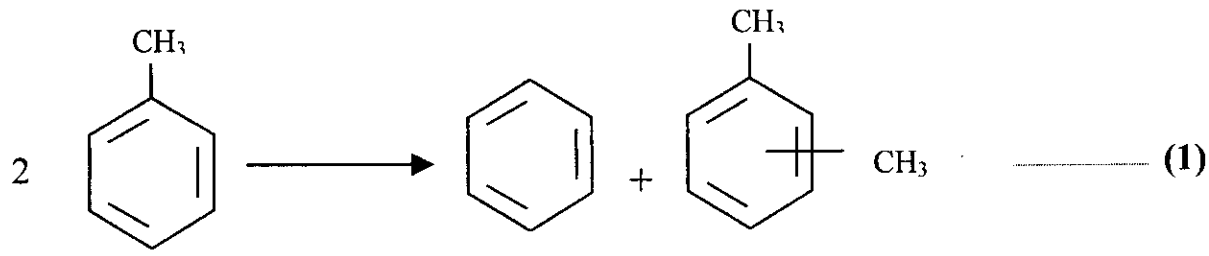
CHAPTER THREE

3. RESULTS AND DISCUSION

3.1. TOLUENE DISPROPORTIONATION REACTION OVER H-ZSM-5 CATALYST:

The present work has been carried out using a fixed – bed flow reactor system in a flowing current of hydrogen at a rate of 25-cm^3 min^{-1}. The catalyst was principally a Chinese ZSM-5 zeolite powder in order to approach the intrinsic activity of the catalyst, i.e., to almost exclude the difference between the apparent and true activities.

The reaction under investigation involves the disproportionation of toluene where one molecule transfers its methyl group to another toluene molecule, producing a benzene molecule and a xylene molecule as follows (reaction 1)

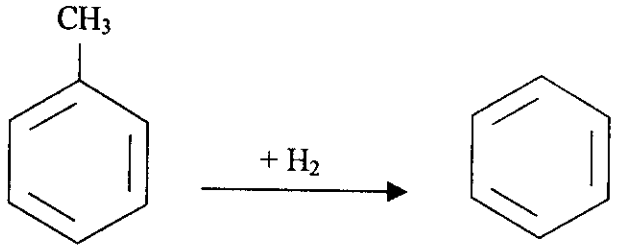


(1)

The xylene product is indeed a mixture of the three xylene isomers, namely o–, m– and p-xylene. The fourth isomer of the C_8 aromatic fraction (ethylbenzene) is not frequently formed using the zeolite catalyst [50]. Hence, ethylbenzene is

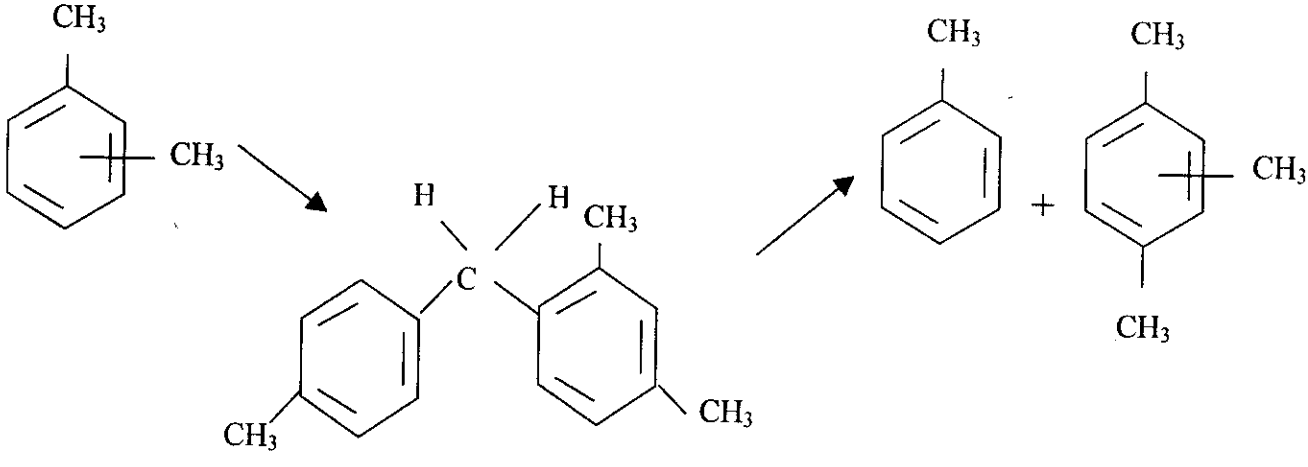
present in the products of the disproportionation reaction under investigation in very low percentages at higher temperatures (or even absent). (Table 3).

A side reaction that can also take place beside the disproportionation of toluene is the hydrocracking of toluene to benzene and methane (reaction 2).



..... (2)

Another side reaction (reaction 3) which may also occur on the external surface of the crystals of H-ZSM-5 zeolite forms trimethylbenzenes. This reaction takes place at a very low extent (Table 3) due to the molecular volume constraint of the reaction transition state. Trimethylbenzenes are to be formed via the voluminous xylene-xylene phase transition state which forms as follows [50]:



..... (3)

Fig.11 shows that toluene conversion over H-ZSM-5 catalyst ranges between 2.28% at 300°C and 34.15 mol% at 500°C at a WHSV of 2.0 g $g^{-1}h^{-1}$. However, using higher severities, namely; higher temperatures (500 – 600°C) and a lower space velocity (WHSV) of 1.0 g $g^{-1}h^{-1}$, toluene conversion is greatly accelerated (41.06 – 61.6 mol%, respectively).

Table 3 shows that the hydrocracking (hydrodealkylation) reaction does not take place during a reaction temperature range of 300–400°C, but starts at 450°C then increases with a further increase of reaction temperature (Fig.12), since this reaction is endothermic. Fig. 13 shows to what extent C_8 aromatics decrease while benzene increases in product. This figure shows that the molar percentage of benzene and C_8 aromatics are equal between 300 and 400°C, but deviate slowly beyond 400°C at a WHSV of 2.0 g $g^{-1}h^{-1}$. However, at a WHSV of 1.0 g $g^{-1}h^{-1}$, the C_8 aromatics decrease with increasing temperature from 15.21 mol% at 500°C to 8.46 mol% at 600°C, principally due to a corresponding increase of benzene production via the dealkylation of toluene and the reverse dealkylation of the formed xylenes. At 500°C, benzene amounts to 25.6 mol% and rises significantly to reach 53.14 mol% at 600°C.

The distribution of the individual xylenes in their mixture in products is frequently described as the xylenes selectivity. Using the H-ZSM-5 catalyst at a temperature of 300°C and a space velocity of 2.0 g $g^{-1}h^{-1}$, the conversion is low (2.28 mol%). However, p-xylene in the xylenes mixture in product (selectivity) is 25.8% compared to a thermodynamic equilibrium value of 23.9%. As temperature increases, the conversion rises up to 34.15 mol % at 500°C (Fig.11), whereas the p-xylene selectivity decreases to 22.6%, due to the increase of o- selectivity.

This latter value does not significantly differ from the thermodynamic value, since the p-xylene thermodynamic values (Table 2) range between 23.9% and 23.2% at temperature between 300 and 500°C, respectively. The p-xylene experimentally obtained (Fig.14) values in total xylenes in product range between 25.8 and 22.6%, respectively.

Table.2. Thermodynamic equilibrium values of para-, meta-, and ortho-xylenes in the gas phase [51] at temperatures of 300 – 600°C:

Temperature,°C	300	350	400	450	500	550	600
para- xylene	23.88	23.73	23.55	23.37	23.19	23.0	22.9
meta-xylene	53.65	52.98	52.42	51.94	51.56	51.4	51.1
ortho-xylene	22.47	23.29	24.03	24.69	25.25	26.0	26.5

Using the as-synthesized zeolite (Table 3), m-xylene selectivity ranges between 53.45% at 300°C and 51.34% at 500°C, which are very close to their thermodynamic equilibrium values. o-Xylene selectivity varying from 20.76% at 300°C to 26.06% at 500°C which do not vary significantly from the thermodynamic equilibrium values at corresponding temperatures (Fig.14). At higher reaction severities (Fig.11) applying a higher temperature range 500- 600°C and a space velocity (WHSV) of 1.0 $g\,g^{-1}h^{-1}$, the conversion greatly increases (41.0 – 61.6 %, respectively), whereas the p-xylene selectivity (Fig.14) significantly decreases (22.31% - 21.51%, respectively).

Fig.14 also shows that the m- xylene selectivity (50.81%-49.9%, respectively) does not vary significantly from the thermodynamics equilibrium values at corresponding temperatures, (Table 2). Nevertheless, the o–xylene selectivities at the severe conditions amount to (26.88%–28.59%, respectively).

The H-ZSM-5 zeolite catalyst examined in this study has been synthesized to acquire a mean pore diameter of 5.5A°. This catalyst produces a very low percentage of TMBs. At temperatures between 300 and 450°C, these voluminous compounds are absent. At the higher reaction severities, TMBs are also of very low concern (Table 3). Hence, these compounds can not be assumed to be of decisive impact on total xylene production or, in particular, on the p-xylene selectivity. However, the enhanced hydrocracking activity of the catalyst as a function of increasing reaction temperature appears to be of a significant impact on decreasing the p-xylene selectivity. This indicates that this p-isomer is the most susceptible to hydrodealkylation. At 600°C and space velocity of 1.0 g $g^{-1}h^{-1}$ benzene resulting via hydrocracking reactions comprises as high as 44.68 mol% (Fig.12).

TABLE 3. TOLUENE DISPROPORTIONATION USING H-ZSM-5 CATALYST - CATALYST (1)

SPACE VELOCITY	2					1		
TEMPERATURE, C° / ITEMS	300	350	400	450	500	500	550	600
CONVERSION, MOL%	2.28	6.80	8.18	19.99	34.15	41.06	53.40	61.60
DISTRIBUTION OF LIQIUD PRODUCTS, WT% :								
BENZENE	0.96	2.87	3.47	9.15	16.69	22.04	36.19	48.33
TOLUENE	97.72	93.22	91.81	80.20	66.31	59.83	48.68	41.19
ETHYL BENZENE	0.00	0.00	0.00	0.19	0.32	0.38	0.27	0.16
p-XYLENE	0.34	0.97	1.12	2.42	3.69	3.89	3.24	2.22
m-XYLENE	0.71	2.07	2.47	5.42	8.38	8.85	7.42	5.15
o-XYLENE	0.27	0.87	1.14	2.62	4.26	4.68	4.10	2.95
TOTAL XYLENES	1.32	3.91	4.72	10.46	16.33	17.42	14.76	10.32
TRIMETHYLBENZENES	0.00	0.00	0.00	0.00	0.35	0.33	0.10	0.00
DISTRIBUTION OF XYLENES % :								
p-XYLENE	25.79	24.72	23.68	23.09	22.60	22.31	21.95	21.51
m-XYLENE	53.45	52.96	52.23	51.86	51.34	50.81	50.27	49.90
o-XYLENE	20.76	22.32	24.09	25.05	26.06	26.88	27.78	28.59
DISTRIBUTION OF LIQIUD PRODUCTS, MOLE% :								
BENZENE (VIA DISPROPORTIONATION)	1.14	3.40	4.09	9.22	14.34	15.21	12.47	8.46
BENZENE (VIA HYDROCRACKING)	0.00	0.00	0.00	1.55	5.20	10.39	28.39	44.68
TOTAL BENZENE	1.14	3.40	4.09	10.77	19.54	25.60	40.86	53.14
TOLUENE	97.72	93.20	91.82	80.01	65.85	58.94	46.60	38.40
ETHYL BENZENE	0.00	0.00	0.00	0.16	0.27	0.32	0.22	0.13
p-XYLENE	0.30	0.84	0.97	2.09	3.18	3.32	2.69	1.79
m-XYLENE	0.61	1.80	2.14	4.70	7.22	7.57	6.16	4.16
o-XYLENE	0.23	0.76	0.98	2.27	3.67	4.00	3.40	2.38
TOTAL XYLENES	1.14	3.40	4.09	9.06	14.07	14.89	12.25	8.33
C8 AROMATICS	1.14	3.40	4.09	9.22	14.34	15.21	12.47	8.46
TRIMETHYLBENZENES	0.00	0.00	0.00	0.00	0.27	0.25	0.07	0.00

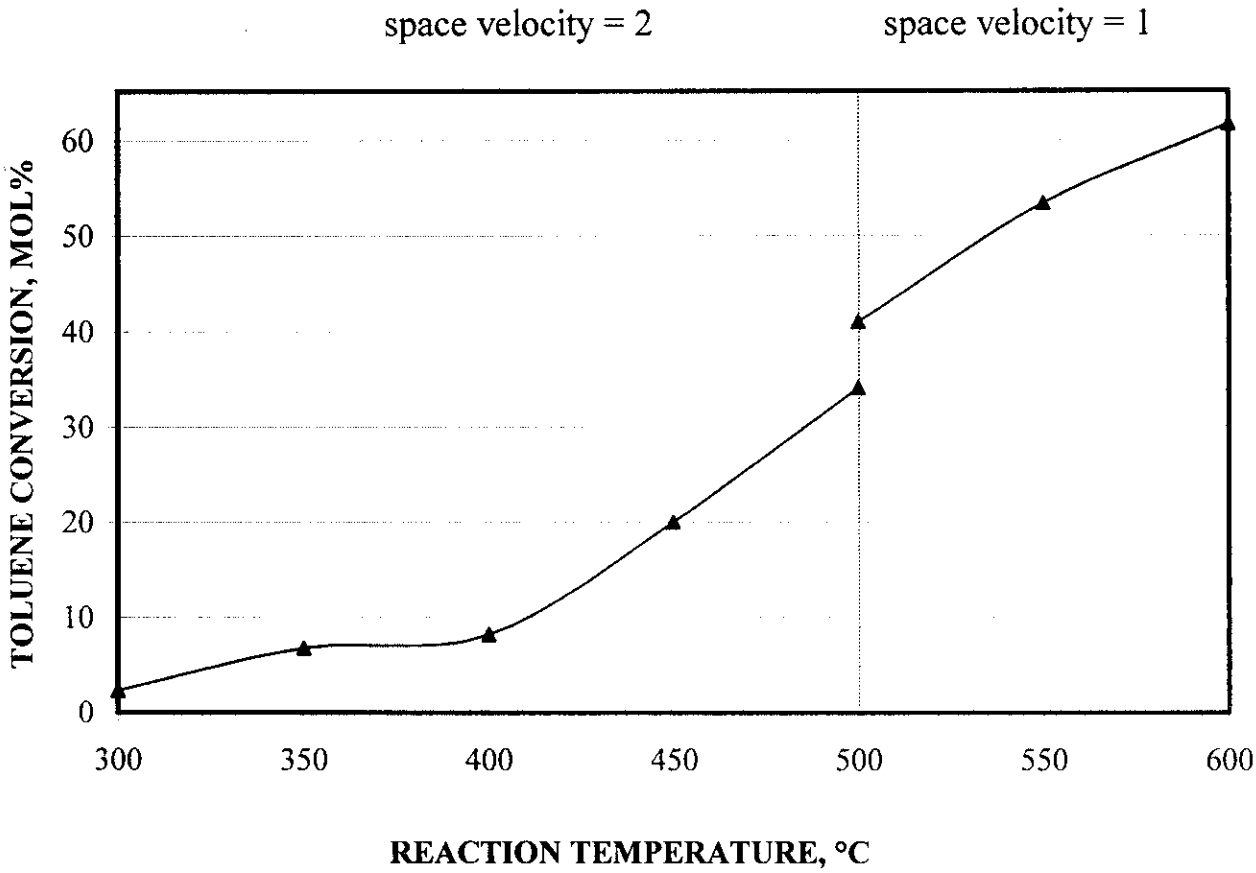


Fig.11 TOTAL TOLUENE CONVERSION AT DIFFERENT REACTION TEMPERATURES AND SPACE VELOCITIES OF TOLUENE DISPROPORTIONATION REACTION ON H-ZSM-5 CATALYST

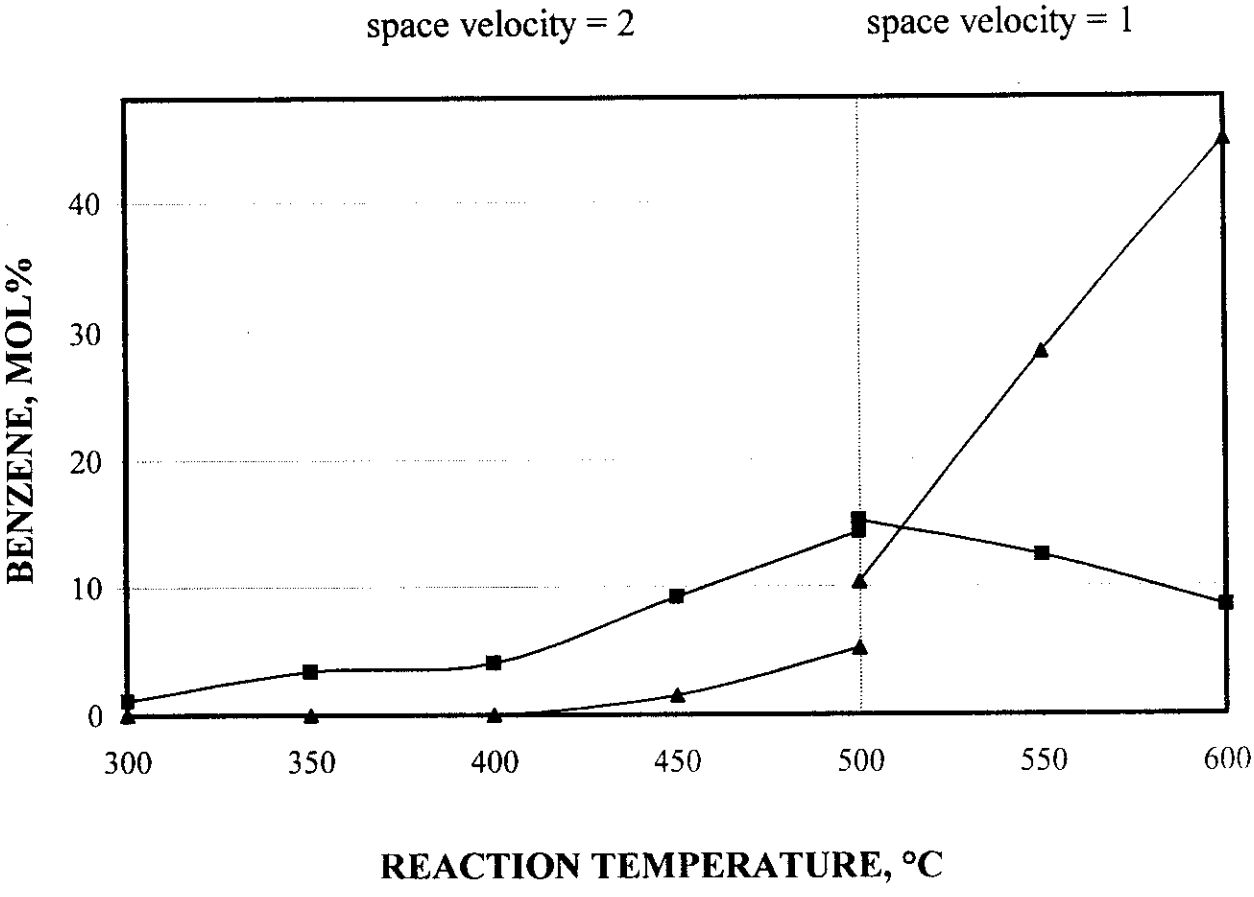


Fig.12 TOTAL BENZENE YIELD AT DIFFERENT TEMPERATURES AND SPACE VELOCITIES OF TOLUENE DISPROPORTIONATION REACTION ON H-ZSM-5 CATALYST

