ZSM-5 catalysts.

Catalysts	Reaction temperature, °C			
	300	350	400	450
0.1%Pt/ H-ZSM-5	$1.68x10^{-4}$	$2.55x10^{-4}$	$3.22x10^{-4}$	$3.51x10^{-4}$
0.1%Pt/H-ZSM-5(1%HF)	$2.16x10^{-4}$	$2.69x10^{-4}$	$3.25x10^{-4}$	$3.80x10^{-4}$
0.1%Pt/H-ZSM-5(2%HF)	$2.20x10^{-4}$	$2.76x10^{-4}$	$3.38x10^{-4}$	$4.02x10^{-4}$
0.1%Pt/H-ZSM-5(3%HF)	$1.82x10^{-4}$	$2.49x10^{-4}$	$3.08x10^{-4}$	$3.80x10^{-4}$
0.1%Pt/H-ZSM-5(4%HF)	$1.90x10^{-4}$	$2.28x10^{-4}$	$3.03x10^{-4}$	$3.75x10^{-4}$

3.1.4.1.7b. Activation energy:

The activation energy (E_a) values are calculated using Arrhenius plot (Fig. 31) and tabulated in Table 31.

Table 31: Activation energy for the alkylation of toluene with methanol reaction using hydrofluorinated 0.1%Pt/H-ZSM-5 catalysts.

Catalyst	Activation Energy (E_a), $kJ.mol^{-1}$
0.1%Pt/ H-ZSM-5	16.8
0.1%Pt/H-ZSM-5(1%HF)	13.0
0.1%Pt/H-ZSM-5(2%HF)	13.5
0.1%Pt/H-ZSM-5(3%HF)	16.5
0.1%Pt/H-ZSM-5(4%HF)	15.6

The data in Table 31 show that the highest catalytic activities are acquired by the catalysts containing 1 and 2%HF, although these catalysts exhibit the lowest E_a values (13.0 and 13.5 kJ/mol, respectively). This regime is compatible with normal kinetic one where activity of the catalyst is inversely proportional with the energy required for activating the catalyst to perform the reaction.

3.1.4.2. Effect of the hydrofluorination degree on 0.3%Pt/H-ZSM-5 catalyst:

3.1.4.2.1. Toluene conversion:

Toluene conversion, during its alkylation with methanol using 0.3%Pt/H-ZSM-5 catalysts treated with different amounts of HF ranging between 1 and 4%, is depicted in Tables 4, 32-35 and Fig. 32. During the low temperature range 300-350^{o}C, the conversion of toluene can be arranged in the order:

0.3%Pt/H-ZSM-5(3%HF) > 0.3%Pt/H-ZSM-5(4%HF) > 0.3%Pt/H-ZSM-5(2%HF) > 0.3%Pt/H-ZSM-5(1%HF) > untreated 0.3%Pt/H-ZSM-5.

The odd HF treatment in this succession is that involving 4%HF. According to a regular order, the 4%HF treatment is expected to be in the first position. However, its shift can be attributed to a decrease in the catalytic activity due to some excessive removal of Al from the supporting zeolite, thus decreasing the number of protons which are equal to the number of framework Al, beside forming silicon and aluminum fluoro-debris which may affect the surface properties including blockage of a position of the catalytic pores which contain platinum and acid sites (Tables 36 and 37).

At higher temperatures, beyond 400^{o}C, the order of toluene conversion can be arranged in the order:

0.3%Pt/H-ZSM-5(1%HF) > 0.3%Pt/H-ZSM-5(2%HF) > untreated 0.3%Pt/H-ZSM-5 > 0.3%Pt/H-ZSM-5(3%HF) > 0.3%Pt/H-ZSM-5(4%HF).

Evidently, the activities of the catalysts, under investigation, have almost been reversed that indicate that the effect of diffusion has became controlling. The diffusion rate is relatively less enhanced than that of the chemical reaction, i.e. becomes rate controlling. Evidently, the data indicate that the diffusion resistance increases with increasing the HF concentration that affects in causing a narrowing of the catalyst pore by the formation of fluoro-aluminum and fluoro-silicon debris **[149].** The lower activity of the catalysts containing 3 and 4% HF than the untreated 0.3%Pt/H-ZSM-5 catalyst is attributed to increasing leaching of aluminum and silicon from the zeolitic framework forming fluoro-aluminum and fluoro-silicon debris, respectively. The 0.3%Pt/H-ZSM-5(1%HF) catalyst is evidently the most active at 450-500°C, since such low HF concentration supplies necessary activity without significantly increasing the diffusion resistance.

Table 36. Effect of HF concentration on surface area and pore volume of the untreated and hydrofluorinated 0.3%Pt/H-ZSM-5 catalysts.

Catalyst	BET surface area (m^2/g)	Total pore volume (ml/g)
Untreated 0.3%Pt/H-ZSM-5	327.1	0.153
0.3%Pt/H-ZSM-5(1%HF)	330.7	0.172
0.3%Pt/H-ZSM-5(2%HF)	332.5	0.198
0.3%Pt/H-ZSM-5(3%HF)	301.6	0.172
0.3%Pt/H-ZSM-5(4%HF)	293.9	0.163

Table 37. Ammonia desorption enthalpy (ΔH_{des}) and peak temperature for 0.3%Pt supported on untreated and hydrofluorinated H-ZSM-5 catalysts.