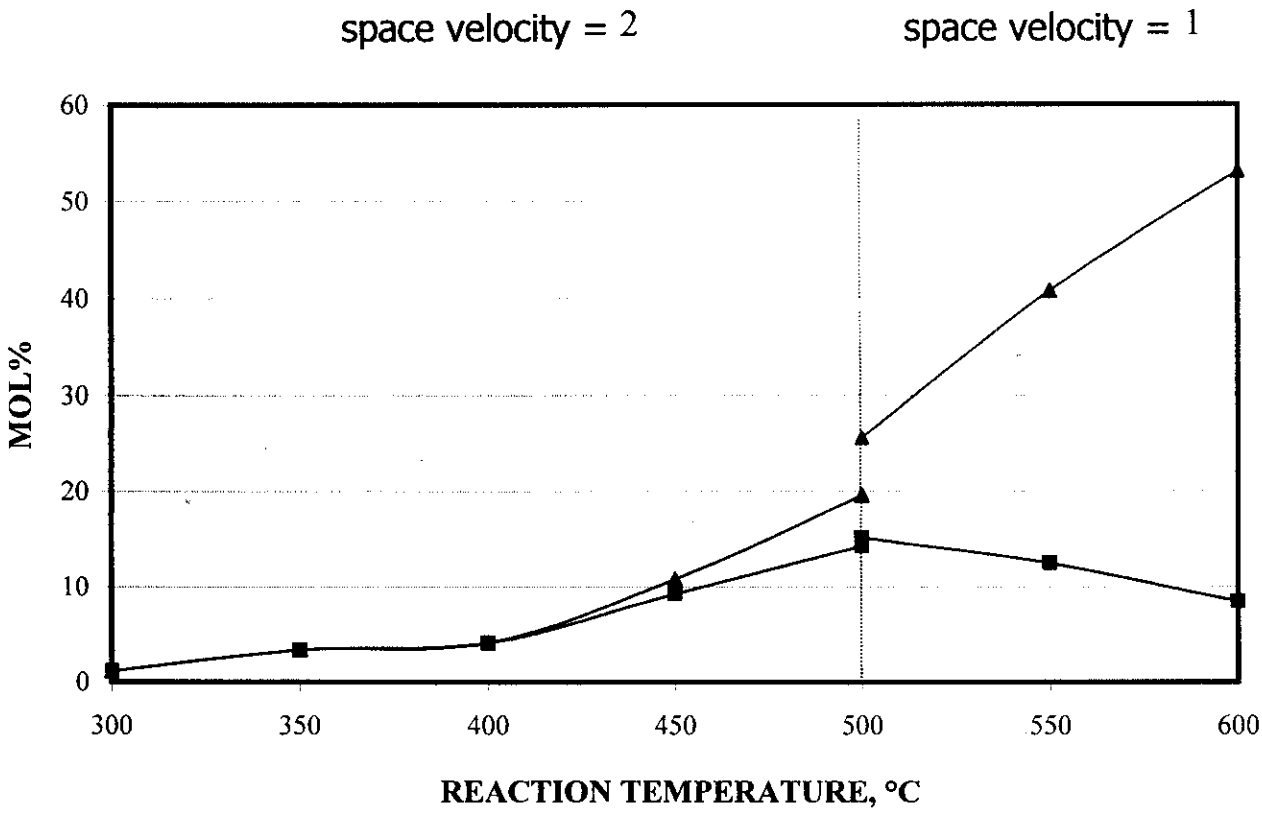


Fig.13 MOL% OF BENZENE AND C_8 AROMATICS IN THE PRODUCT OF TOLUENE DISPROPORTIONATION AT DIFFERENT REACTION TEMPERATURES AND SPACE VELOCITIES USING H- ZSM-5

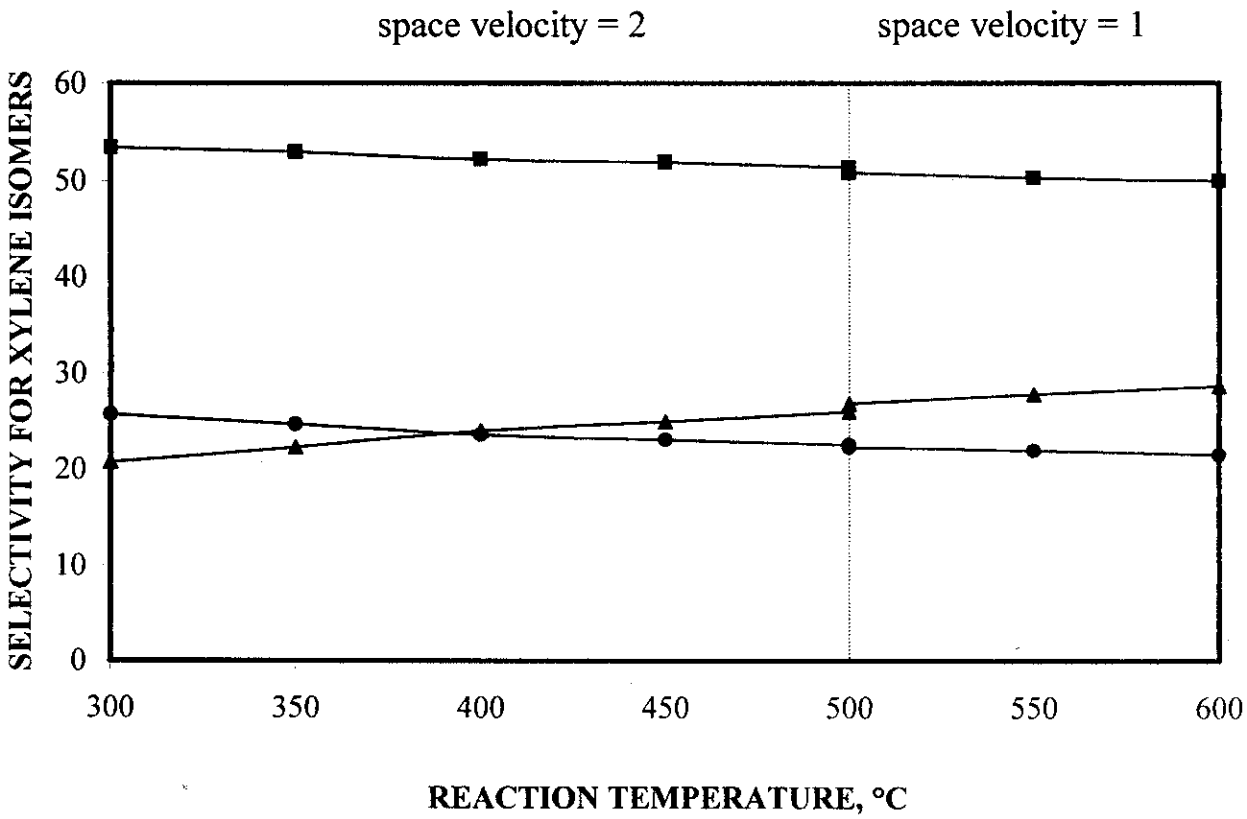


Fig.14 SELECTIVITY OF XYLENE ISOMERS AT DIFFERENT REACTION TEMPERATURES AND SPACE VELOCITIES OF TOLUENE DISPROPORTIONATION REACTION ON H-ZSM-5 CATALYST.

3.1.1. EFFECT OF SILICONIZATION OF H-ZSM-5 CATALYST ON THE DISPROPORTIONATION OF TOLUENE:

In the present investigation, it is attempted to improve further the p-selectivity of the ZSM-5 zeolite for toluene disproportionation. Hence we have treated H-ZSM-5 zeolite with a silicon-containing material (silicon grease) in a trial to precipitate some silicon (3.0 wt.% Si / 1gm H-ZSM-5 catalyst) in the zeolitic pores, i.e., siliconized in order to tailor a pore diameter adequate for faster p-xylene diffusion relative to that of m- and o-xylene isomers, thus increasing the rate of production of p-xylene relative to those of m- and o- xylenes.

The addition of silicon decreased the total toluene conversion from 2.28% to 0.96 mol% at 300°C and from 34.15% to 13.83 mol% at 500°C and a space velocity of 2.0 g $g^{-1}h^{-1}$. This is attributed to a decrease in the catalytic activity due to the masking of strong acid sites by silicon atoms (Fig.15). Also, the total xylenes production decreased from 1.14 to 0.48 mol% at 300°C and from 14.07 to 6.38 mol% at 500°C, using a space velocity of 2.0 g $g^{-1}h^{-1}$ (Tables 3 and 4). However, the p-xylene selectivity increases from 25.79% to 60.23% at temperature of 300°C and a space velocity of 2.0 g $g^{-1}h^{-1}$. Moreover, at 500°C, p-xylene selectivity increases from 22.6% to 52.16%. Also at the more severe conditions, (high temperature and space velocity of 1.0 g $g^{-1}h^{-1}$), the production of total xylenes decreases from 14.89 to 8.81 mol% at temperature of 500°C, while increases from 8.33 % to 9.86 mol% at temperature of 600°C, this is attributed to a decrease in hydrocracking (hydrodealkylation) reaction of xylenes due to the addition of silicon (Tables 3 and 4) (Fig.16), while p-xylene selectivity increases due to addition of silicon from (22.31 – 21.51 mol%) to (49.06 – 40.1mol%) at temperatures of 500 – 600 °C. o-Xylene has been greatly diminished on the siliconized catalyst compared to using

the untreated zeolite catalyst. At temperatures of 300-500°C, o-xylene comprises (20.76–26.06mol%, respectively), using the untreated catalyst (Table 3) (Fig.14), and decreases to (8.25–12.47mol%) (Table 4) (Fig.17), after incorporation of silicon in the zeolite catalyst. This may be attributed to the larger molecular size of o-xylene, relative to those of the para- and meta- isomers. Although Wei calculated the diameter of o- and m-xylenes to be equal to 6.9°A, whereas that of p-xylene to be 6.3°A, Choudhary et al. [52] estimated a bigger volume of o-xylene than the other two isomers (p-and m-xylenes). Moreover, o-xylene has been found to acquire lower values than the thermodynamic equilibrium values on pore–selective catalysts.

Fig.16 shows that at space velocity of 1.0 g $g^{-1}h^{-1}$, total xylene production increases till reaching a temperature of 550°C then decreases after that. This indicates that the addition of silicon decreases the rate of hydrocracking (hydrodealkylation) reaction of xylenes.

The competition of toluene hydrocracking (hydrodealkylation) with the formation of xylenes during the course of the reaction, under study, is more pronounced using the parent H-ZSM-5 zeolite catalyst than using the siliconized one. On the former catalyst benzene resulting from hydrocracking amounts to 5.2 mol% at 500°C and a WHSV of 2.0 g $g^{-1}h^{-1}$ and greatly enhances to reach 44.68 mol% at 600°C and WHSV of 1.0 g $g^{-1}h^{-1}$ (Table 3), while it comprises only 1.07mol% at 500°C and a WHSV of 2.0 g $g^{-1}h^{-1}$ and 8.77 mol% at 600°C and a WHSV of 1.0 g $g^{-1}h^{-1}$ (Table 4). This lower hydrocracking activity of the siliconized zeolite catalyst can be attributed to masking a part of the strong acid sites in the channels of H-ZSM-5 zeolite. However, lower hydrocracking is advantageous when the reaction is primarily directed towards xylenes production.

*TABLE 4. TOLUENE DISPROPORTIONATION USING SILICONIZED H-ZSM-5 CATALYST - CATALYST (1 *)*

SPACE VELOCITY	2					1		
TEMPERATURE, C° / ITEMS	300	350	400	450	500	500	550	600
CONVERSION, MOL%	0.96	2.00	4.60	6.76	13.83	19.43	24.66	29.06
DISTRIBUTION OF LIQIUD PRODUCTS, WT% :								
BENZENE	0.41	0.86	1.95	3.09	6.33	8.70	11.13	16.10
TOLUENE	99.04	97.99	95.39	93.30	86.30	80.68	75.48	71.82
ETHYL BENZENE	0.00	0.00	0.00	0.00	0.00	0.19	0.21	0.15
p-XYLENE	0.33	0.68	1.53	2.02	3.84	4.99	5.99	4.62
m-XYLENE	0.17	0.37	0.86	1.19	2.61	3.79	4.95	4.93
o-XYLENE	0.05	0.11	0.27	0.40	0.92	1.39	1.90	1.97
TOTAL XYLENES	0.55	1.15	2.66	3.61	7.37	10.17	12.84	11.52
TRIMETHYLBENZENES	0.00	0.00	0.00	0.00	0.00	0.26	0.34	0.41
DISTRIBUTION OF XYLENES % :								
p-XYLENE	60.23	58.70	57.29	55.95	52.16	49.06	46.65	40.10
m-XYLENE	31.52	32.10	32.42	33.02	35.37	37.27	38.55	42.76
o-XYLENE	8.25	9.20	10.29	11.03	12.47	13.67	14.80	17.14
DISTRIBUTION OF LIQIUD PRODUCTS, MOLE% :								
BENZENE (VIA DISPROPORTIONATION)	0.48	1.00	2.30	3.13	6.38	8.98	11.31	9.99
BENZENE (VIA HYDROCRACKING)	0.00	0.00	0.00	0.50	1.07	1.27	1.78	8.77
TOTAL BENZENE	0.48	1.00	2.30	3.63	7.45	10.25	13.09	18.76
TOLUENE	99.04	98.00	95.40	93.24	86.17	80.57	75.34	70.94
ETHYL BENZENE	0.00	0.00	0.00	0.00	0.00	0.17	0.18	0.13
p-XYLENE	0.29	0.59	1.32	1.75	3.33	4.33	5.19	3.95
m-XYLENE	0.15	0.32	0.75	1.03	2.26	3.28	4.29	4.23
o-XYLENE	0.04	0.09	0.24	0.35	0.80	1.20	1.65	1.68
TOTAL XYLENES	0.48	1.00	2.30	3.13	6.38	8.81	11.13	9.86
C8 AROMATICS	0.48	1.00	2.30	3.13	6.38	8.98	11.31	9.99
TRIMETHYLBENZENES	0.00	0.00	0.00	0.00	0.00	0.20	0.26	0.31

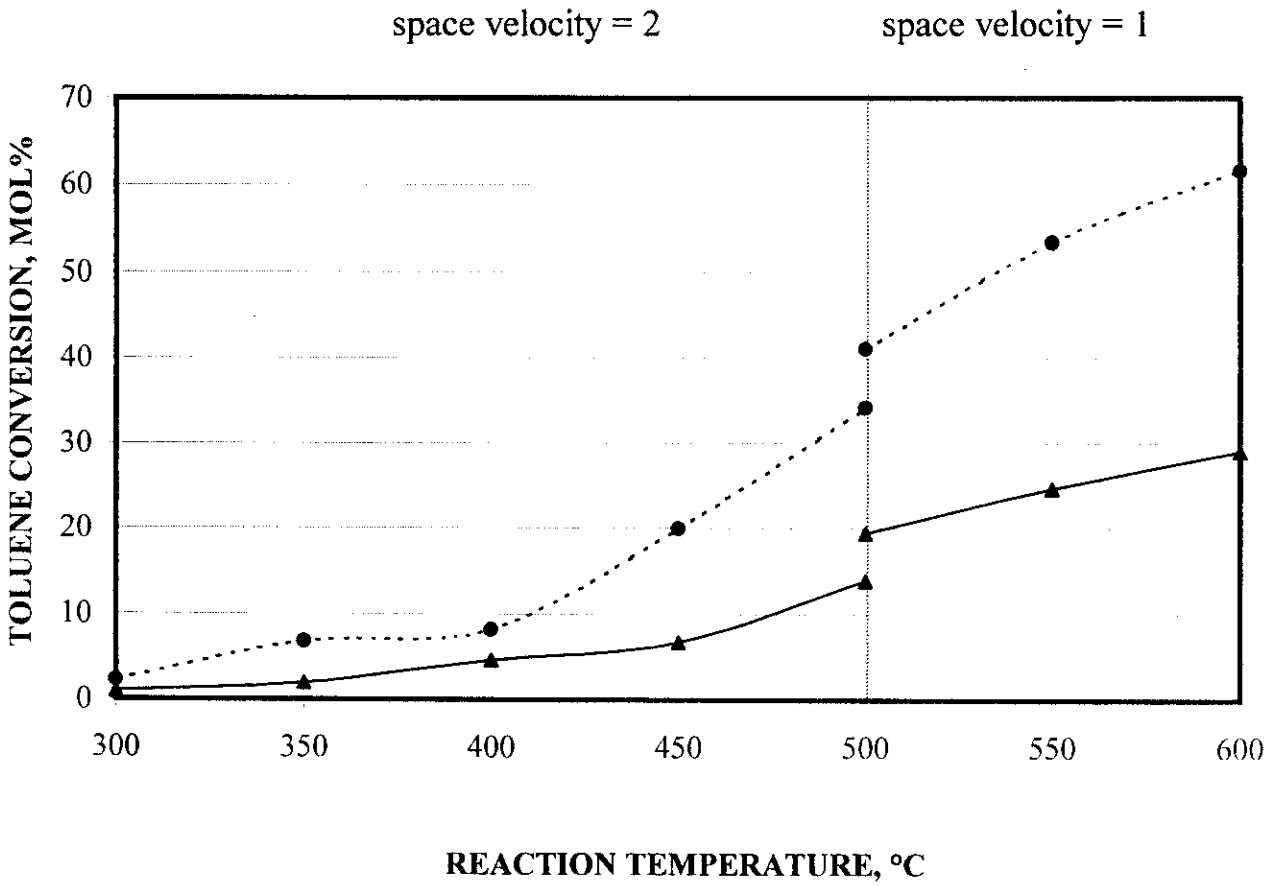


Fig.15 TOTAL TOLUENE CONVERSION AT DIFFERENT REACTION TEMPERATURES AND SPACE VELOCITIES OF TOLUENE DISPROPORTIONATION REACTION ON Si-H-ZSM-5 & H-ZSM-5 CATALYSTS.

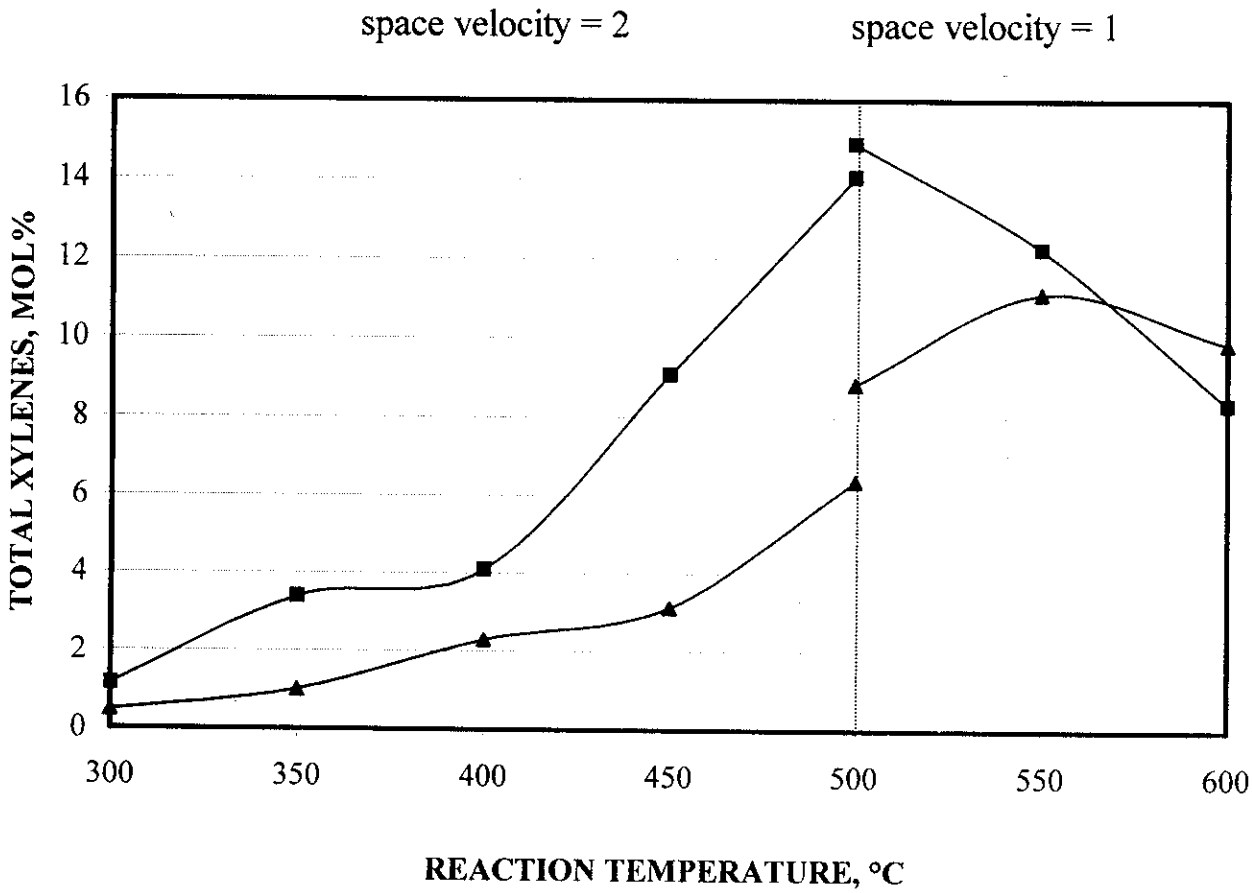


Fig.16 TOTAL XYLENES YIELD, MOL% AT DIFFERENT REACTION TEMPERATURES AND SPACE VELOCITIES OF TOLUENE DISPROPORTIONATION REACTION ON H-ZSM-5 & Si-H-ZSM-5 CATALYSTS.

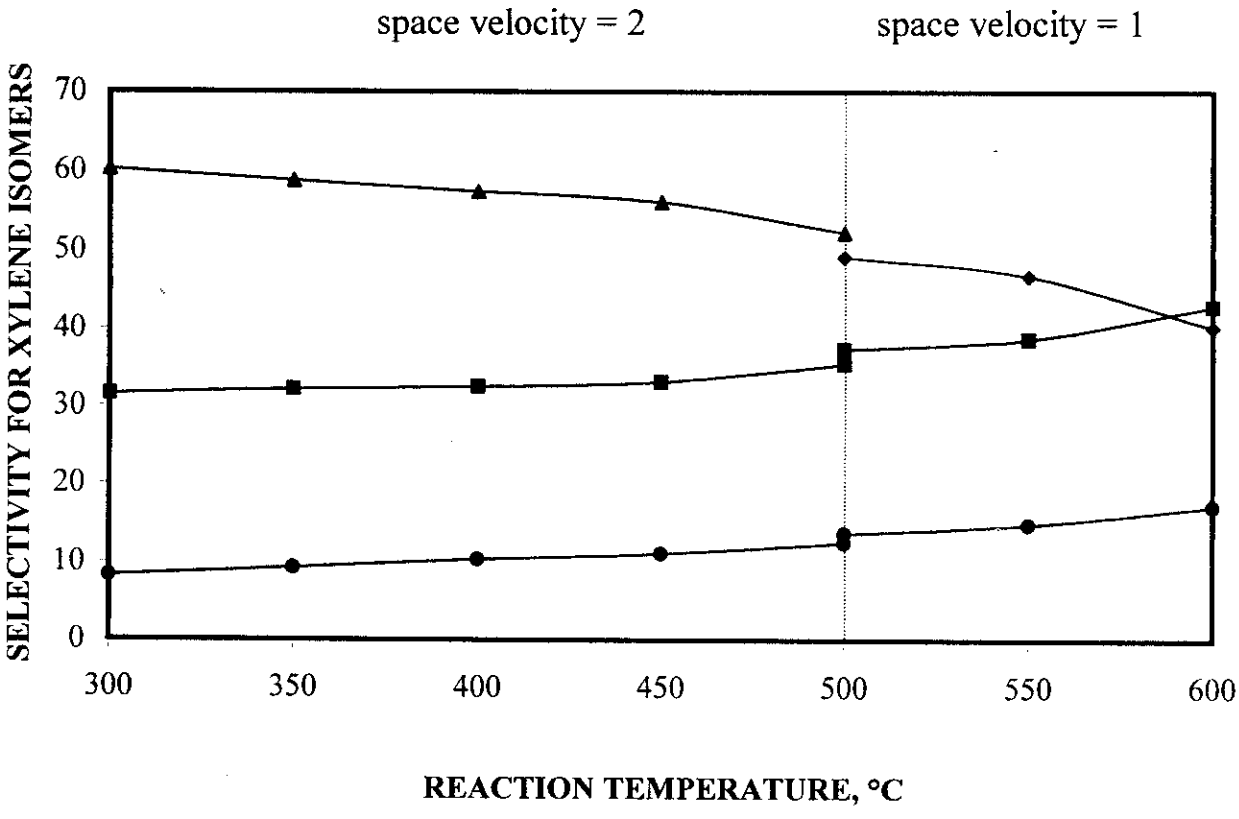


Fig.17 SELECTIVITY OF XYLENE ISOMERS AT DIFFERENT REACTION TEMPERATURES AND SPACE VELOCITIES OF TOLUENE DISPROPORTIONATION REACTION ON Si-H-ZSM-5 CATALYST.

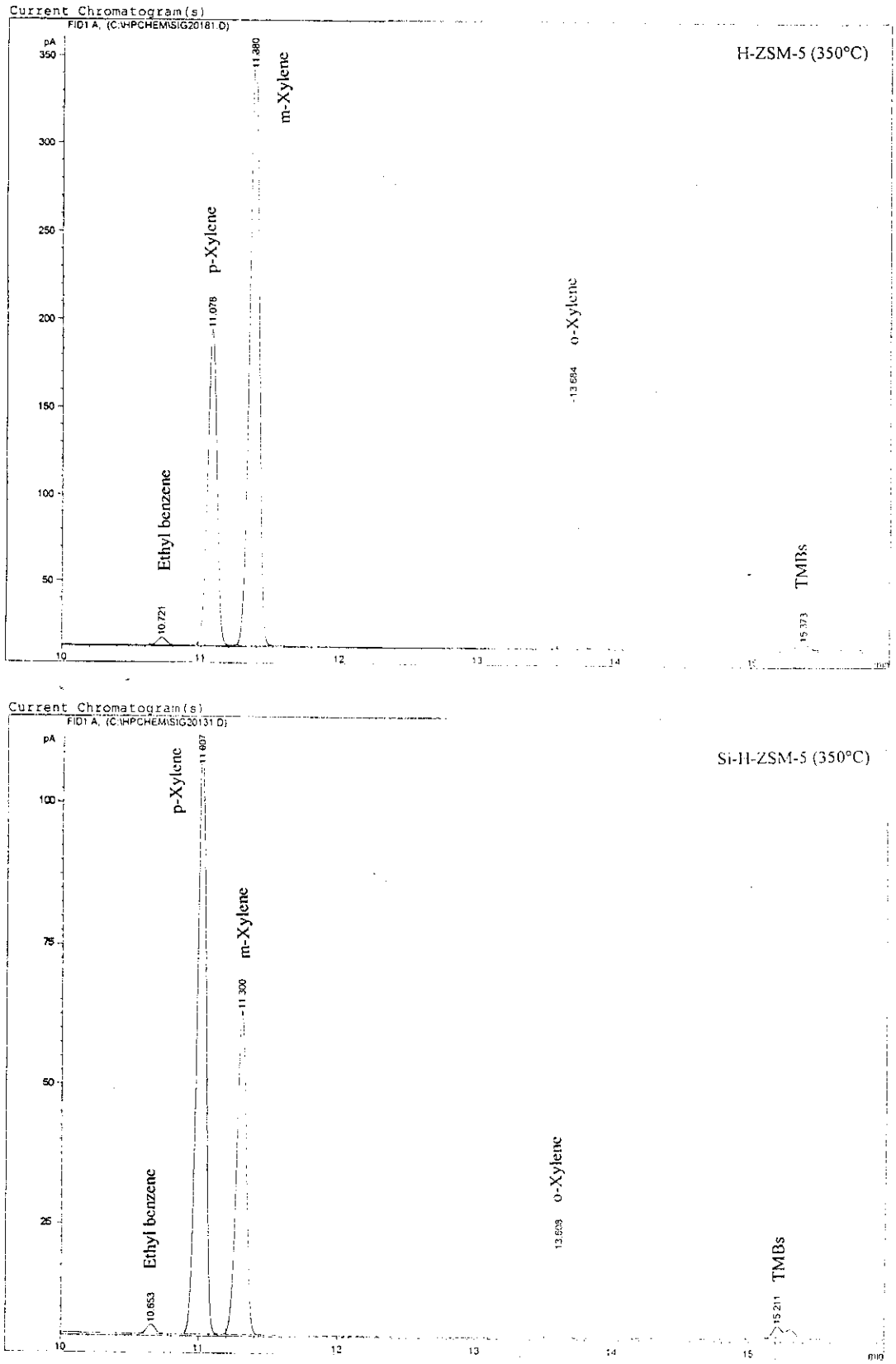


FIG.18 GAS CHROMATOGRAM OF THE C_8 & C_9 AROMATIC PRODUCT USING H-ZSM-5 & Si-H-ZSM-5 CATALYSTS, (REACTION TEMPERATURE = 350°C; SPACE VELOCITY = 2.0 $g\ g^{-1}\ h^{-1}$)

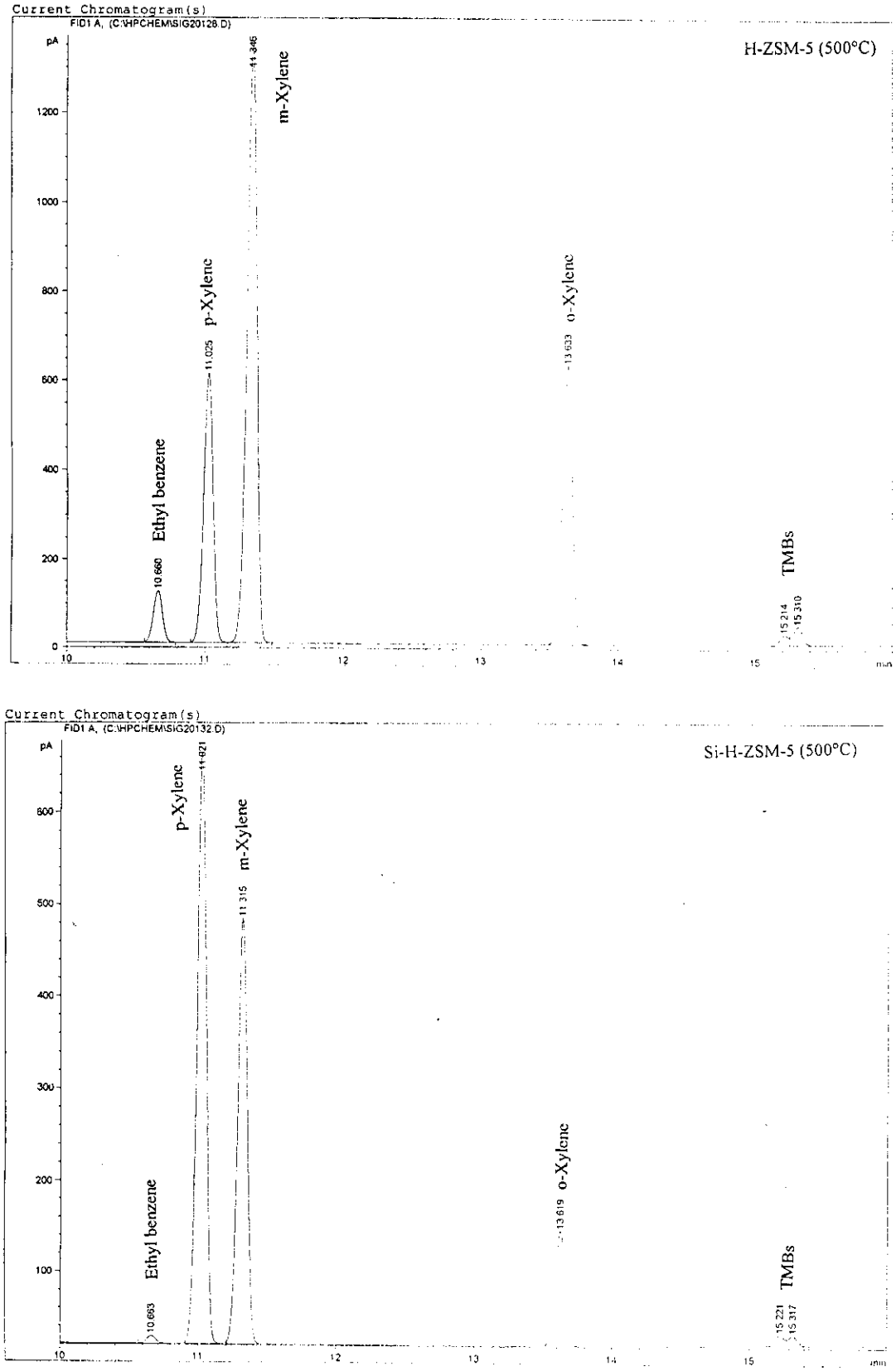


FIG.19 GAS CHROMATOGRAM OF THE C_8 & C_9 AROMATIC PRODUCT USING H-ZSM-5 & Si-H-ZSM-5 CATALYSTS, (REACTION TEMPERATURE = 500°C; SPACE VELOCITY = 2.0 g g^{-1} h^{-1})

3.1.2. EFFECT OF DEALUMINATION OF H-ZSM-5 ZEOLITE ON TOLUENE DISPROPORTIONATION:

The H-ZSM-5 zeolite under study has been dealuminated for partial removal of the framework aluminum (F-Al) such as to increase the Si/Al ratio and transforming the zeolite to a more hydrophobic form, which resists deactivation by carbon deposition.

The dealuminaion treatment removes a significant numbers of Brönsted acid sites since these sites are normally associated with the F-Al, which has been removed via HCl leaching [53]. However, the strength of the acid sites remaining in the zeolite after dealumination is somewhat higher than that of the parent zeolite due to excluding the interaction between neighboring H^+ when their concentration is high. The increase of Brönsted acid site strength seems to have decreased the selectivity of p-xylene via reisomerization to the two other isomers. The pore size (channel diameter) and the channels intersection space also widens via dealumination [54] as evidenced by the increase of ortho-xylene in product which has been found to posses a larger molecular size than para- and meta- xylenes. Although trimethylbenzenes are of low concern, they show a slight increase via dealumination, since these voluminous compounds require much larger channels to be formed therein. Tables 3 and 5 show that the zeolite dealumination for a period of 4h increases the conversion from 2.28% to 3.8 mol% at 300C°, and from 34.15% to 42.93 mol% at 500C° at a space velocity of 2.0 g $g^{-1}h^{-1}$ (Fig.20).

Dealumination increases the total xylene production from 1.14% to 1.9 mol% at temperature of 300°C, and from 14.07% to 17.39 mol% at temperature of 500°C, and a space velocity of 2.0 g $g^{-1}h^{-1}$. However, using higher severities (higher temperature and space velocity of 1.0 g $g^{-1}h^{-1}$), the total xylene production increases

from 14.89% to 17.26 mol% at temperature of 500°C, and from 8.33 to 9.83 mol% at temperature of 600°C (Fig.21). Dealumination also has slightly decreased the para-selectivity; for instance, from 25.79% to 24.36% at 300°C and from 22.6% to 21.66% at 500°C at a space velocity of 2.0 g g^{-1} h^{-1} (Fig.22). The m-xylene encountered almost the same decrease in selectivity, which is favorable since m-xylene is the least required petrochemical material. However, the selectivity for o-xylene shows some increase (from 20.8% to 23.5% at 300°C and from 26.1% to 27.8% at 500°C) (Tables 3 and 5). Again, o-xylene enhancement is favorable since it has a larger petrochemical market than m-xylene.

Benzene produced via toluene dealkylation (hydrocracking) during the disproportionation process under investigation shows some increase; e.g., it rises from 5.2% to 7.3 mol% at 500°C and a space velocity of 2.0 g g^{-1} h^{-1} using the dealuminated catalyst.

TABLE 5. TOLUENE DISPROPORTIONATION USING H-ZSM-5 CATALYST DEALUMINATED FOR 4 HOURS - CATALYST (4)

SPACE VELOCITY	*2*					*1*		
TEMPERATURE, C° / *ITEMS*	**300**	**350**	**400**	**450**	**500**	**500**	**550**	**600**
CONVERSION, MOL%	3.80	8.38	14.14	32.79	42.93	47.09	63.46	66.87
DISTRIBUTION OF LIQIUD PRODUCTS, WT% :								
BENZENE	1.62	3.55	6.00	14.71	21.30	25.10	44.31	51.69
TOLUENE	96.19	91.62	85.84	67.39	57.98	53.80	38.61	35.64
ETHYL BENZENE	0.00	0.00	0.00	0.20	0.37	0.43	0.33	0.19
p-XYLENE	0.53	1.12	1.83	3.84	4.35	4.28	3.39	2.50
m-XYLENE	1.14	2.50	4.18	8.93	10.15	10.08	8.05	5.90
o-XYLENE	0.52	1.20	2.15	4.80	5.58	5.85	4.92	3.78
TOTAL XYLENES%	2.19	4.83	8.16	17.57	20.07	20.22	16.36	12.18
TRIMETHYLBENZENES	0.00	0.00	0.00	0.13	0.28	0.45	0.39	0.30
DISTRIBUTION OF XYLENES % :								
p-XYLENE	24.36	23.29	22.46	21.84	21.66	21.19	20.73	20.53
m-XYLENE	52.12	51.77	51.24	50.83	50.56	49.86	49.20	48.44
o-XYLENE	23.52	24.94	26.30	27.33	27.78	28.95	30.07	31.03
DISTRIBUTION OF LIQIUD PRODUCTS, MOLE% :								
BENZENE (VIA DISPROPORTIONATION)	1.90	4.19	7.07	15.38	17.71	17.63	13.71	9.98
BENZENE (VIA HYDROCRACKING)	0.00	0.00	0.00	1.93	7.30	11.49	35.76	46.69
TOTAL BENZENE	1.90	4.19	7.07	17.31	25.01	29.12	49.47	56.67
TOLUENE	96.20	91.62	85.86	67.21	57.07	52.91	36.54	33.13
ETHYL BENZENE	0.00	0.00	0.00	0.17	0.32	0.37	0.27	0.15
p-XYLENE	0.46	0.98	1.59	3.32	3.77	3.66	2.79	2.02
m-XYLENE	0.99	2.17	3.62	7.73	8.79	8.61	6.61	4.76
o-XYLENE	0.45	1.05	1.86	4.16	4.83	5.00	4.04	3.05
TOTAL XYLENES	1.90	4.19	7.07	15.21	17.39	17.26	13.44	9.83
C8 AROMATICS	1.90	4.19	7.07	15.38	17.71	17.63	13.71	9.98
TRIMETHYLBENZENES	0.00	0.00	0.00	0.10	0.21	0.34	0.28	0.22

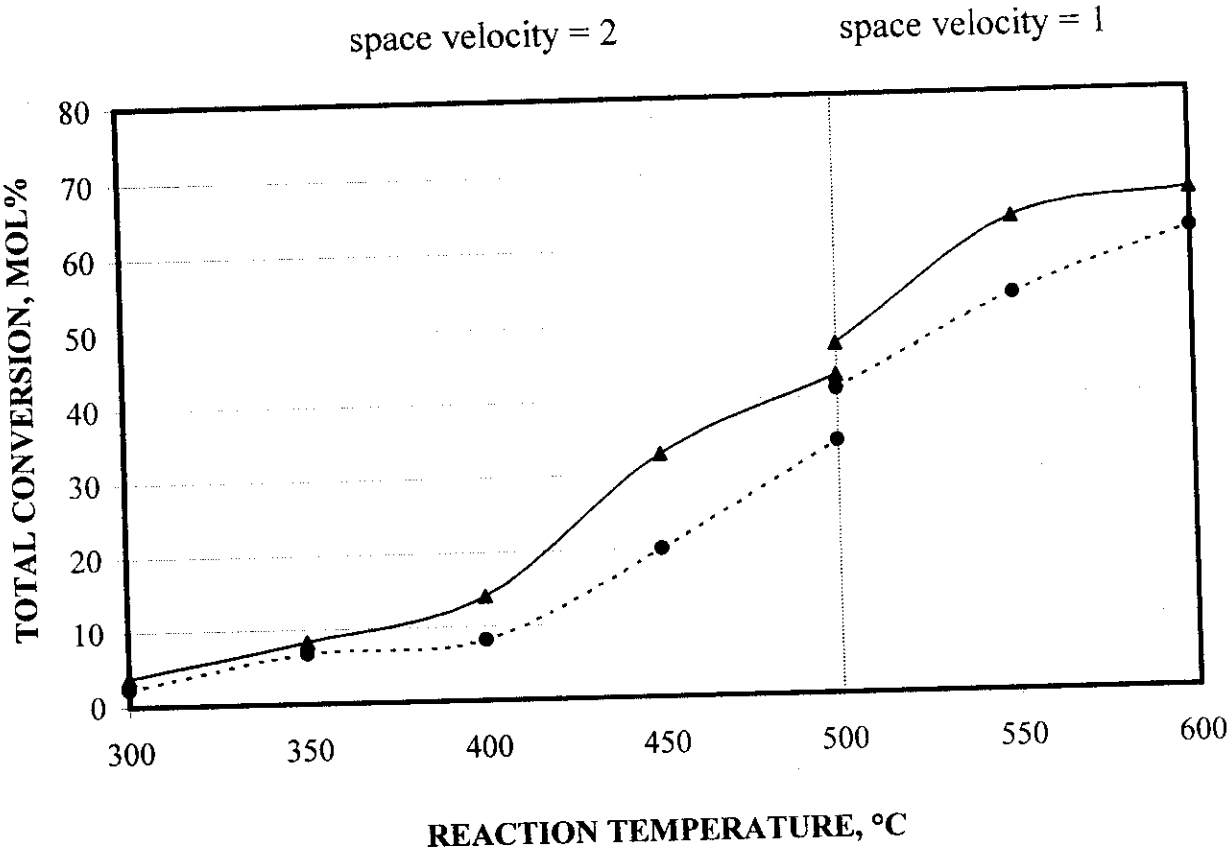


Fig.20 TOTAL TOLUENE CONVERSION AT DIFFERENT REACTION TEMPERATURES AND SPACE VELOCITIES OF TOLUENE DISPROPORTIONATION REACTION ON DA- H-ZSM-5 (4h) & H-ZSM-5 CATALYSTS.