Catalyst	TPD of Ammonia	
	ΔH_{des} (J/g) [a]	Peak Temp. (°C) [b]
Untreated 0.3%Pt/H-ZSM-5	74.0	355
0.3%Pt/H-ZSM-5(1%HF)	77.8	380
0.3%Pt/H-ZSM-5(2%HF)	81.1	381
0.3%Pt/H-ZSM-5(3%HF)	79.5	383
0.3%Pt/H-ZSM-5(4%HF)	75.5	383

[a] proportional to acid sites number

[b] proportional to acid sites strength

3.1.4.2.2. Total xylenes in product:

The effect of hydrofluorination of the current catalysts on the production of total xylenes (Tables 4, 32-35 and Fig. 33) resembles that obtained during the conversion of toluene with methanol (Fig. 32), throughout the lower temperature range (300-400^{o}C), beyond which, the diffusion restriction effect and the metal inclusion play their roles. At these temperatures, the 0.3%Pt/H-ZSM-5(1%HF) catalyst is the most effective, whereas the untreated 0.3%Pt/H-ZSM-5 catalyst is the least effective. The remaining catalysts show almost equal activities.

3.1.4.2.3. Para-xylene selectivity:

Tables 4, 32-35 and Fig. 34 show that at temperatures between 300 and 400^{o}C, the selectivity for producing para-xylene during the alkylation of toluene with methanol using the fluorinated catalysts under study can be arranged in the following order:

0.3%Pt/H-ZSM-5(4%HF) > 0.3%Pt/H-ZSM-5(3%HF) > 0.3%Pt/H-ZSM-5(2%HF) > 0.3%Pt/H-ZSM-5(1%HF)

The enhancement of para-xylene selectivity by increasing the concentration of HF from 1 to 4% can be attributed to the formation of fluoro-aluminum debris which deposited inside the pore of the H-ZSM-5 zeolite and then increases the diffusional constraints of the bulkier isomers (ortho- and meta-xylenes) **[153-155]**. However, the decline of para-xylene selectivity beyond 400^{o}C on the 4%HF treated catalyst may be due to the increasing of isomerization with increasing the acid sites strength **[160]**. The acid sites located on the external surface are responsible for isomerization reactions **[161,162]**. The para-xylene selectivity is the lowest on the 0.3%Pt/H-ZSM-5(1%HF) catalyst. This can be attributed to the higher activity of the latter catalyst to produce the side products trimethylbenzenes (Fig. 35) and the hydrocracking gases (Fig. 36).

3.1.4.2.4. Trimethylbenzenes in product (TMBs):

Tables 4, 32-35 and Fig. 35 show that at a temperature of 350°C, all of the current catalysts exhibit almost the same activity for producing the side products trimethylbenzenes. The increase of reaction temperature increases the production of these larger molecules with different extents. This increase seems to increase with decreasing the treating HF concentration, which indicates that HF concentration has an obvious effect upon modifying the pore dimension of H-ZSM-5 zeolite. Obviously, the higher concentration of HF, the larger the amount of fluoro-silicon and aluminum debris that is deposited on the inner sides of the zeolitic channels and hence resulting in producing narrower pore dimensions, and hence lower percentages of TMBs are produced.

3.1.4.2.5. Gas production:

Tables 4, 32-35 and Fig. 36 show that the most active catalyst for production of gases is the 0.3%Pt/H-ZSM-5(2%HF) catalyst. However, the lowest gaseous production is obtained at the highest HF concentrations (3 and 4%HF), which may be attributed to enhancing the removal of the aluminum in the zeolitic framework and decreasing the surface area (Tables 36). To each zeolitic Al atom, one photonic hydrogen is attached, and hence the Brönsted acidity decreases. This may indicate that the hydrocracking reactions primarily depends on the diffusivity and effective pore diameter of the catalysts which have been altered by the fluoro-aluminum debris formed via 3 and 4%HF treatments, rather than the acid sites strength. These species deposited in the pores may also hide a part of the strongest acid sites in the zeolite channels, thus reducing the hydrocracking activities of the catalysts with the highest HF concentrations (3 and 4%HF).

3.1.4.2.6. The individual xylene isomers in the xylenes mixture relative to the corresponding equilibrium values (X/Xe):

Tables 32-35 and Fig. 37 show that in general, the para-xylene X/Xe values increase with increasing the concentration of HF from 1 to 4% in the 0.3%Pt/H-ZSM-5 catalyst, at most reaction temperatures. Using the 0.3%Pt/H-ZSM-5(4%HF) catalyst, the para-xylene X/Xe values are highest than on the other catalysts between 300 and 400°C. The 0.3%Pt/H-ZSM-5(4%HF) catalyst attains the highest production of para-xylene at temperatures between 300-400°C, whereas, the 0.3%Pt/H-ZSM-5(3%HF) catalyst attains the highest production of para-xylene at temperatures between 400 and 500°C. On the other hand, ortho- and meta-xylenes exhibit X/Xe values lower than unity at all HF concentrations on the 0.3%Pt/H-ZSM-5 (HF= 1-4%) catalysts except for the reaction at 300°C using the 0.3%Pt/H-ZSM-5(1%HF) catalyst.