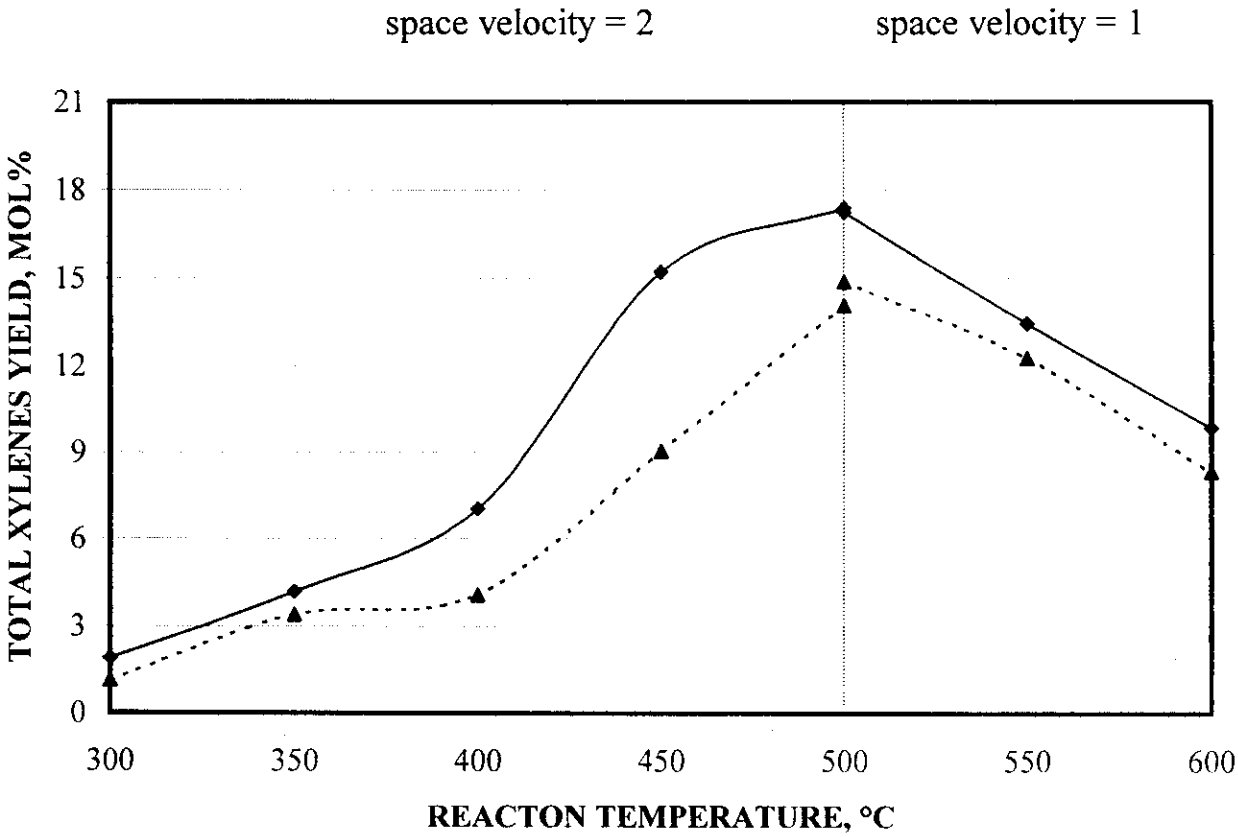


Fig.21 MOL% OF TOTAL XYLENES YIELD AT DIFFERENT REACTION TEMPERATURES AND SPACE VELOCITIES OF TOLUENE DISPROPORTIONATION REACTION ON DA- H-ZSM-5 (4h) & H-ZSM-5 CATALYSTS.

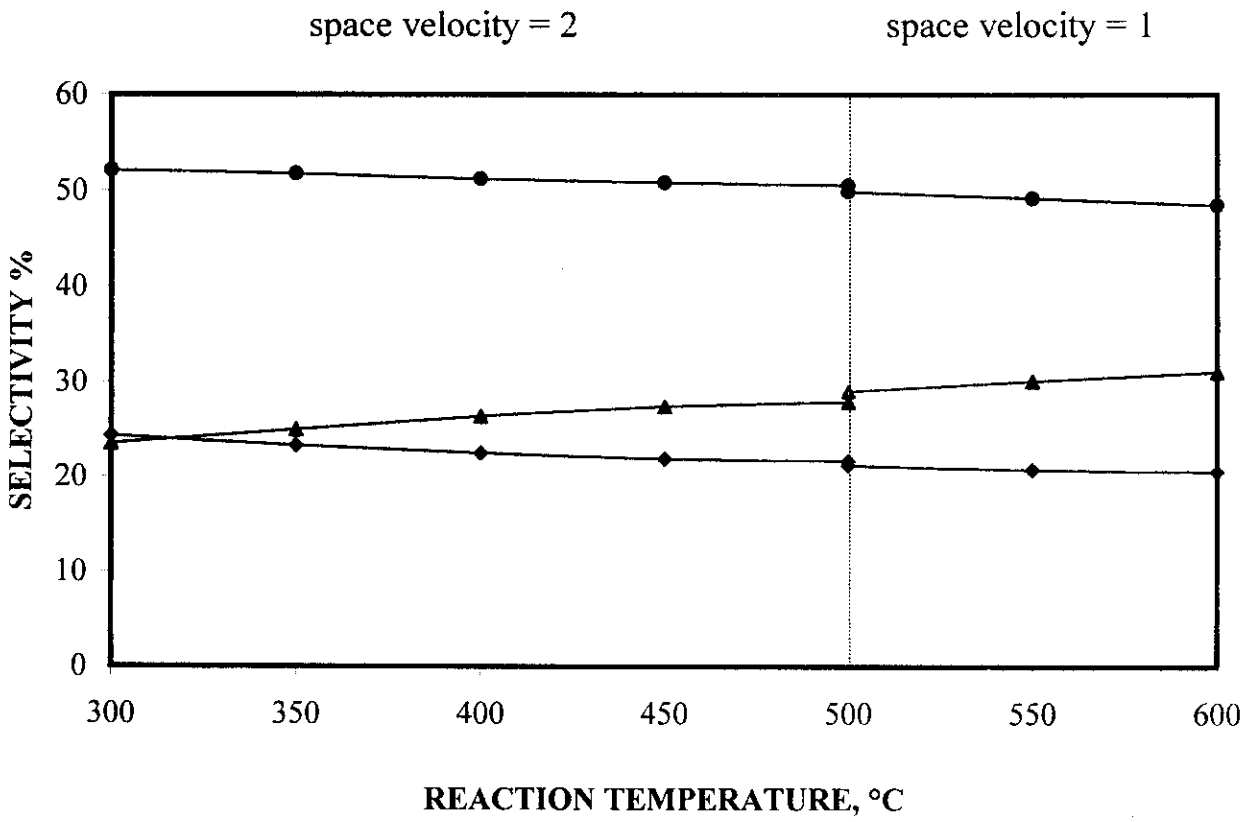


Fig.22 SELECTIVITY OF XYLENE ISOMERS AT DIFFERENT REACTION TEMPERATURES AND SPACE VELOCITIES OF TOLUENE DISPROPORTIONATION REACTION ON DA-H-ZSM-5 (4h) CATALYST.

3.1.3. EFFECT OF DEALUMINATION EXTENT ON ACTIVITIES OF THE SILICONIZED CATALYST:

Addition of a fixed amount of silicon grease (equivalent to 3.0 wt.% Si) to the different dealuminated zeolite catalysts has been carried out.

The data in Table 6 show that the increase of the dealumination period using 0.5M HCl, increases the Si/Al ratio from 23.7 in the as-synthesized zeolite up to 37.7 in the zeolite dealuminated for 4h. The increase of the Si/Al ratio leads to the increase of the catalytic activity of the zeolite for toluene conversion. Both at space velocities of 2.0 and 1.0 $g\,g^{-1}h^{-1}$, the catalytic activity is more evidently enhanced via increasing the Si/Al ratio from 26.5 to 30.3 (Fig.23)

Fig.24 shows that at a space velocity of 1.0 $gg^{-1}h^{-1}$, the production of total xylenes at 550°C is highest. However, at a higher temperature of 600C°, hydrocracking reactions are enhanced and xylenes production is thus becomes lower.

Fig.25 shows that the selectivity for p-xylene production at a space velocity of 2.0 $g\,g^{-1}h^{-1}$ decreases with increasing temperature. Also the increase in Si/Al ratio from 26.5 to 30.3 gives a significant decrease in selectivity especially beyond a temperature of 350°C. The same behavior takes place at space velocity of 1.0 $g\ g^{-1}h^{-1}$ where a significant decrease in selectivity is observed at Si/Al ratios between 26.5 to 30.3 (Fig.25)

Generally, as the Si/Al ratio increases, the activity of catalyst increases due to the increase of the strength of acid sites which leading to high toluene conversion, high benzene yield and high total xylenes yield which decreased after 550°C due to dehydroalkylation reaction. The selectivity of p-xylene decreases with Si/Al ratio due

TABLE. 6 EFFECT OF DEALUMINATION EXTENT ON THE Si/Al OF H-ZSM-5 CATALYST

Catalyst	Dealumination period,h	Si/Al
1*	As synthesized	23.7
2*	1	26.5
3*	2	30.3
4*	4	37.7

* Designates silicon incorporation after dealumination.

*TABLE 7. TOLUENE DISPROPORTIONATION USING SILICONIZED H-ZSM-5 CATALYST DEALUMINATED FOR 1 HOUR - CATALYST (2 *)*

SPACE VELOCITY	2					1		
TEMPERATURE, C° / ITEMS	300	350	400	450	500	500	550	600
CONVERSION, MOL%	1.32	2.64	4.72	9.08	16.92	20.93	27.29	31.86
DISTRIBUTION OF LIQIUD PRODUCTS, WT% :								
BENZENE	0.55	1.12	2.01	4.03	7.61	9.41	12.48	17.13
TOLUENE	98.69	97.35	95.26	90.97	83.17	79.18	72.90	68.95
ETHYL BENZENE	0.00	0.00	0.00	0.09	0.15	0.27	0.39	0.32
p-XYLENE	0.42	0.83	1.45	2.41	4.16	4.82	5.73	5.01
m-XYLENE	0.27	0.55	0.98	1.78	3.46	4.33	5.86	5.80
o-XYLENE	0.07	0.16	0.30	0.59	1.22	1.67	2.26	2.32
TOTAL XYLENES	0.76	1.53	2.73	4.78	8.84	10.81	13.85	13.13
TRIMETHYLBENZENES	0.00	0.00	0.00	0.13	0.23	0.33	0.38	0.47
DISTRIBUTION OF XYLENES % :								
p-XYLENE	55.28	53.96	52.96	50.37	47.09	44.57	41.37	38.16
m-XYLENE	35.44	35.77	35.93	37.20	39.13	40.02	42.31	44.17
o-XYLENE	9.28	10.27	11.11	12.43	13.78	15.41	16.32	17.67
DISTRIBUTION OF LIQIUD PRODUCTS, MOLE% :								
BENZENE (VIA DISPROPORTIONATION)	0.66	1.32	2.36	4.23	7.78	9.60	12.32	11.35
BENZENE (VIA HYDROCRACKING)	0.00	0.00	0.00	0.52	1.18	1.48	2.36	8.62
TOTAL BENZENE	0.66	1.32	2.36	4.75	8.96	11.08	14.68	19.97
TOLUENE	98.68	97.36	95.28	90.92	83.08	79.07	72.71	68.14
ETHYL BENZENE	0.00	0.00	0.00	0.08	0.13	0.23	0.34	0.27
p-XYLENE	0.36	0.71	1.25	2.09	3.60	4.18	4.96	4.30
m-XYLENE	0.24	0.47	0.85	1.54	2.99	3.75	5.07	4.97
o-XYLENE	0.06	0.14	0.26	0.52	1.05	1.44	1.95	1.99
TOTAL XYLENES	0.66	1.32	2.36	4.15	7.65	9.37	11.98	11.26
C8 AROMATICS	0.66	1.32	2.36	4.23	7.78	9.60	12.32	11.53
TRIMETHYLBENZENES	0.00	0.00	0.00	0.10	0.18	0.25	0.29	0.36

TABLE 8. TOLUENE DISPROPORTIONATION USING SILICONIZED H-ZSM-5 CATALYST DEALUMINATED FOR 2 HOURS - CATALYST (3)*

SPACE VELOCITY	2					1		
TEMPERATURE, C° / ITEMS	300	350	400	450	500	500	550	600
CONVERSION, MOL%	2.18	4.14	6.86	17.72	25.11	32.07	39.91	47.38
DISTRIBUTION OF LIQIUD PRODUCTS, WT% :								
BENZENE	0.93	1.76	2.91	7.76	11.21	14.12	17.81	25.46
TOLUENE	97.80	95.84	93.13	82.33	75.01	68.01	60.23	53.53
ETHYL BENZENE	0.00	0.00	0.00	0.14	0.29	0.36	0.43	0.40
p-XYLENE	0.68	0.97	1.32	2.51	3.34	3.92	4.70	4.41
m-XYLENE	0.47	1.11	2.00	4.91	6.83	8.92	10.92	10.37
o-XYLENE	0.12	0.32	0.64	2.16	3.06	4.12	5.29	5.16
TOTAL XYLENES	1.27	2.40	3.96	9.58	13.22	16.96	20.91	19.94
TRIMETHYLBENZENES	0.00	0.00	0.00	0.19	0.27	0.55	0.62	0.67
DISTRIBUTION OF XYLENES % :								
p-XYLENE	53.63	40.25	33.31	26.24	25.25	23.10	22.50	22.10
m-XYLENE	36.75	46.42	50.63	51.26	51.63	52.60	52.20	52.00
o-XYLENE	9.62	13.33	16.06	22.50	23.12	24.30	25.30	25.90
DISTRIBUTION OF LIQIUD PRODUCTS, MOLE% :								
BENZENE (VIA DISPROPORTIONATION)	1.09	2.07	3.43	8.43	11.70	15.01	18.48	17.49
BENZENE (VIA HYDROCRACKING)	0.00	0.00	0.00	0.72	1.50	1.63	2.48	12.03
TOTAL BENZENE	1.09	2.07	3.43	9.15	13.20	16.64	20.96	29.52
TOLUENE	97.82	95.86	93.14	82.28	74.89	67.93	60.09	52.62
ETHYL BENZENE	0.00	0.00	0.00	0.12	0.25	0.31	0.37	0.34
p-XYLENE	0.58	0.83	1.14	2.18	2.89	3.40	4.07	3.76
m-XYLENE	0.40	0.96	1.74	4.26	5.91	7.73	9.45	8.85
o-XYLENE	0.10	0.28	0.55	1.87	2.65	3.57	4.58	4.41
TOTAL XYLENES	1.09	2.07	3.43	8.31	11.45	14.70	18.11	17.02
C8 AROMATICS	1.09	2.07	3.43	8.43	11.70	15.01	18.48	17.36
TRIMETHYLBENZENES	0.00	0.00	0.00	0.14	0.21	0.42	0.47	0.50

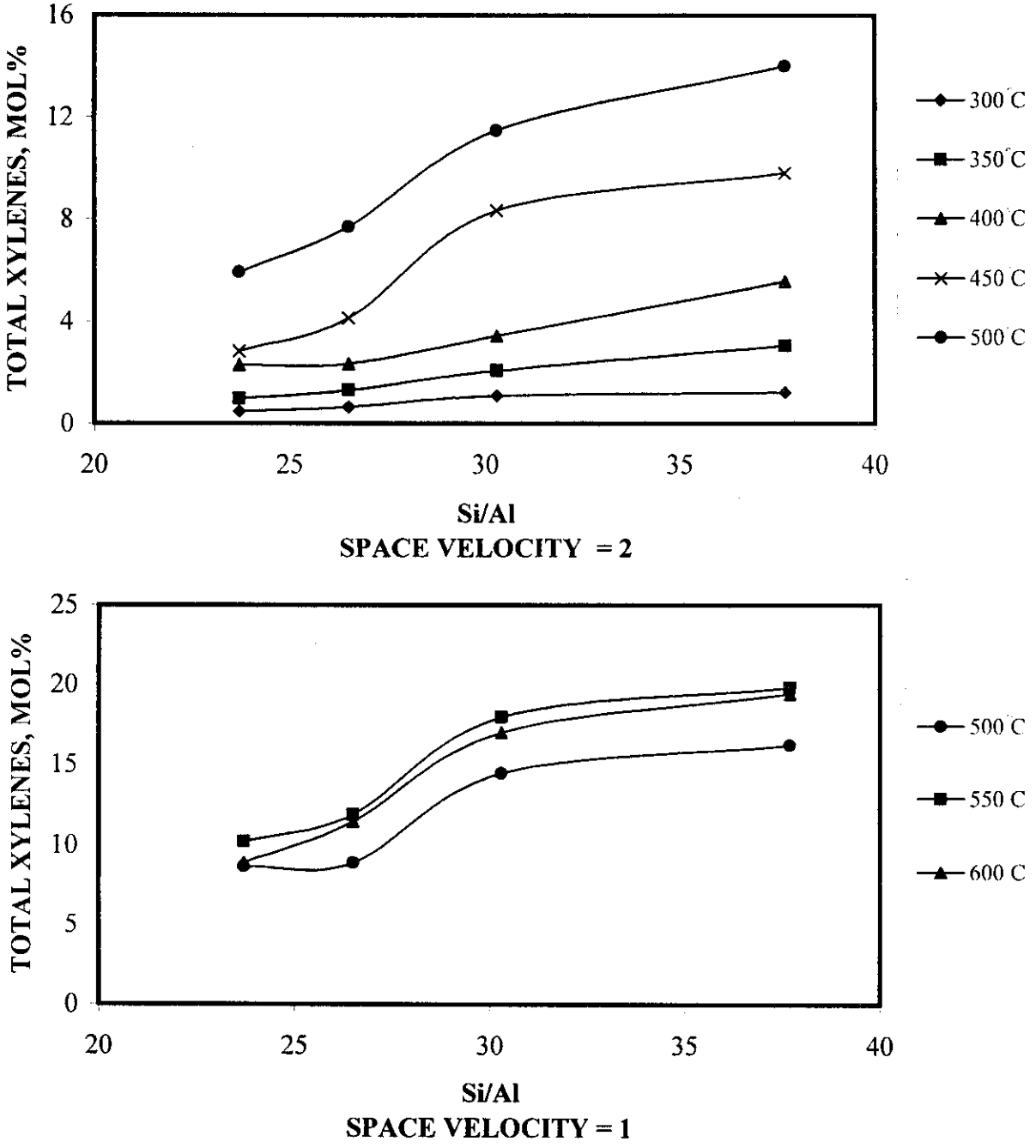


Fig. 24 EFFECT OF Si/Al RATIO AT DIFFRENT REACTION TEMPERATURES ON TOTAL XYLENES YIELD
(Si/Al : CAT.1* = 23.7, CAT.2* = 26.5, CAT.3* = 30.3, CAT.4* = 37.7)
(see Table 6)

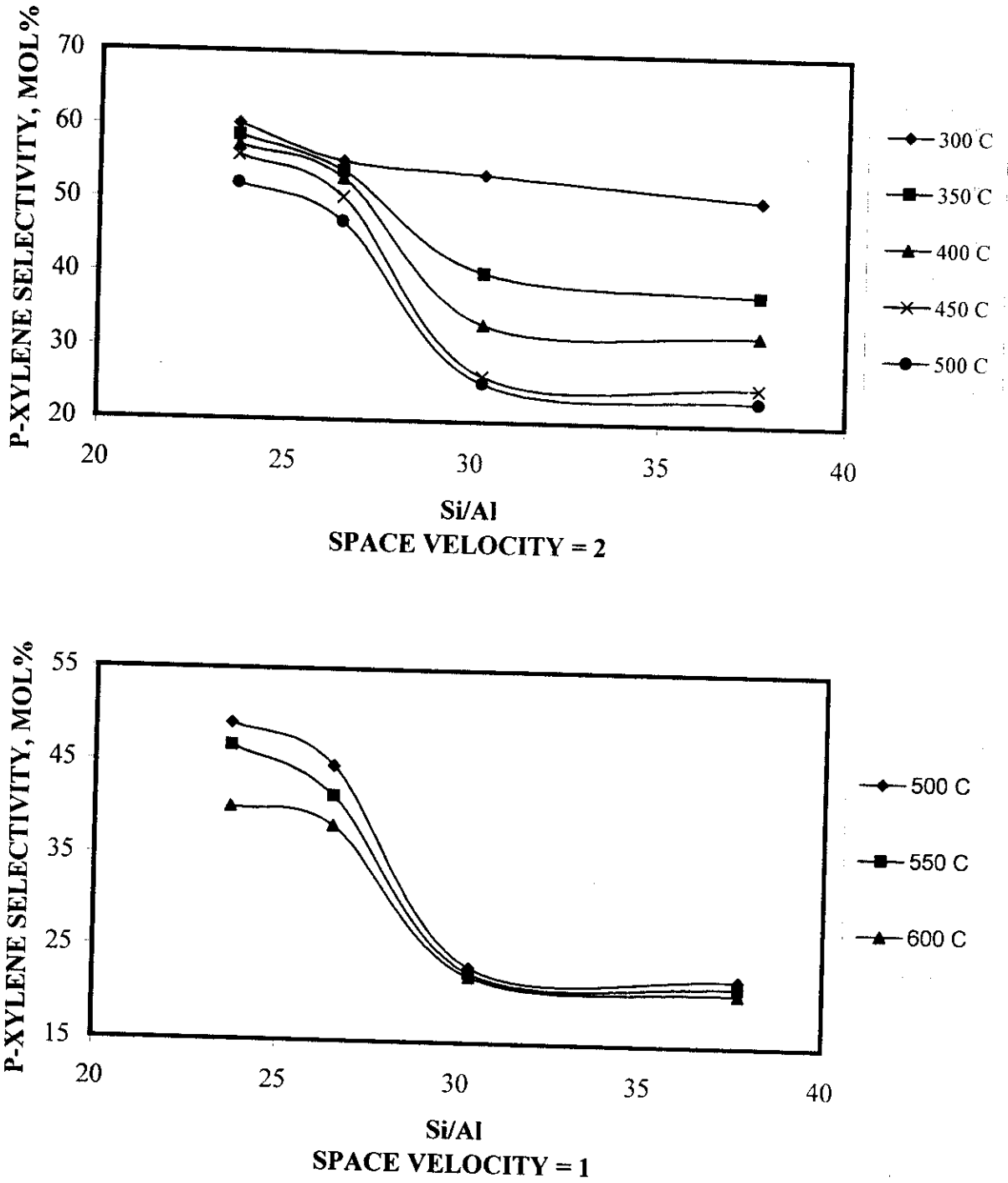


Fig. 25 EFFECT OF Si/Al RATIO AT DIFFRENT REACTION TEMPERATURES ON P- XYLENE SELECTIVITY
(Si/Al : CAT.1* = 23.7, CAT.2* = 26.5, CAT.3* = 30.3, CAT.4* = 37.7)
(see Table 6)

to increase in acid strength, which lead to increase the reisomerisation reaction of p-xylene to m- and o-xylene. The increase of the zeolite pore diameter with increasing dealumination decreases also the selectivity for p-xylene production.

3.1.4. EFFECT OF SILICONIZATION EXTENT ON DA-H-ZSM-5 CATALYST:

After addition of the silicon-containing component (equivalent to 3.0 wt.% of Si / 1 gm catalyst) to the dealuminated zeolite for 4h, the conversion of toluene has been diminished i.e., decreased the catalytic activity, since conversion on the unsiliconized catalyst reaches 42.93 mol% at 500°C and space velocity of 2.0 g $g^{-1}h^{-1}$ (Table 5), compared to 30.53 mol% using the siliconized catalyst (Table 8) (Fig.26). Moreover, total xylenes amount to 17.39 mol% at 500°C and space velocity of 2.0 g $g^{-1}h^{-1}$ using the unsiliconized catalyst, compared to 14.02mol% using the siliconized one (Fig 27).

The selectivity for p-xylene formation increases significantly, particularly, at the lower reaction temperatures. At 300°C p-xylene amounts to 50.6 % on the Si-treated catalyst (containing 3.0 wt.% of Si) (Table 8), compared to 24.4% on the unsiliconized dealuminated catalyst. The ortho-xylene production greatly decreases, particularly, at the lower reaction temperatures (10.3% at 300°C compared to 23.5% using the unsiliconized dealuminated catalyst) (Fig.28).

Increasing the incorporated silicon in the H-ZSM-5 zeolite, under investigation, to the double (equivalent to 6.0 wt.% Si / 1gm catalyst), has greatly decreased the conversion of toluene. Comparing tables 8 and 10, show that the conversion decreases from 2.46% to 0.64 mol% at temperature of 300°C and from 30.53% to 14.06 mol% at temperature of 500°C and a space velocity of 2.0 g $g^{-1}h^{-1}$ (Fig.26).

Also total xylenes decreased from 14.02% to 6.73 mol% at 500°C and space velocity of 2.0 g $g^{-1}h^{-1}$ (Fig.27). Another function of addition of silicon in the zeolite is the significant of the para-xylene selectivity. Tables 9 and 10 and (Fig.28) Show that the para-xylene selectivity increases from 50.6% to 55.4% at temperature of 300°C, and from 23.2% to 41.6% at temperature of 500°C and a space velocity of 2.0 g $g^{-1}h^{-1}$ via doubling the quantity of silicon in the dealuminated H-ZSM-5.

It has to be pointed out that the formation of TMBs using the double siliconized DA-H-ZSM-5 catalyst has been completely inhibited, indicating a greater restriction of this reaction. Also, ethylbenzene production on this catalyst has been completely stopped.

On the other hand, m- and o- xylenes selectivities has been significantly decreased. m-Xylene selectivity decreases from 39.2% to 35.4% at temperature of 300°C and from 52.1% to 43.2% at temperature of 500°C and a space velocity of 2.0 g $g^{-1}h^{-1}$. As indicated above, m-xylene is the least required petrochemical C_8 aromatic hydrocarbon. However, o-xylene selectivity decreases from 10.3% to 9.3% at temperature of 300°C and from 24.7% to 15.2 % at temperature of 500°C and a space velocity of 2.0 g $g^{-1}h^{-1}$. Evidently, para–xylene in the xylenes mixture in product increases on the expense of a corresponding decrease of the m- and o-isomers (Fig.28).

The hydrocracking reaction forming benzene and methane is a competitive reaction to benzene formation via disproportionation of toluene to produce xylenes and benzene. So, the ratio of benzene production via disproportionation divided by benzene production via cracking will be a clear indication of the catalytic disproportionation selectivity.

Fig.29 shows that the data obtained from Tables (5, 8 and 10) give an evidence of the importance of siliconizing the H-ZSM-5 zeolite for decreasing the hydrocracking activity and hence increasing the disproportionation activity. Further increase of silicon-loading is found to produce a further increase of the disproportionation selectivity which attributed to the masking of strong acid sites in the zeolite channels.

TABLE 10. TOLUENE DISPROPORTIONATION USING DOUBLE SILICONIZED H-ZSM-5 CATALYST DEALUMINATED FOR 4 HOURS - CATALYST (4 **)

SPACE VELOCITY	*2*					*1*		
TEMPERATURE, C° / *ITEMS*	**300**	**350**	**400**	**450**	**500**	**500**	**550**	**600**
CONVERSION, MOL%	0.64	1.48	3.06	7.35	14.06	18.09	21.72	27.03
DISTRIBUTION OF LIQIUD PRODUCTS, WT% :								
BENZENE	0.27	0.63	1.30	3.12	6.22	8.01	9.60	14.30
TOLUENE	99.36	98.51	96.94	92.68	86.01	82.00	78.35	73.65
ETHYL BENZENE	0.00	0.00	0.00	0.00	0.00	0.09	0.15	0.10
p-XYLENE	0.20	0.45	0.90	1.88	3.23	3.23	3.39	2.80
m-XYLENE	0.13	0.32	0.65	1.74	3.35	4.77	5.92	6.03
o-XYLENE	0.03	0.09	0.21	0.58	1.18	1.75	2.28	2.67
TOTAL XYLENES%	0.37	0.86	1.76	4.20	7.77	9.76	11.59	11.50
TRIMETHYLBENZENES	0.00	0.00	0.00	0.00	0.00	0.14	0.31	0.45
DISTRIBUTION OF XYLENES % :								
p-XYLENE	55.39	52.65	51.15	44.79	41.63	33.12	29.25	24.38
m-XYLENE	35.35	36.78	37.08	41.38	43.16	48.91	51.08	52.41
o-XYLENE	9.26	10.57	11.77	13.83	15.21	17.97	19.67	23.21
DISTRIBUTION OF LIQIUD PRODUCTS, MOLE% :								
BENZENE (VIA DISPROPORTIONATION)	0.32	0.74	1.53	3.62	6.73	8.54	10.17	9.98
BENZENE (VIA HYDROCRACKING)	0.00	0.00	0.00	0.11	0.60	0.90	1.14	6.73
TOTAL BENZENE	0.32	0.74	1.53	3.73	7.33	9.44	11.31	16.71
TOLUENE	99.36	98.52	96.94	92.65	85.94	81.91	78.28	72.97
ETHYL BENZENE	0.00	0.00	0.00	0.00	0.00	0.08	0.13	0.08
p-XYLENE	0.18	0.39	0.78	1.62	2.80	2.80	2.93	2.41
m-XYLENE	0.11	0.27	0.57	1.50	2.90	4.14	5.13	5.19
o-XYLENE	0.03	0.08	0.18	0.50	1.02	1.52	1.98	2.30
TOTAL XYLENES	0.32	0.74	1.53	3.62	6.73	8.46	10.04	9.90
C8 AROMATICS	0.32	0.74	1.53	3.62	6.73	8.54	10.17	9.98
TRIMETHYLBENZENES	0.00	0.00	0.00	0.00	0.00	0.11	0.24	0.34

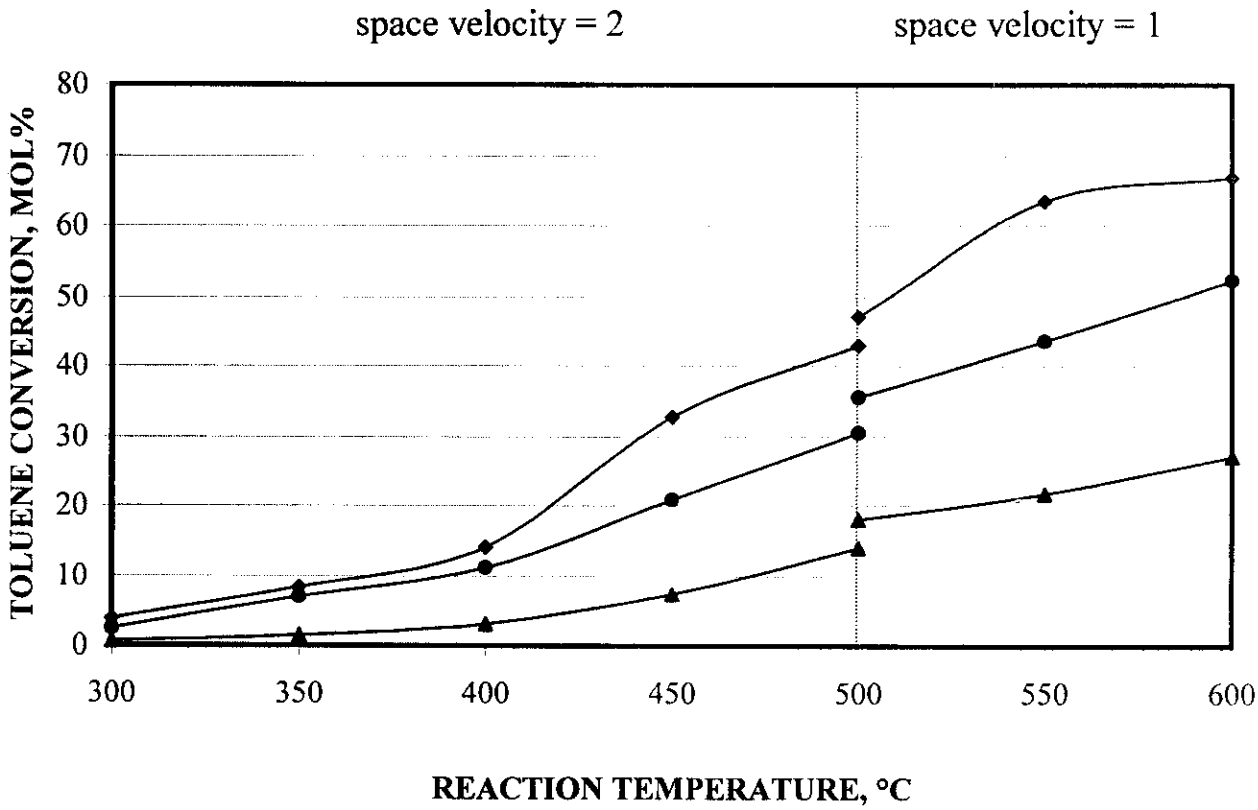


Fig.26 TOTAL TOLUENE CONVERSION AT DIFFERENT REACTION TEMPERATURES AND SPACE VELOCITIES FOR TOLUENE DISPROPORTIONATION REACTION ON DA-HZSM-5 (4h), SILICONIZED & DOUBLE SILICONIZED CATALYSTS

—◆— DA-H-ZSM-5, (4h), cat.4 —●— siliconized DA-H-ZSM-5, (4h), cat.4*
—▲— double siliconized DA-H-ZSM-5, (4h), cat.4**

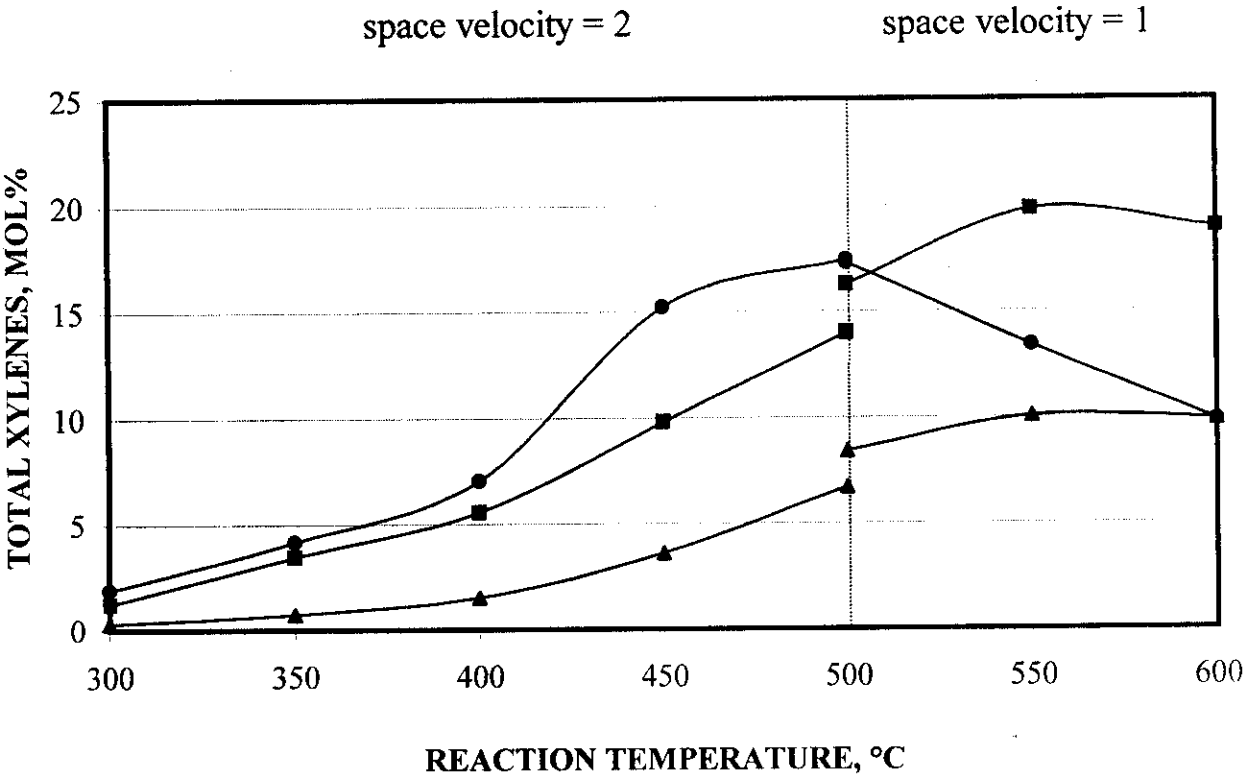


Fig.27 TOTAL XYLENES YIELD AT DIFFERENT REACTION TEMPERATURES AND SPACE VELOCITIES FOR TOLUENE DISPROPORTIONATION REACTION ON DA-HZSM-5 (4h), SILICONIZED & DOUBLE SILICONIZED CATALYSTS

—●— DA-H-ZSM-5, (4h), cat.4 —■— siliconized DA-H-ZSM-5, (4h), cat.4*
—▲— double siliconized DA-H-ZSM-5, (4h), cat.4**