3.1.4.2.7. Kinetics of toluene alkylation with methanol using the hydrofluorinated 0.3%Pt/H-ZSM-5 catalysts:

3.1.4.2.7a. Reaction rate constant:

From the reaction data of total xylenes in Fig. 33 and Tables 32-35, the reaction rate constant (k) has been calculated and listed in Table (38).

Table 38: Apparent reaction rate constant, k (h^{-1}), for the alkylation reaction using the current untreated and hydrofluorinated 0.3%Pt/ H-ZSM-5 catalysts.

Catalyst	**Reaction temperature, °C**			
	300	**350**	**400**	**450**
0.3%Pt/ H-ZSM-5	1.51×10^{-4}	1.87×10^{-4}	2.79×10^{-4}	3.35×10^{-4}
0.3%Pt/H-ZSM-5(1%HF)	1.45×10^{-4}	2.05×10^{-4}	2.80×10^{-4}	3.57×10^{-4}
0.3%Pt/H-ZSM-5(2%HF)	1.78×10^{-4}	2.14×10^{-4}	2.82×10^{-4}	3.44×10^{-4}
0.3%Pt/H-ZSM-5(3%HF)	2.19×10^{-4}	2.78×10^{-4}	3.23×10^{-4}	3.48×10^{-4}
0.3%Pt/H-ZSM-5(4%HF)	2.15×10^{-4}	2.57×10^{-4}	3.01×10^{-4}	3.43×10^{-4}

3.1.4.2.7b. Activation energy:

Using Arrhenius plot (Fig. 38), the activation energy (E_a) values are calculated and tabulated in Table 39, which shows that the highest catalytic activities are acquired by the catalyst containing 3%HF, although this catalyst exhibits the lowest E_a value (10.4 kJ/mol).

Table 39: Activation energy values for the alkylation reaction using the untreated and hydrofluorinated 0.3%Pt/ H-ZSM-5 catalysts.

Catalyst	**Activation Energy (E_a), kJ.mol^{-1}**
0.3%Pt/ H-ZSM-5	18.8
0.3%Pt/H-ZSM-5(1%HF)	20.2
0.3%Pt/H-ZSM-5(2%HF)	15.2
0.3%Pt/H-ZSM-5(3%HF)	10.4
0.3%Pt/H-ZSM-5(4%HF)	10.4

3.1.4.2.8. Diffusion effects resulting via hydrofluorination of 0.3%Pt/H-ZSM-5 catalysts:

Using equations 22 and 23, the diffusion restriction (Φ_L) are calculated. Fig. 39 and Table 40 show that irrespective of the Pt incorporation in this series of catalysts, it is evident that diffusion restriction, increases continually with increasing the percentage of HF doped in the 0.3%Pt/H-ZSM-5 catalysts.

Table 40: Thiele modulus values (Φ_L) for the alkylation reaction using the untreated and hydrofluorinated 0.3%Pt/H-ZSM-5 catalysts.

Catalyst	**Φ_L**			
	300	**350**	**400**	**450**
0.3%Pt/H-ZSM-5	9.69	10.53	12.62	13.44
0.3%Pt/H-ZSM-5(1%HF)	10.11	11.87	13.56	15.02
0.3%Pt/H-ZSM-5(2%HF)	12.68	13.58	15.24	16.5
0.3%Pt/H-ZSM-5(3%HF)	15.96	17.56	18.52	18.82
0.3%Pt/H-ZSM-5(4%HF)	17.61	18.78	19.93	20.86

3.1.5. Methylation of Toluene Using Pt-Pd Bimetallic Catalysts supported on untreated and hydro-fluorinated H-ZSM-5:

The introduction of second metal influences the property of first dispersed metal, due to the formation of bimetallic clusters **[163]**. In a variety of reactions, alloying of platinum with other metals results in a beneficial effect on catalytic performance **[164]**. The use of the bimetallic Pt–Pd-supported catalyst has been reported to enhance its hydrogenation activity with respect to a mono-metallic catalyst **[165]**.

3.1.5.1. Toluene conversion:

In this study, bimetallic catalysts, namely: 0.1%Pt+0.2%Pd/H-ZSM-5, 0.2%Pt+0.1%Pd/H-ZSM-5, 0.1%Pt+0.2%Pd/H-ZSM-5(3%HF) and 0.2%Pt+0.1%Pd/H-ZSM-5(3%HF) are used to investigate the alkylation of toluene with methanol reaction, in the temperatures range 300-500^{o}C (Tables 41-44 and Fig. 40). The evident variation between these catalysts is attributed to doping with 3%HF. The HF doped catalysts show a continuous increase of toluene conversion as a function of temperature, whereas the unhydrofluorinated catalysts show an increase of conversion with increasing the temperature from 300 to 450^{o}C, beyond which a further increase of temperature decreases the conversion. This behavior can be attributed to the physical effect introduced by some debris of fluoro-aluminum and fluoro-silicon derivatives that produced diffusion restriction effects **[149]**, since the decrease of activity at the higher temperatures is known to be due to lower acceleration of the diffusion rate relative to the chemical reaction, such that diffusion becomes rate-controlling. Another observation wherein the two metal combinations participate is that 0.1%Pt+0.2%Pd combination is somewhat more active than the 0.2%Pt+0.1%Pd combination, whether these catalysts are treated with 3%HF or not. In other words, the lower Pt combined with higher Pd gives higher toluene conversion.

3.1.5.2. Total xylenes in product:

Total xylenes production during toluene alkylation with methanol (Tables 41-44 and Fig. 41) may resemble to great extent the conversion of toluene shown in Fig. 40, at least during the temperature range 300-400^{o}C. Beyond 400^{o}C, the superiority of higher Pd than Pt gives reversed activities.

3.1.5.3. Para-xylene selectivity:

The para-xylene selectivities (Tables 41-44 and Fig. 42) on the bimetallic Pt-Pd/H-ZSM-5 catalysts have widely different trend and order. Using the two unhydrofluorinated catalysts, the para-xylene selectivity remains almost unchanged as a function of temperature between 300 and 450^{o}C, then increases beyond 450^{o}C to attain the highest value at 500^{o}C; 37.5% using the 0.1%Pt+0.2%Pd catalyst and 40.4% using the 0.2%Pt+0.1%Pd catalyst. The 0.2%Pt+0.1%Pd/H-ZSM-5 catalyst always shows higher para-xylene selectivities over the 0.1%Pt+0.2%Pd/H-ZSM-5 catalyst at all reaction temperatures. It may be concluded that in absence of HF doping, a higher Pt than Pd favors para-xylene selectivity.

On the other hand, in the same Fig. 42, the para-xylene selectivities of the HF-treated Pt-Pd/H-ZSM-5 catalysts acquire different behaviors both of trend and order. These two HF-treated catalysts show significantly lower para-xylene selectivities compared to the untreated catalysts versions and that the selectivity decreases with temperature but with a higher decreasing rates at 300-400^{o}C. However, the order of para-xylene selectivity is found to be reversed via HF doping; at all reaction temperatures, i.e., unhydrofluorinated 0.2%Pt+0.1%Pd/H-ZSM-5 catalyst gives higher para-selectivity than the 0.1%Pt+0.2%Pd/H-ZSM-5 catalyst, whereas the HF treated 0.1%Pt+0.2%Pd/H-ZSM-5 catalyst gives much higher para-selectivity than the HF treated 0.2%Pt+0.1%Pd/H-ZSM-5 catalyst. It may be agreed that a higher platinum content than Pd in presence of HF may not be in favor of para-xylene. In fact, with respect to why this metals combination or that gives higher or lower para-xylene selectivity than another can not be precisely attributed.

3.1.5.4. Trimethylbenzenes in product (TMBs):

The behavior of producing trimethylbenzenes (TMBs) as a function of reaction temperature during the alkylation of toluene with methanol (Tables 41-44 and Fig. 43) reveals some similarity of the TMBs production with production of total xylenes (Fig. 41). This can be attributed to the fact that production of both TMBs and total xylenes are merely via alkylation reaction.

3.1.5.5. Gas production:

The cracked gases product on all catalysts increases almost linearly as a function of reaction temperature (Tables 41-44 and Fig. 44). It can be concluded that the catalysts containing higher platinum than palladium acquire higher cracking activities than those containing higher palladium than platinum. The catalysts containing 0.2%Pt+0.1%Pd are more active in producing gases than those containing 0.1%Pt+0.2%Pd.

On the other hand, Fig.44 also shows that the catalysts containing HF are more active for gas production than the untreated versions. Evidently, the 0.2%Pt+0.1%Pd/H-ZSM-5(3%HF) catalyst is more active than the 0.2%Pt+0.1%Pd/H-ZSM-5 catalyst, and the 0.1%Pt+0.2%Pd/H-ZSM-5(3%HF) catalyst is more active than the 0.1%Pt+0.2%Pd/H-ZSM-5 catalyst. The data obtained in this work is compatible with previously published data **[166],** and the higher cracking activity of the HF treated catalysts is attributed to their higher acidity.

3.1.5.6. The individual xylene isomers in the xylenes mixture relative to the corresponding equilibrium values (X/Xe):

using all catalysts under investigation, it is evident that the para-xylene occupies the highest position among the three xylene isomers relative to its thermodynamic equilibrium values at the different reaction temperatures from 300-500°C (Tables 41-44 and Fig. 45). Using the 0.1%Pt+0.2%Pd and the 0.2%Pt+0.1%Pd containing catalysts, without HF treatment, para-xylene in product relative to its thermodynamic equilibrium (X/Xe) values range between 1.44-1.62 and 1.47-1.74, respectively. Whereas for meta-xylene, the produced (X/Xe) values range between 0.60-0.82 using the 0.1%Pt+0.2%Pd or the 0.2%Pt+0.1%Pd containing catalyst. The economic (industrial value) of meta-xylene is the lowest, whereas that of para-xylene is the highest due to its known requirement as starting material for the synthesis of polyester fibers. Roughly speaking, using the above mention two catalysts, para-xylene production relative to its equilibrium values amounts to almost double these relative values of meta-xylene and ortho-xylene.

On the other hand, using the HF treated versions of the above mentioned two catalysts, para-xylene production relative to the thermodynamic equilibrium values, is still higher than the corresponding values of meta- and ortho-xylenes, though para-xylene values on the HF treated catalysts are significantly lower than those produced on the untreated catalysts; i.e., 1.40-1.11 and 1.34-1.02, respectively. On these catalysts, the meta-xylene is 0.78-1.00 and 0.67-1.00, respectively, and the ortho-xylene is 0.89-1.09 and 0.98-1.42, respectively.