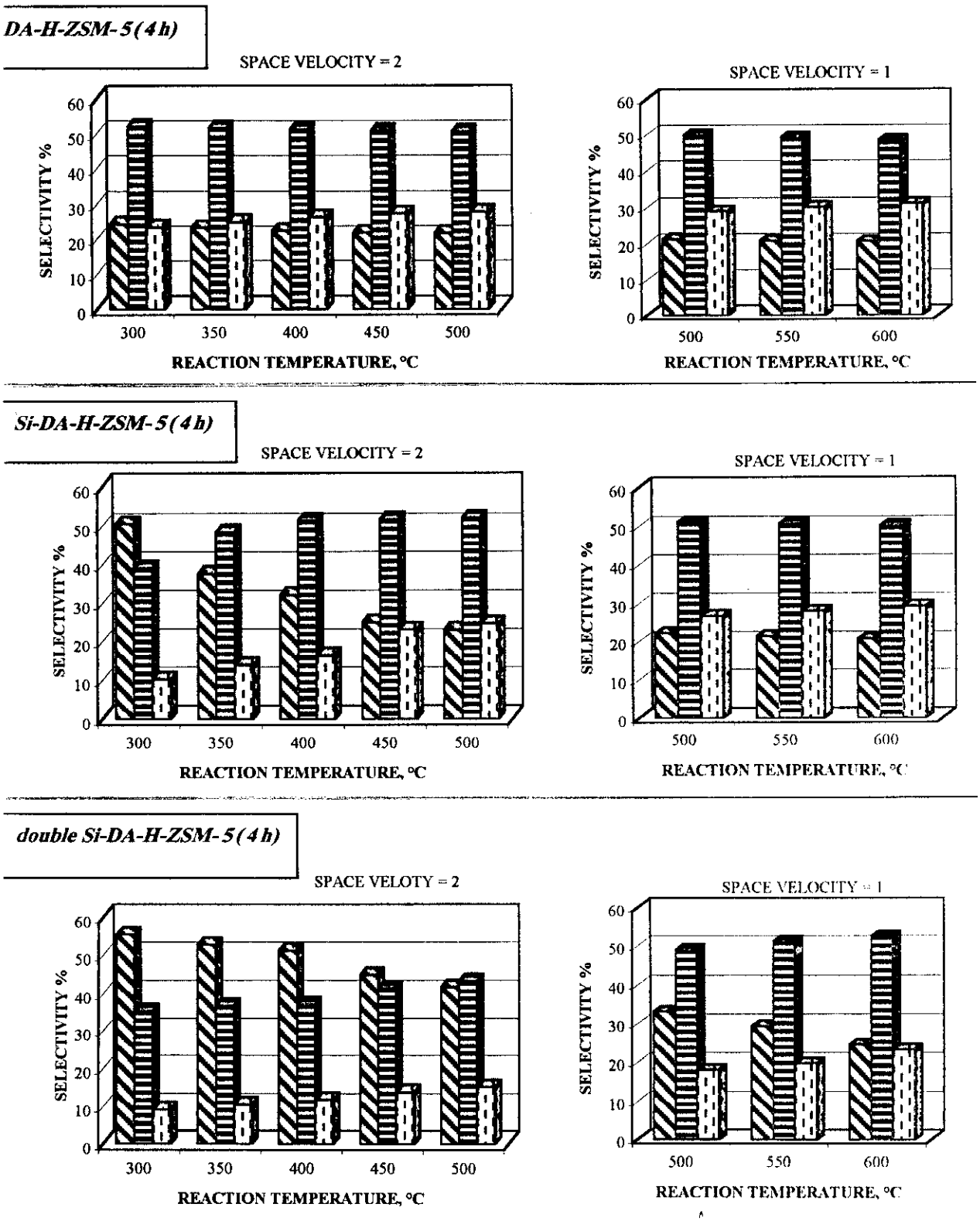


Fig.28 SELECTIVITY OF XYLENE ISOMERS AT DIFFERENT REACTION TEMPERATURES AND SPACE VELOCITIES OF TOLUENE DISPROPORTIONATION REACTION ON DA-HZSM-5 (4h), SILICONIZED & DOUBLE SILICONIZED CATALYSTS

P-XYLENE M-XYLENE O-XYLENE

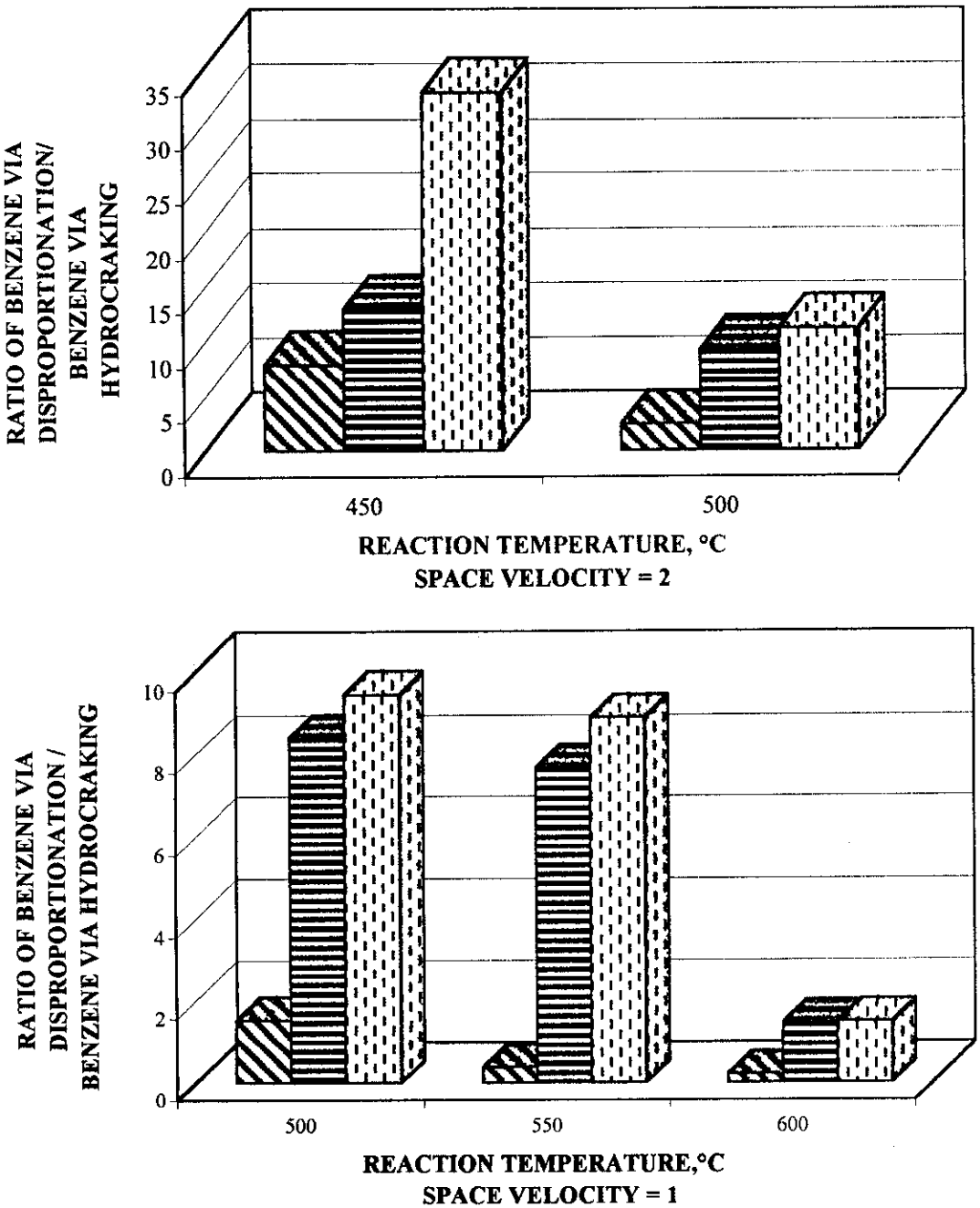


Fig.29 RATIO OF BENZENE VIA DISPROPORTIONATION, MOL% / BENZENE VIA HYDROCRAKING,MOL% AT DIFFERENT REACTION TEMPERATURES AND SPACE VELOCITIES FOR TOLUENE DISPROPORTIONATION REACTION ON DA-HZSM-5 (4h), SILICONIZED & DOUBLE SILICONIZED CATALYSTS.

DA-H-ZSM-5 siliconized DA-H-ZSM-5 double siliconized DA-H-ZSM-5

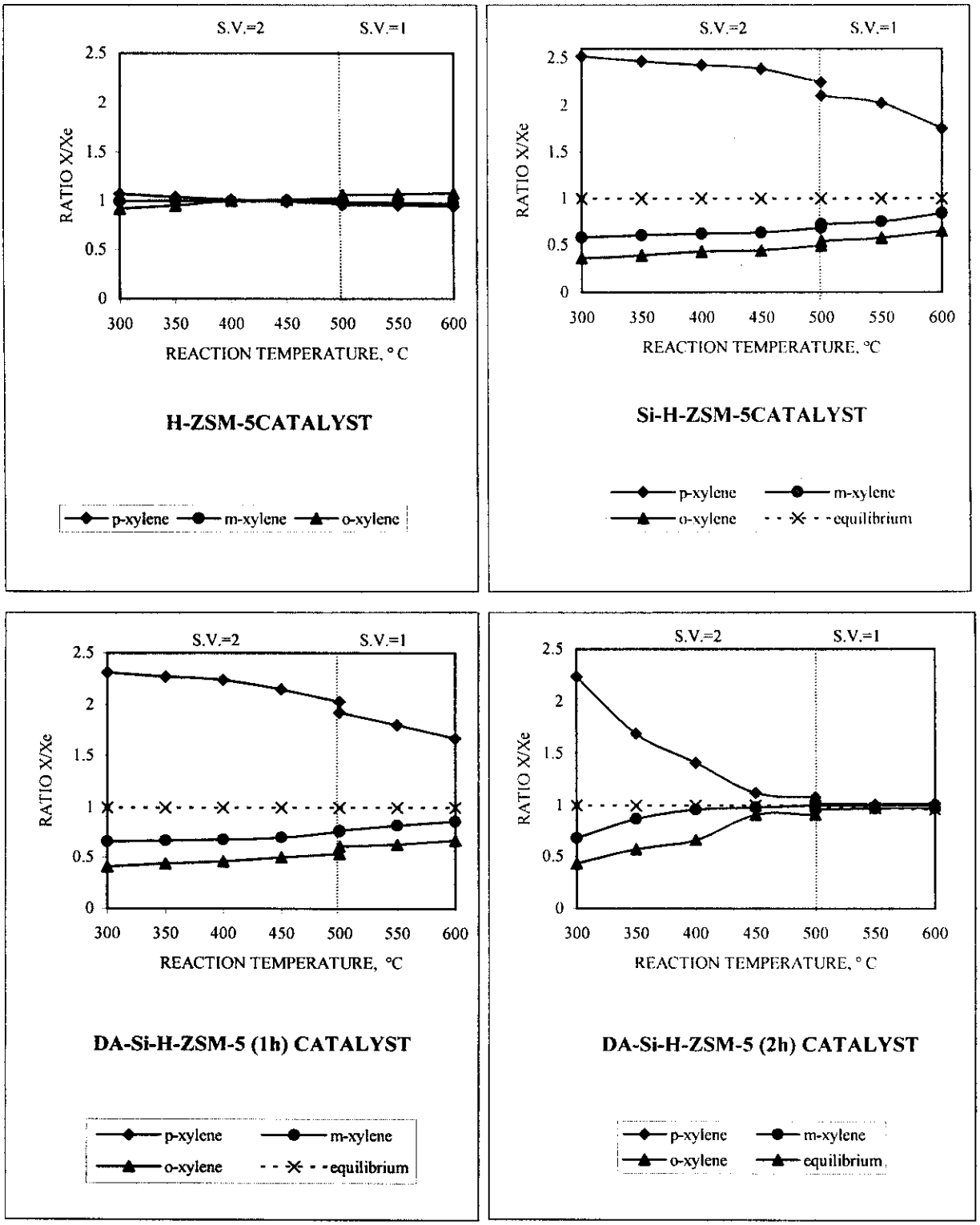
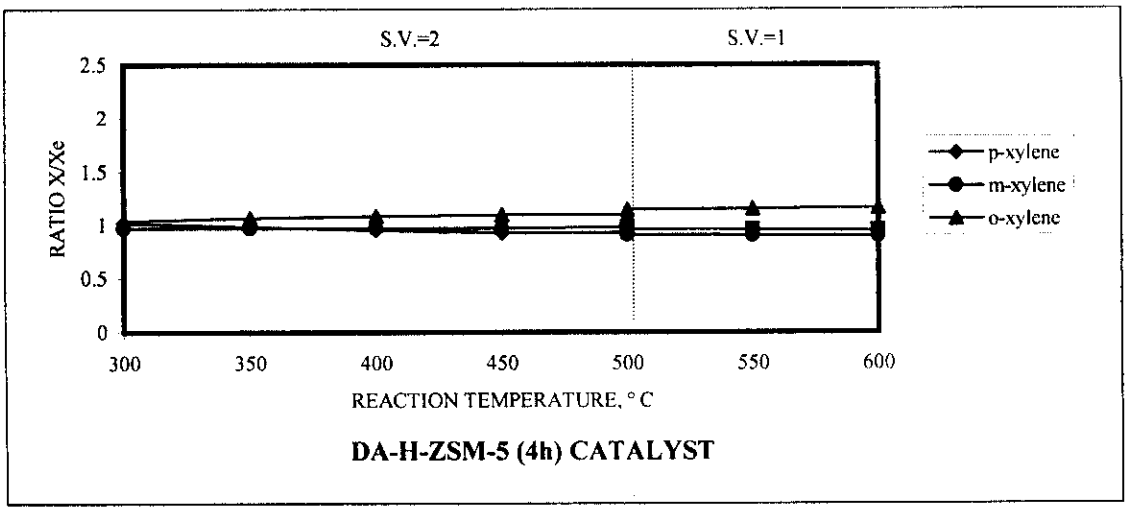
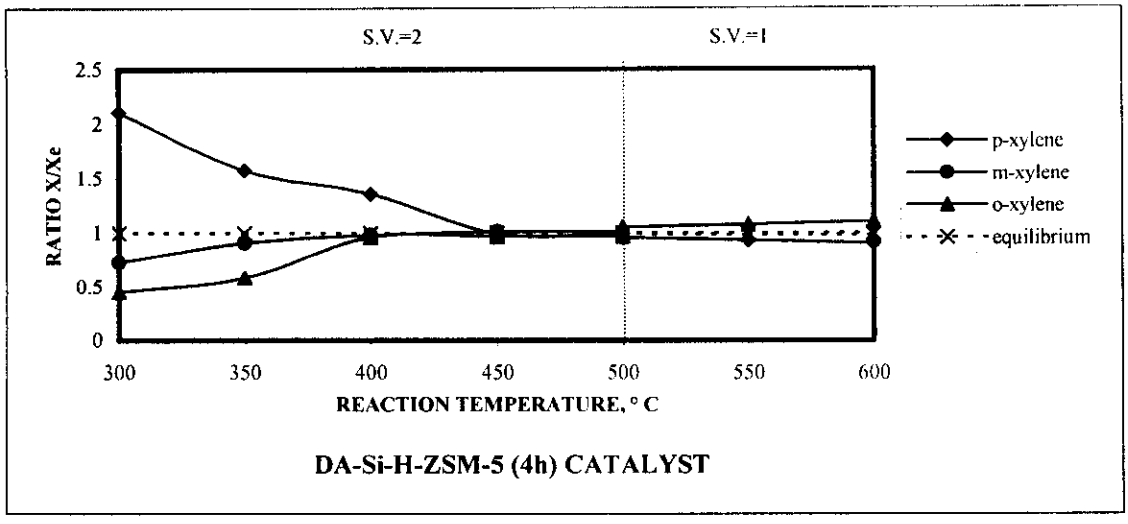


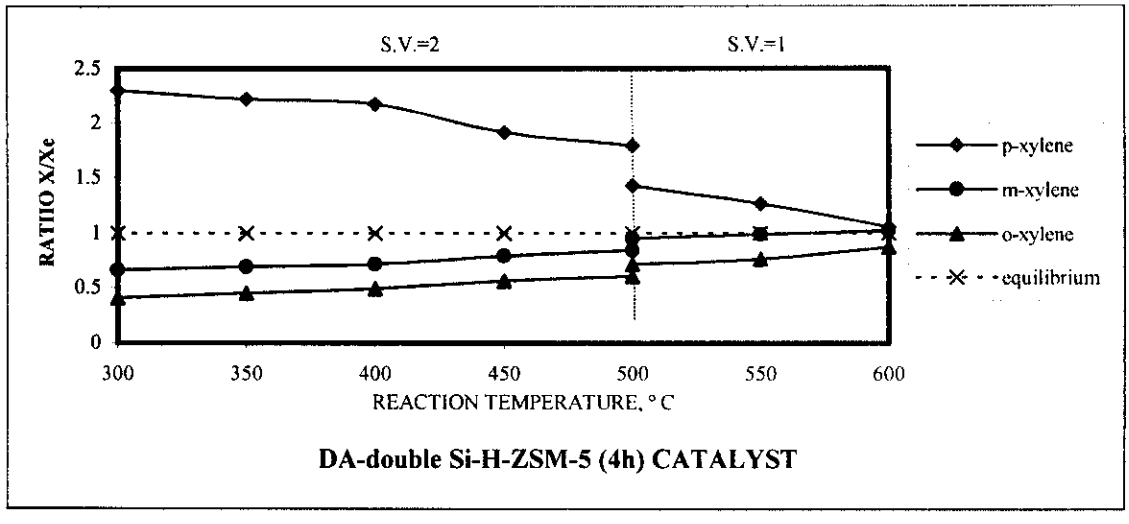
Fig.30 COMPARISON OF O-, M- AND P-XYLENE SELECTIVITY FOR TOLUENE DISPROPORTIONATION REACTION RELATIVE TO THEIR THERMODYNAMIC EQUILIBRIUM (X/Xe)



DA-H-ZSM-5 (4h) CATALYST



DA-Si-H-ZSM-5 (4h) CATALYST



DA-double Si-H-ZSM-5 (4h) CATALYST

3.2. TOLUENE DISPROPORTIONATION REACTION OVER H-MORDENITE CATALYST:

Fig.31 shows that toluene conversion ranges between 2.04% and 32.28 mol% at temperatures ranging between 300 and 500°C and a space velocity of 2.0 g $g^{-1}h^{-1}$. However, at more severe conditions; 500 - 600°C and a WHSV of 1.0 g $g^{-1}h^{-1}$, the conversion of toluene decreases sharply to range between 9.76% and 29.45 mol%, respectively, which may be attributed to deactivation of the catalyst as a result of coke formation at high temperatures [55].

Fig. 32 shows a total xylenes yield which ranges between 1.02% and 12.99 mol% at temperature of 300 and 500°C and a space velocity of 2.0 g $g^{-1}h^{-1}$.while at severe conditions, the xylenes yield is decreased to 4.6 mol% at temperature of 500°C and 14.14 mol% at temperature of 600°C (due to formation of coke).

The selectivity of p-, m- and o-xylene do not widely differ from their value at thermodynamic equilibrium (Table 2). For instance, the selectivity of p-xylene at a space velocity of 2.0 g $g^{-1}h^{-1}$ and temperature of 300°C is 24.65% and at temperature of 500°C is 21.93% (Fig.33). However, these selectivities at thermodynamic equilibrium are 23.88% and 23.19%.

The total benzene yield ranges between 1.02% and 18.24 mol% at temperatures ranging between 300 and 500°C, respectively, using a space velocity of 2.0 g $g^{-1}h^{-1}$ (Fig. 34) (Table 11).

3.2.1. EFFECT OF SILICONIZATION OF H-MORDENITE CATALYST ON THE DISPROPORTIONATION OF TOLUENE:

Addition of silicon to H-mordenite catalyst give the same behaviour as that encountered using the H-ZSM-5 zeolite, where silicon mask a part of the strong acid sites and leads to a decrease of the activity of the mordenite catalyst as manifested by decreasing toluene conversion (Table 12) (Fig.31).

Total xylenes yield also decrease from 1.02% to 0.3 mol% at temperature of 300°C and from 12.99% to 5.29 mol% at temperature of 500°C using a space velocity of 2.0 g $g^{-1}h^{-1}$. At space velocity of 1.0 g $g^{-1}h^{-1}$ total xylenes decrease from 4.6% to 2.2 mol% at temperature of 500°C and from 14.14% to 7.0 mol% at temperature of 600°C (Fig.32).