3.1.5.7. Kinetics of toluene alkylation with methanol using the Pt-Pd bimetallic catalysts:

3.1.5.7a. Reaction rate constant:

From the reaction data of total xylene in Fig. 41 and Tables 41-44, the apparent reaction rate constant (k) has been calculated at different reaction temperatures according to the first order flow reactor equation (17). The k values are listed in Table 45.

Table 45: Apparent reaction rate constant, k (h^{-1}), for the alkylation reaction using the current bimetallic catalysts.

Catalyst	**Reaction temperature, ^oC**			
	300	**350**	**400**	**450**
0.1%Pt+0.2%Pd/H-ZSM-5	**$1.68x10^{-4}$**	**$2.43x10^{-4}$**	**$3.42x10^{-4}$**	**$3.90x10^{-4}$**
0.2%Pt+0.1%Pd/H-ZSM-5	**$1.42x10^{-4}$**	**$2.18x10^{-4}$**	**$3.22x10^{-4}$**	**$4.00x10^{-4}$**
0.1%Pt+0.2%Pd/H-ZSM-5(3%HF)	**$2.14x10^{-4}$**	**$2.58x10^{-4}$**	**$3.02x10^{-4}$**	**$3.35x10^{-4}$**
0.2%Pt+0.1%Pd/H-ZSM-5(3%HF)	**$1.90x10^{-4}$**	**$2.40x10^{-4}$**	**$2.82x10^{-4}$**	**$3.32x10^{-4}$**

3.1.5.7b. Activation energy:

The activation energy (E_a) for the alkylation reaction using the current catalysts has been calculated using Arrhenius plot, which is given in Fig. 46. The E_a values calculated accordingly are tabulated in Table 46.

Table 46: Activation parameters for the alkylation reaction using the current bimetallic catalysts.

Catalyst	**Activation Energy (E_a), $kJ.mol^{-1}$**
0.1%Pt+0.2%Pd/H-ZSM-5	19.5
0.2%Pt+0.1%Pd/H-ZSM-5	23.8
0.1%Pt+0.2%Pd/H-ZSM-5(3%HF)	10.3
0.2%Pt+0.1%Pd/H-ZSM-5(3%HF)	12.7

The data in Table 46 show that 0.2%Pt+0.1%Pd catalyst gives higher activation energy for toluene alkylation reaction than catalyst containing 0.1%Pd+0.2%Pt, whether these catalysts are hydrofluorinated or not. Evidently, the addition of 3%HF to these catalysts under study has decreased significantly the E_a values.

3.1.6. Effect of Methanol/Toluene Molar Ratio:

3.1.6.1. Toluene conversion:

Tables 47-49 and Fig. 47 show that the conversion of toluene increases with increasing the methanol/toluene molar ratio (M/T) from 1.0 up to 2.5 at 400°C reaction temperature and 2.6h^{-1} weight hourly space velocity (WHSV) using untreated H-ZSM-5, H-ZSM-5(3%HF) and 0.3%Pt/H-ZSM-5(3%HF) catalysts. This behavior is compatible with a previous work, in which, the toluene conversion increase with increasing the concentration of methanol in the feed **[167]**. This behavior can be interpreted by supposing that the first step in toluene-methanol alkylation is forming methoxy groups **[53]**, which results from chemisorption of methanol on Brönsted acid sites of the zeolite **[168-170]**. The activities of the catalysts under study are in the order: H-ZSM-5(3%HF) > untreated H-ZSM-5 > 0.3%Pt/H-ZSM-5(3%HF), at methanol/toluene molar ratios of 1.5-2.0.

3.1.6.2. Total xylenes in product:

Both catalysts containing HF, i.e., H-ZSM-5(HF) and 0.3%Pt/H-ZSM-5(3%HF) are found more active for producing total xylenes than the untreated H-ZSM-5 catalyst (Tables 47-49 and Fig. 48). However, Pt incorporation appears inhibiting at methanol/toluene molar ratio of 1.5-2.0; however, at a molar ratio of 1.0 the Pt containing catalyst is the most active.

3.1.6.3. Para-xylene selectivity:

Tables 47-49 and Fig. 49 show that the para-xylene selectivity is significantly affected by doping the zeolite with HF. At a molar ratio of methanol/toluene of 1.0, para-xylene selectivity increases from 24.3 to 30.5% via doping H-ZSM-5 with 3%HF and from 27.9 to 37.8% at a molar ratio of 2.5. During the molar ratio range 1.0-2.0 of methanol to toluene, Pt incorporation in presence of HF increases the para-xylene selectivity from 24.3 to 31.8% at a molar ratio of 1.0 and from 27.2 to 39.2% at a molar ratio of 2.0.

3.1.6.4. Trimethylbenzenes in product (TMBs):

Tables 47-49 and Fig. 50 show that the decrease of TMBs is compatible with the increase of dopants, such that the order of formation of these products (TMBs) can be arranged in the following order: untreated H-ZSM-5 > H-ZSM-5(3%HF) > 0.3%Pt/H-ZSM-5(3%HF). Using all the catalysts under study, TMBs increase with increasing the methanol/toluene molar ratio from 1.0 to 2.5.