The selectivity of p-xylene increases sharply with addition of silicon where it increases from 24.65% to 56.78% at temperature of 300°C and from 21.93% to 26.31% at temperature of 500°C and a space velocity of 2.0 g $g^{-1}h^{-1}$.however, at space velocity of 1.0 g $g^{-1}h^{-1}$, selectivity of p-xylene increases from 22.97% to 28.04 % at temperature of 500°C and from 21.08% to 26.17% at temperature of 600°C (Fig.33).

TABLE. 11. TOLUENE DISPROPORTIONATION USING H-MORDENITE CATALYST - CATALYST (5)

SPACE VELOCITY	2					1		
TEMPERATURE, C° / ITEMS	300	350	400	450	500	500	550	600
CONVERSION, MOL%	2.04	5.16	7.71	17.48	32.28	9.76	17.12	29.45
DISTRIBUTION OF LIQIUD PRODUCTS, WT% :								
BENZENE	0.87	2.19	3.38	7.64	15.56	4.38	7.55	12.88
TOLUENE	97.94	94.84	92.32	82.57	68.11	90.31	82.97	70.64
ETHYL BENZENE	0.00	0.00	0.00	0.17	0.72	0.00	0.00	0.16
p-XYLENE	0.29	0.71	0.99	2.09	3.30	1.22	2.12	3.44
m-XYLENE	0.64	1.60	2.30	5.00	7.96	2.86	5.00	8.55
o-XYLENE	0.25	0.66	1.01	2.32	3.79	1.24	2.36	4.33
TOTAL XYLENES%	1.19	2.97	4.30	9.41	15.05	5.31	9.48	16.32
TRIMETHYLBENZENES	0.00	0.00	0.00	0.21	0.56	0.00	0.00	0.00
DISTRIBUTION OF XYLENES % :								
p-XYLENE	24.65	23.88	22.91	22.22	21.93	22.97	22.37	21.08
m-XYLENE	54.05	53.88	53.56	53.14	52.92	53.77	52.69	52.36
o-XYLENE	21.30	22.24	23.53	24.64	25.15	23.26	24.94	26.56
DISTRIBUTION OF LIQIUD PRODUCTS, MOLE% :								
BENZENE (VIA DISPROPORTIONATION)	1.02	2.58	3.73	8.31	13.61	4.60	8.22	14.28
BENZENE (VIA HYDROCRACKING)	0.00	0.00	0.25	0.70	4.63	0.56	0.68	0.89
TOTAL BENZENE	1.02	2.58	3.98	9.01	18.24	5.16	8.90	15.17
TOLUENE	97.96	94.84	92.29	82.52	67.72	90.24	82.88	70.55
ETHYL BENZENE	0.00	0.00	0.00	0.15	0.62	0.00	0.00	0.14
p-XYLENE	0.25	0.62	0.85	1.81	2.85	1.06	1.84	2.98
m-XYLENE	0.55	1.39	2.00	4.34	6.87	2.47	4.33	7.40
o-XYLENE	0.22	0.57	0.88	2.01	3.27	1.07	2.05	3.76
TOTAL XYLENES	1.02	2.58	3.73	8.16	12.99	4.60	8.22	14.14
C8 AROMATICS	1.02	2.58	3.73	8.31	13.61	4.60	8.22	14.28
TRIMETHYLBENZENES	0.00	0.00	0.00	0.16	0.43	0.00	0.00	0.00

TABLE. 12. TOLUENE DISPROPORTIONATION USING SILICONIZED H-MORDENITE CATALYST - CATALYST (5)*

SPACE VELOCITY	*2*					*1*		
TEMPERATURE, C° / *ITEMS*	**300**	**350**	**400**	**450**	**500**	**500**	**550**	**600**
CONVERSION, MOL%	0.60	1.50	2.60	4.89	12.15	4.51	8.07	14.25
DISTRIBUTION OF LIQIUD PRODUCTS, WT% :								
BENZENE	0.26	0.64	1.10	2.15	5.83	1.96	3.43	6.15
TOLUENE	99.38	98.50	97.41	95.14	88.06	95.50	91.99	85.78
ETHYL BENZENE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
p-XYLENE	0.20	0.43	0.61	0.90	1.61	0.71	1.28	2.11
m-XYLENE	0.13	0.32	0.65	1.37	3.13	1.28	2.31	4.06
o-XYLENE	0.03	0.11	0.23	0.45	1.37	0.55	1.00	1.90
TOTAL XYLENES%	0.36	0.86	1.49	2.71	6.11	2.54	4.58	8.07
TRIMETHYLBENZENES	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
DISTRIBUTION OF XYLENES % :								
p-XYLENE	56.78	50.10	40.85	33.10	26.31	28.04	27.89	26.17
m-XYLENE	35.72	36.92	43.59	50.37	51.27	50.45	50.38	50.34
o-XYLENE	7.50	12.98	15.56	16.53	22.42	21.51	21.73	23.49
DISTRIBUTION OF LIQIUD PRODUCTS, MOLE% :								
BENZENE (VIA DISPROPORTIONATION)	0.30	0.75	1.30	2.35	5.29	2.20	3.96	7.00
BENZENE (VIA HYDROCRACKING)	0.00	0.00	0.00	0.19	1.57	0.11	0.15	0.25
TOTAL BENZENE	0.30	0.75	1.30	2.54	6.86	2.31	4.11	7.25
TOLUENE	99.40	98.50	97.40	95.11	87.85	95.49	91.93	85.75
ETHYL BENZENE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
p-XYLENE	0.17	0.38	0.53	0.78	1.39	0.62	1.10	1.83
m-XYLENE	0.11	0.28	0.57	1.18	2.71	1.11	2.00	3.52
o-XYLENE	0.02	0.10	0.20	0.39	1.19	0.47	0.86	1.64
TOTAL XYLENES	0.30	0.75	1.30	2.35	5.29	2.20	3.96	7.00
C8 AROMATICS	0.30	0.75	1.30	2.35	5.29	2.20	3.96	7.00
TRIMETHYLBENZENES	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

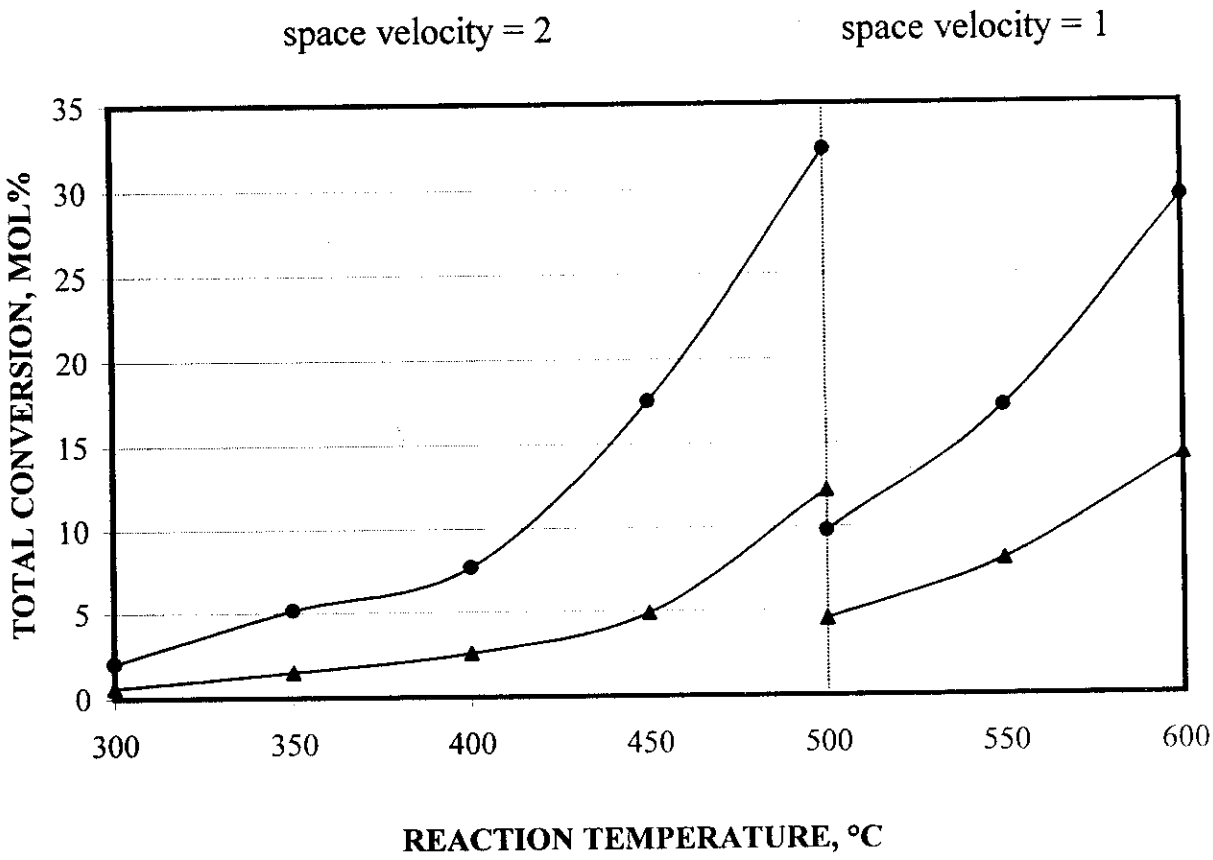


Fig.31 TOTAL TOLUENE CONVERSION, MOL% AT DIFFERENT REACTION TEMPERATURES AND SPACE VELOCITIES FOR TOLUENE DISPROPORTIONATION REACTION ON H-M AND Si-H-M CATALYSTS

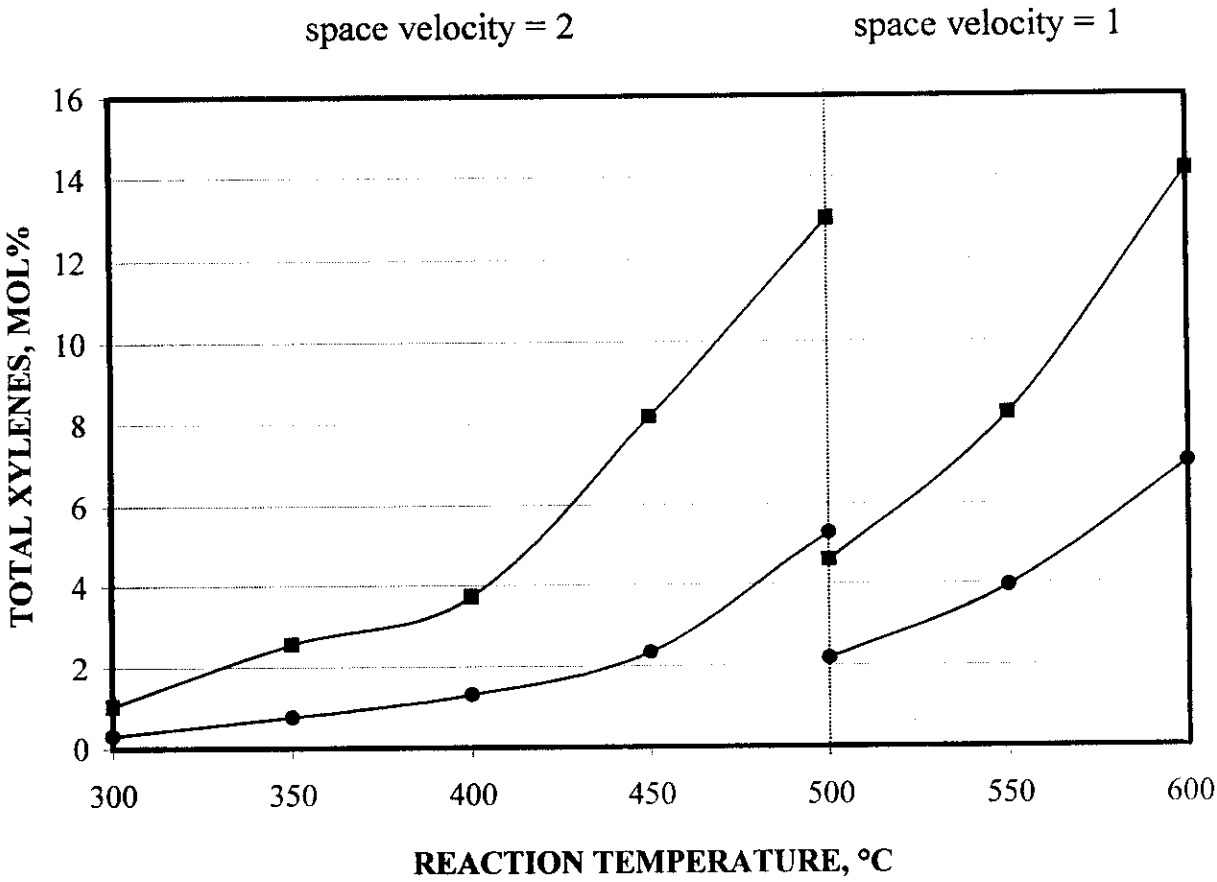
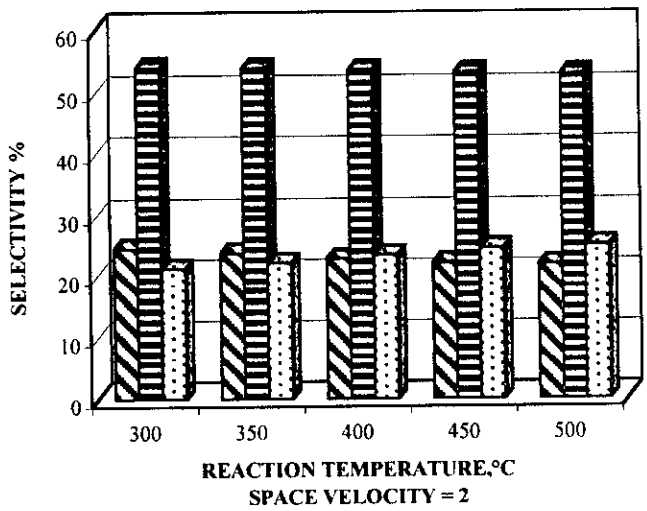
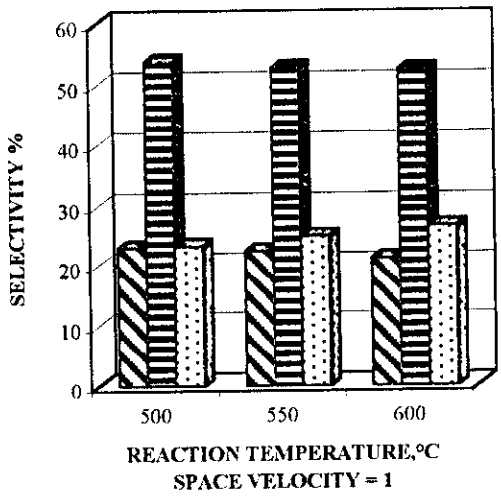


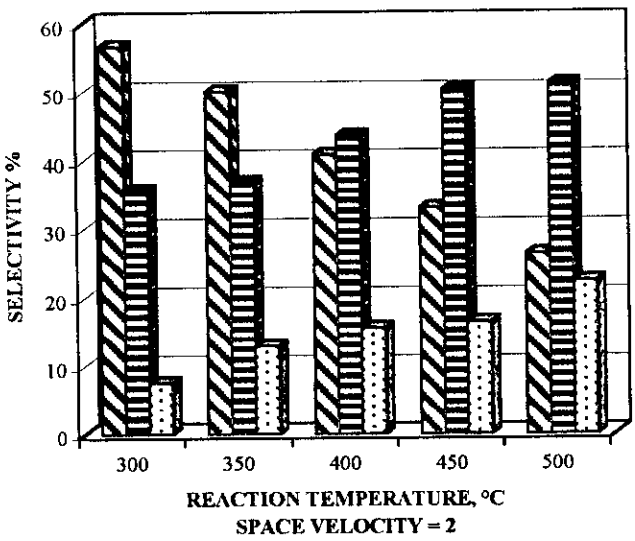
Fig.32 TOTAL XYLENES YIELD, MOL% AT DIFFERENT REACTION TEMPERATURES AND SPACE VELOCITIES FOR TOLUENE DISPROPORTIONATION REACTION ON H-M AND Si-H-M CATALYSTS

H-MORDENITE





Si-H-MORDENITE



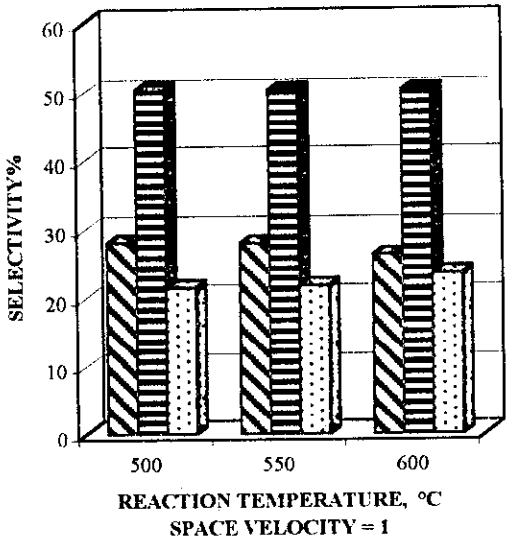


Fig. 33 SELECTIVITY OF XYLENE ISOMERS AT DIFFERENT REACTION TEMPERATURES AND SPACE VELOCITIES FOR TOLUENE DISPROPORTIONATION REACTION ON H-M AND Si-H-M CATALYSTS

▨ p-xylene ▤ m-xylene ▥ o-xylene

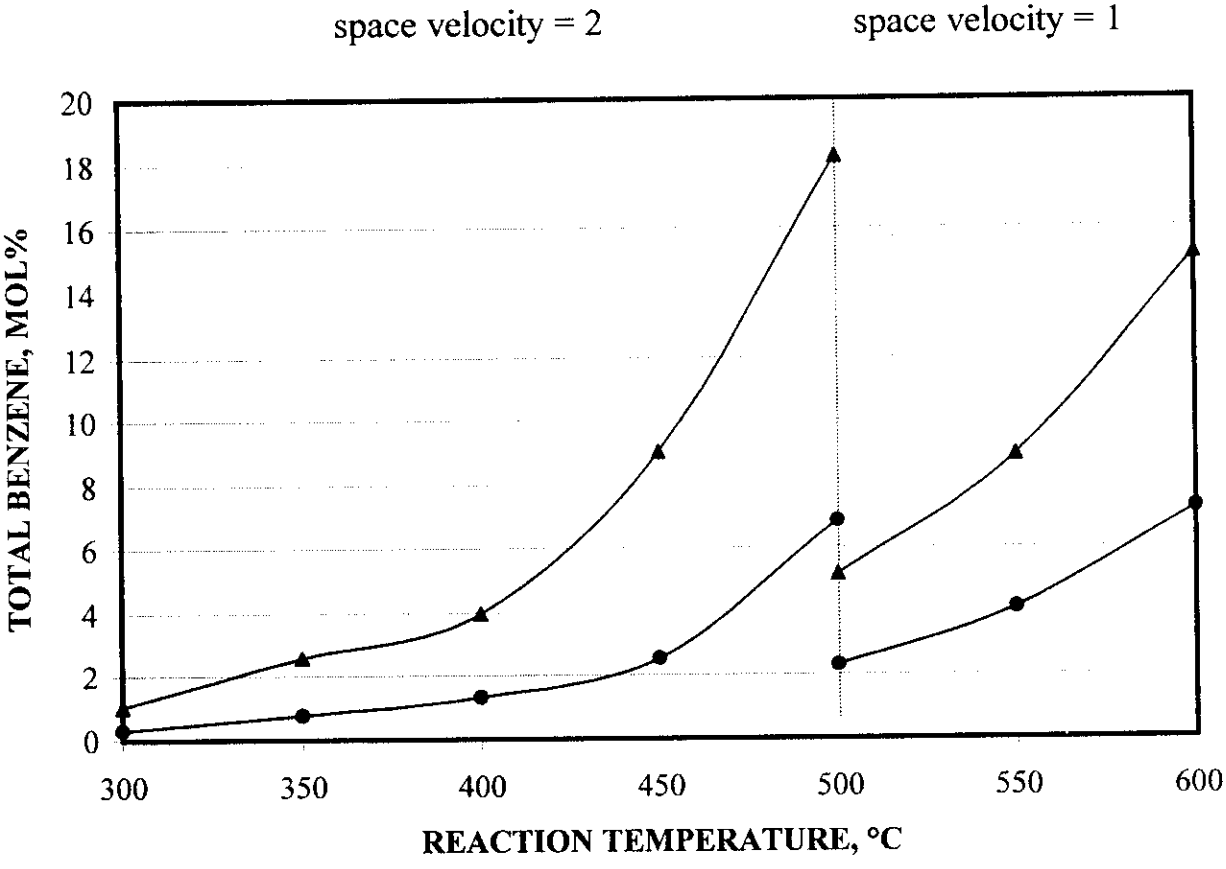


Fig.34 TOTAL BENZENE YIELD, MOL% AT DIFFERENT REACTION TEMPERATURES AND SPACE VELOCITIES FOR TOLUENE DISPROPORTIONATION REACTION ON H-M AND Si-H-M CATALYSTS