3.1.6.5. The individual xylene isomers in the xylenes mixture relative to the corresponding equilibrium values (X/Xe):

An important variation occurs via treating the H-ZSM-5 zeolite with 3%HF and with HF before incorporation of 0.3%Pt (Tables 47-49 and Fig. 51). Using the untreated H-ZSM-5 zeolite, both ortho-xylene and para-xylene acquire X/Xe values higher than unity at methanol/toluene molar ratios of 1.0-2.5. Even though, ortho-xylene is higher than para-xylene. This indicates that the isomerization activity of the H-ZSM-5 zeolite is in favor of ortho-position than the para-position. However, the meta-xylene isomer is lower than unity at all molar ratios on this catalyst. This is logic, since the methyl group in toluene is ortho- / para-directing.

Treatment of H-ZSM-5 with 3%HF makes the para-isomer X/Xe value jumps, amounting to 1.29-1.60 at molar ratios of 1.0-2.5, respectively, whereas ortho-xylene drops to values below unity at methanol/toluene molar ratios of 1.0-2.0. Also, meta-xylene acquires the lowest X/Xe value which is an important accomplishment, since meta-xylene is the cheapest xylene isomer. Using the 0.3%Pt/H-ZSM-5(3%HF) catalyst, the highest value of X/Xe for para-xylene is 1.66 at a methanol/toluene molar ratio of 2.0.

3.2. DISPROPORTIONATION OF TOLUENE:

3.2.1. Disproportionation of Toluene Using Hydrofluorinated H-ZSM-5 Catalysts:

3.2.1.1. Toluene conversion:

The effect of reaction temperature on toluene conversion during the toluene disproportionation reaction, using untreated and hydrofluorinated H-ZSM-5 catalysts doped with 2, 3 and 4%HF, is illustrated in Tables 50-53 and Fig. 52. In a systematic regime, it is evident that the increase of HF concentration in H-ZSM-5 zeolite decreases the activity (toluene conversion) of the catalysts under study according to the following order:

untreated H-ZSM-5 > H-ZSM-5 (2%HF) > H-ZSM-5 (3%HF) > H-ZSM-5 (4%HF)

Although the acid sites strength increases with increasing the HF concentration from 2 up to 4% (Table 21), the toluene Disproportionation activity decreases, which is evidently attributed to a physical rather than to a chemical effect. The leaching of aluminum and silicon atoms in the skeletal structure of the zeolite framework followed by the deposition of the fluoro-aluminum and fluoro-silicon phases formed in the form of amorphous debris in the zeolitic channels should be increased with increasing the HF concentration used. Hence, the diffusion restriction of reactants and products molecules, in particular the intermediate bimolecular phase **[171]**, will become more significant with increasing the concentration of the HF used.

The behavior of toluene conversion at 450-500^{o}C using the 4%HF treated catalyst differs markedly than the cases using the untreated H-ZSM-5, 2% and 3%HF treated catalysts which is supportive to the belief that diffusion restriction plays a significant role in the current reaction. Between 450 and 500°C, where the rate of diffusion should be the lowest, toluene conversion on the 4%HF treated catalyst does not show a significant increase as occurs with the other catalyst.

3.2.1.2. Total xylenes in product:

A close similarity of the general behavior of the catalysts investigated in Figures 52 and 53 is evident. The succession of catalysts is the same; the total xylenes decrease with the increase of the treating HF concentration, and the significant increase of catalytic activity with increasing temperature from 450 to 500°C, using the 4%HF treated catalyst, does not take place (Fig. 53).

3.2.1.3. Para-xylene selectivity:

Tables 50-53 and Fig. 54 show that para-xylene selectivity is almost 25% at all used reaction temperatures, using the untreated H-ZSM-5 catalyst. This selectivity is the lowest, since all HF treated catalysts exhibit much higher selectivities. Using the 2% and 3% HF treated zeolite catalysts, the difference in selectivities is not large but still the 3%HF treated catalyst is more selective than the 2%HF treated catalyst. However, the 4%HF treated catalyst is much more selective than the 3%HF treated catalyst. Using the 4%HF treated catalyst, as high as 78.6% of the xylene is the para-isomer at a temperature of 300°C. The equilibrium para-xylene at this temperature is only 23%. The reason for enhancing para-xylene selectivity is undoubtedly the deposition of hydrofluorinated Al and Si debris in the channels of the H-ZSM-5 zeolite, whereby these channels become narrow and encounter diffusion restriction **[70,71]** which serves as a sieve allowing the formation of highest quantities of the para-xylene relative to the other xylenes. Then, the resultant para-xylene formed diffuses out of the pores at relatively fast rate. In addition, ortho-and meta-isomers move within the pores relatively slow and further convert to the para-isomer before escaping from the channel system.

Young, et al. [12] has suggested that differences of diffusivity, however, may not be the only reason for the high selectivity observed in toluene disproportionation. In addition to diffusional effects, restrictions of the xylene-forming transition state may also contribute to para-selectivity here.

3.2.1.4. The individual xylene isomers in the xylenes mixture relative to the corresponding equilibrium values (X/Xe):

Using untreated H-ZSM-5 catalyst, disproportionation of toluene gives X/Xe values of the three xylenes that does not markedly differ, i.e., all are around unity. However, the effect of HF concentration in treating these catalysts is evident (Tables 50-53 and Fig. 55). The para-xylene X/Xe values are greatly increasing, particularly at lower reaction temperatures, where on the H-ZSM-5(4%HF) catalyst, the X/Xe value at 300^{o}C amounts to as high as 3.29. Correspondingly, the X/Xe values for the production of meta- and ortho-xylenes significantly decrease below unity with increasing the HF concentration used to treat the catalyst.

3.2.2. Disproportionation of Toluene Using Unloaded and Pt-Loaded H-ZSM-5 Catalysts:

The disproportionation of toluene is acid catalyzed reaction **[152]**.The addition of metal to the acidic supported catalyst plays an important role in the suppression of the formation of the condensation products as coke precursors. It is also known that when metals with hydrogenation properties are deposited on the catalyst surface, a considerable increase in the catalytic activity is observed, for reaction such as disproportionation of toluene **[172,173]**.

3.2.2.1. Toluene conversion:

Tables 54, 55 and Fig 56 show that the toluene conversion activity via increasing the Pt content from 0.1 to 0.3wt% in H-ZSM-5 zeolite is negligible, but markedly differs than the activity change of the unloaded H-ZSM-5 zeolite for the disproportionation of toluene to xylenes. On the Pt containing catalysts, the conversion of toluene rises from ~ 5%up to ~ 40% via increasing the reaction temperature from 300 to 500°C, whereas using the unloaded H-ZSM-5 catalyst, the conversion of toluene starts with higher activity 21.4% at 300°C up to 37.8% at 500°C.

3.2.2.2. Total xylenes in product:

Tables 54, 55 and Fig. 57 show that the activities of the Pt-/H-ZSM-5 catalysts for xylenes production exceed that of the unloaded H-ZSM-5 catalyst, at higher temperatures (400-500°C); however, at lower temperatures, the reverse occurs. This superiority of the Pt/H-ZSM-5 catalysts is attributed to the stabilization of the carbocation ion necessary for the disproportionation (methyl group transfer) reaction. Whereas, the lower activities, in the temperature range 300-400°C, is due to decreasing of the acid sites number and strength with increasing the Pt content (Table 6).

3.2.2.3. Para-xylene selectivity:

Although the difference in total xylenes production is insignificant on the 0.1 and 0.3wt%Pt/H-ZSM-5 catalysts (Fig. 57), it is evident in Fig. 58 that the para-xylene selectivity on these two catalysts is rather significant. The lower Pt containing catalyst gives higher selectivity at the lower temperature than the 0.3%Pt containing catalyst which can be attributed to the more suitable pore loading with 0.1%Pt since the intermediate formed during this reaction is a voluminous molecule composed of two toluene molecules in contact inside the Pt containing channels. However, on the other hand, the pores of the catalyst containing 0.3%Pt are mostly incapable of including such two-contacted intermediate because Pt causes a relatively higher crowd. Therefore, during the lower temperatures region (300-400^{o}C), the reaction may preferably take place on the outer surface, where the shape selectivity for para-xylene production is relatively lower. Nevertheless, during the higher temperature region (450-500^{o}C), the effect of Pt in forming and stabilizing the carbocation ion is evident, since this action requires higher Pt sites to increase the d-bonding character. Both arguments at lower and higher temperature regions on the Pt containing catalysts can be supported by the behavior of the unloaded H-ZSM-5 catalyst, which possesses lower activities during the whole range of reaction temperatures examined.

3.2.3. Disproportionation of Toluene Using Hydrofluorinated Pt-Loaded H-ZSM-5 Catalysts:

3.2.3.1. Toluene conversion:

A correlation of the curves in Figs. 56 and 59 shows the effect of doping 3%HF in the catalysts containing 0.1 and 0.3%Pt supported on H-ZSM-5 zeolite. Evidently, this trial of HF doping gives negative results. Both catalysts show a deteriorative effect during the temperature range of 350-500^{o}C. A simple correlation can be accomplished by comparing the difference between toluene conversion on the unloaded H-ZSM-5 catalyst and those containing 0.1 and 0.3%Pt (Fig. 56), then comparing the difference between the untreated H-ZSM-5 activity and those containing 0.1 and 0.3%Pt plus 3%HF on both catalysts (Fig. 59).

3.2.3.2. Total xylenes in product:

Again, the same results obtained through comparing the toluene conversions before and after addition of 3%HF (Figs. 56 and 59) correlated with Figs. 57 and 60 for total xylenes production show that HF is deteriorative.

3.2.3.3. Para-xylene selectivity:

Tables 56, 57 and Fig. 61 show that the lower Pt content (0.1wt%) in the catalysts gives higher para-xylene selectivity than the higher Pt content (0.3wt%) due to pore blockage by Pt crystallites in the later catalyst. However, the unloaded untreated H-ZSM-5 zeolite, although the most acidic, gives the lowest para-xylene selectivity because of its wider channels.

3.2.4. Disproportionation of Toluene Using Hydrochlorinated H-ZSM-5 Catalyst:

3.2.4.1. Toluene conversion:

The effect of H-ZSM-5 zeolite treated with 3%HCl on toluene conversion during toluene disproportionation reaction is illustrated in Table 59 and Fig. 62. It is clear that, the activity of the H-ZSM-5 (3%HCl) catalyst exceeds that of the untreated H-ZSM-5 catalyst at all reaction temperatures (300-500°C). This higher activity of the hydrochlorinated catalyst is attributed to the higher acid sites number and strength of the hydrochlorinated catalyst than the untreated H-ZSM-5 catalyst (Table 58). **Vinek et al. [152]** has concluded that the catalytic activity of H-ZSM-5 catalyst for disproportionation of toluene reaction increases with increasing the number of strong Brönsted acid sites.

Table 58. Ammonia desorption enthalpy (ΔH) and peak temperature for untreated and hydrofluorinated H-ZSM-5 catalysts.

Catalyst	TPD of Ammonia	
	ΔH_d (Jg^{-1}) [a]	**Peak Temperature (°C) [b]**
Untreated H-ZSM-5	105.1	380
H-ZSM-5 (3%HCl)	108.5	383

[a] proportional to acid sites number
[b] proportional to acid sites strength

3.2.4.2. Total xylenes in product:

Tables 50, 59 and Fig. 63 illustrate the effect of increasing the catalyst acid sites number and to some extent increasing the acid site strength, thereby increasing the catalytic activity for producing total xylenes during the disproportionation of toluene reaction.

3.2.4.3. Para-xylene selectivity:

Treating the H-ZSM-5 zeolite with 3%HCl increases the para-xylene selectivity (Fig. 64). Para-xylene selectivity slightly increases with increasing the reaction temperature to reach 26.6% as a maximum value at 400^{o}C. Para-xylene as a product of disproportionation on the 3%HCl treated zeolite is enhanced by enhancing the acidity. Moreover, the para-selectivity is related to decreasing the pore dimension, which can occur by deposition of amorphous debris obtained as a result of leaching aluminum from the zeolitic structure **[174]**.

3.2.5. Disproportionation of Toluene Using Hydrofluorinated H-Mordenite Catalysts:

3.2.5.1. Toluene conversion:

Fig. 65 shows that 2%HF treatment of H-mordenite (H-MOR) zeolite increases toluene conversion during its disproportionation due to increasing the acid sites strength **[141]** associated with a reasonable deposition of debris in the mordenite zeolitic channels. However, the 4%HF treatment decreases the toluene conversion due to excessive leaching of fluoro-aluminum and fluoro-silicon debris followed by the deposition of excessive debris in the zeolitic channels **[158].**

3.2.5.2. Total xylenes in product:

The activities of the untreated and hydrofluorinated H-MOR catalysts for total xylenes production (Fig. 66) resemble to large extent the activities of these catalysts for toluene conversion (Fig. 65). Total xylenes production is the highest on the H-MOR(2%HF) catalyst, but the lowest on the H-MOR(4%HF) catalyst.

3.2.5.3. Para-xylene selectivity:

The general behavior of response of para-xylene selectivity, using the HF treated H-MOR catalysts (Tables 60-62 and Fig. 67), resembles to a large extent the behavior of a similar treatment of H-ZSM-5 catalysts (Fig. 54). The principle difference between the two series is the much higher para-xylene selectivities evidently obtained using the respective H-ZSM-5 catalysts. Fig. 67 shows that the maximum para-xylene selectivity amounts to 30.9%, using the H-MOR(4%HF) catalyst, at 300^{o}C.

3.2.5.4. The individual xylene isomers in the xylenes mixture relative to the corresponding equilibrium values (X/Xe):

Tables 60-62 and Fig. 68 show that using the untreated H-MOR catalyst, the para-xylene X/Xe values are intermingling since the ortho-xylene curve increases with temperature to a maximum at 400°C, beyond which it decreases with a further increase of temperature. However, in general, the distribution of these isomers can be arranged at higher temperatures as follow, para-xylene > meta-xylene > ortho-xylene.

Treatment of the mordenite with 2%HF improves the selectivity of production of para-xylene relative to the other xylenes, where X/Xe values for ortho- and meta-xylenes are lower than unity, whereas para-xylene X/Xe values are above unity. A further increase of HF concentration in the catalyst to 4% shows a more significant improvement of the para-xylene X/Xe values, particularly at the lower temperatures.

3.3. COKE DEPOSITION

The amount of deposited coke on the surface of the catalysts under study is determined using thermal gravitational analysis technique. The data are given in Tables 63 and 64, which show that the coke deposition on the catalysts containing Pt or Pd metal decreases with increasing the noble metal content which is attributed to the hydrogenating activities of these metals. Moreover, Pt is more efficient than Pd for reducing the coke formation activity of the zeolite catalyst. However, the effectiveness of the Pd containing catalyst change more positively via increasing the Pd content from 0.2 to 0.3%, whereby the coke formed on the 0.3%Pd/H-ZSM-5 catalyst becomes very close to that formed with 0.3%Pt/H-ZSM-5 catalyst.

The amount of deposited coke increases from 7.53% to 7.79% with increasing the HF concentration doping in the H-ZSM-5 zeolite from 1 to 3%. However, a further increase of HF to 4% lowers deposited coke to 6.60%. This is attributed to significant closure of pores and a large decrease of surface area of the zeolite.