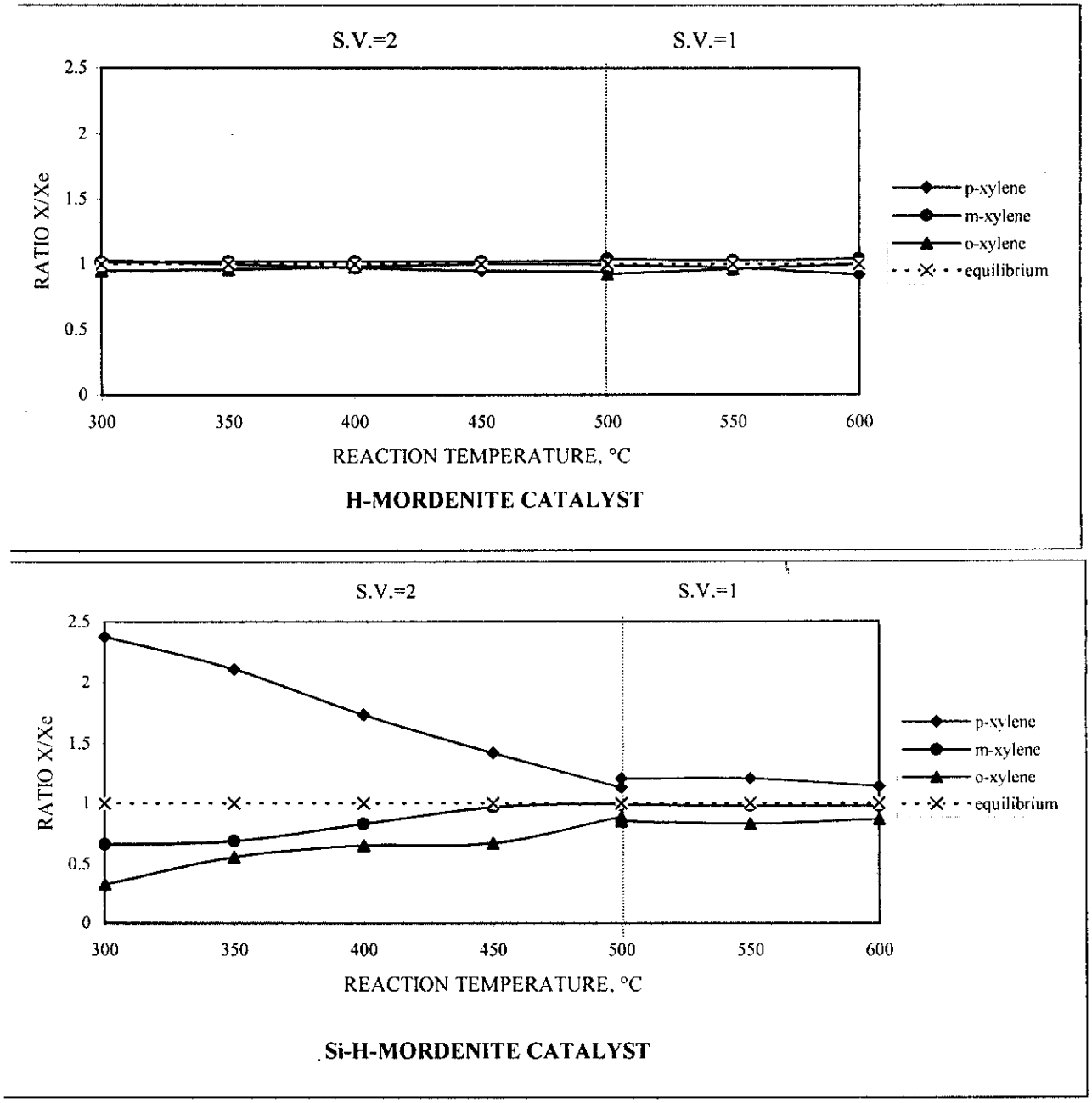
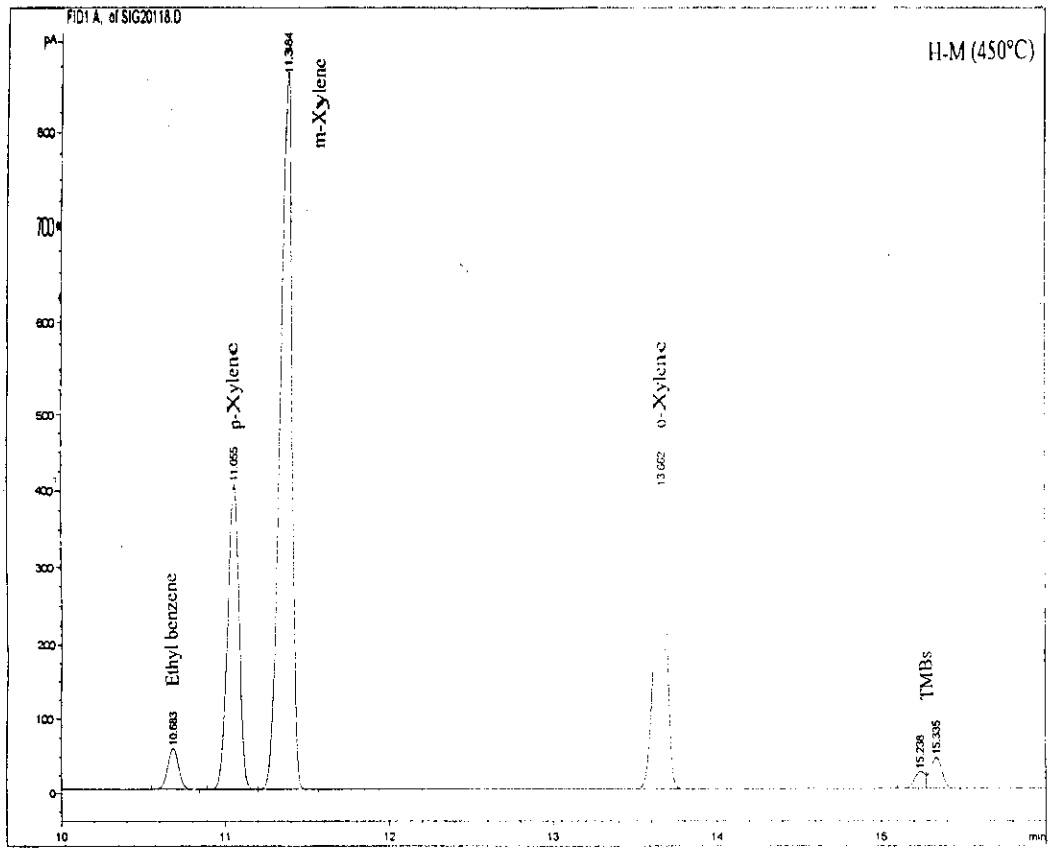


Fig 35 COMPARISON OF O-, M- AND P-XYLENE SELECTIVITY FOR TOLUENE DISPROPORTIONATION REACTION RELATIVE TO THEIR THERMODYNAMIC EQUILIBRIUM (X/Xe)



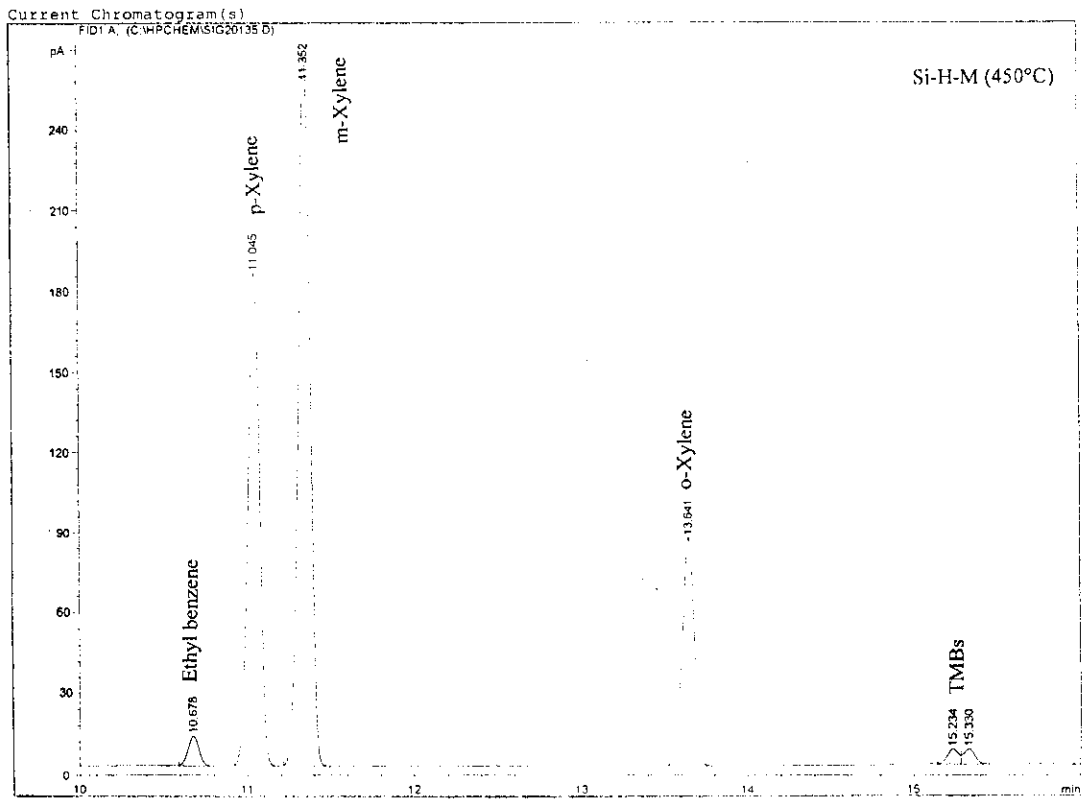


FIG.36 GAS CHROMATOGRAM OF THE C_8 & C_9 AROMATIC PRODUCT USING H-MOR & Si- H-MOR CATALYSTS, (REACTION TEMPERATURE = 450°C; SPACE VELOCITY = 2.0 $g\ g^{-1}\ h^{-1}$)

3.3. THREE COMPONENET SELECTIVITY OF XYLENE ISOMERS: -

All points representing the isomers distribution in the triangular plot (Fig.37 a), show a significant gathering towards the m-isomer. The position of these points in the plot do not differ significantly from those calculated at the thermodynamic equilibrium at various reaction temperatures.

Fig.b shows that siliconization of the H-ZSM-5 zeolite with the silicon grease has shifted the position of the points in the triangle to the higher percentages of the p-xylene isomer, indicating a better para-selectivity. At the same time the points are shifted to lower o- and m-isomers.

Fig.c acquire points insignificantly different from the m-isomer. This substantiates the single treatment of the zeolite siliconization alone. The combination of dealumination with siliconization does not exhibit improvement of the p-selectivity.

Again, a longer dealumination of 4h appears to decrease the p-selectivity, whereby a larger shift of the points towards the m-isomer occurs. The dealumination has yet an important advantage although it does not improve the para-selectivity. This advantage is related to the increase of the total xylenes in product. Dealumination widens the channels and increases the acidity strength. Both characteristics are in favor of decreasing the p-selectivity but in favor of increasing the total xylenes production, (see Fig.37 e-g).

Fig. h & i show that using H-MOR zeolite, the p-xylene selectivity at space velocity of 1.0 $g\ g^{-1}h^{-1}$ does not significantly differ from that obtained

obtained using the siliconized catalyst. However at a space velocity of 2.0 g $g^{-1}h^{-1}$, the para–selectivity has evidently increased and the points on plot i are shifted towards the p-xylene corner in the plot. It is to be pointed out that the production of xylenes on the H-MOR catalysts are lower than on the H-ZSM-5 catalysts.

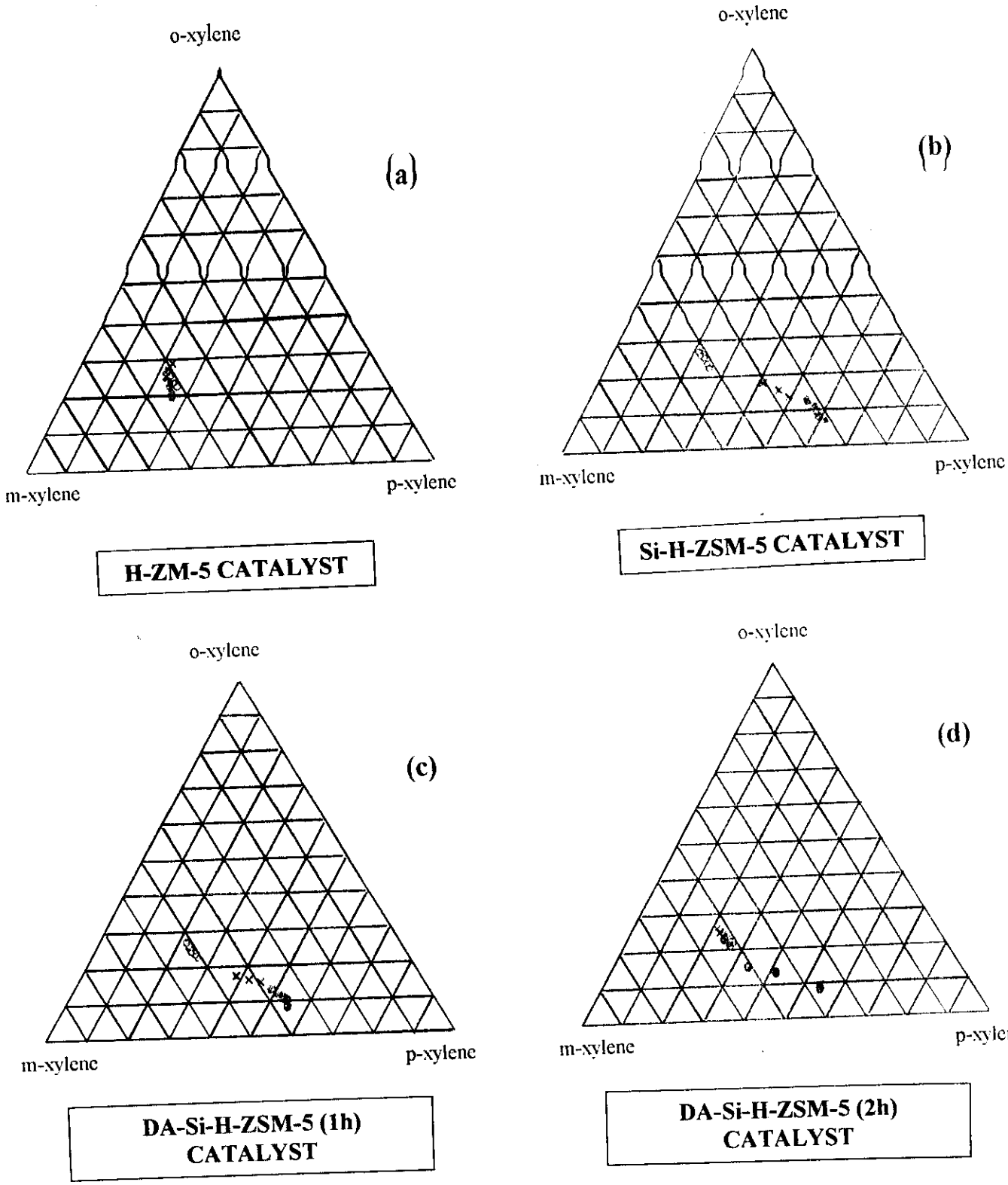
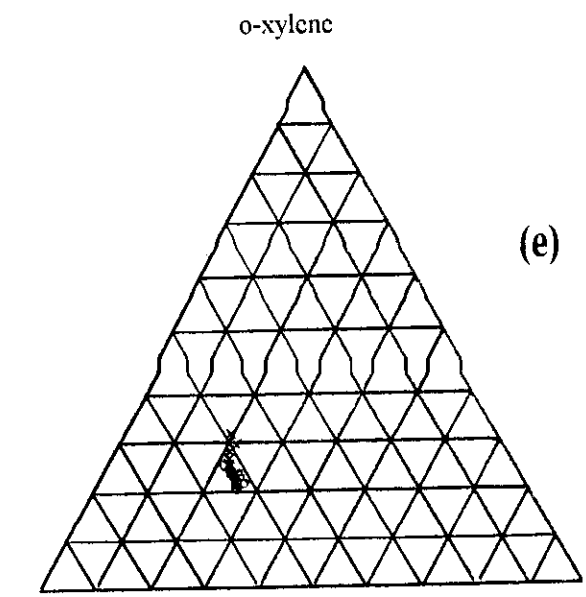
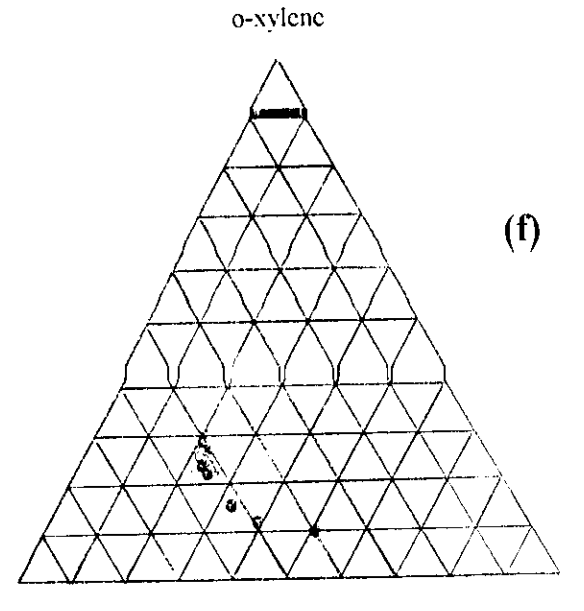


Fig. 37 THREE COMPONENT SELECTIVITY PLOTS OF XYLENE ISOMERS.



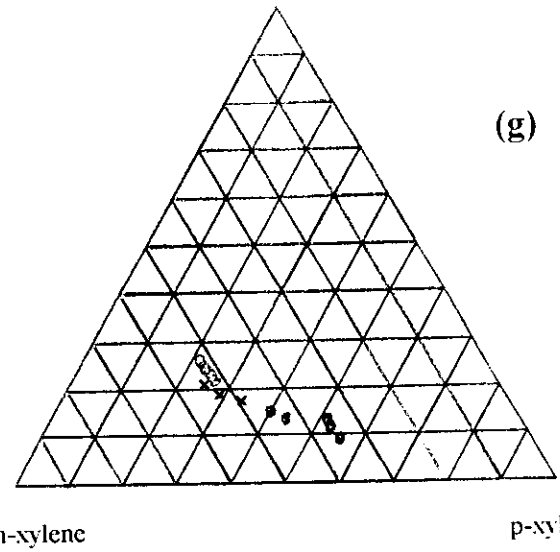
(e)

DA-H-ZSM-5 (4h) CATALYST



(f)

DA-Si-H-ZSM-5 (4h) CATALYST

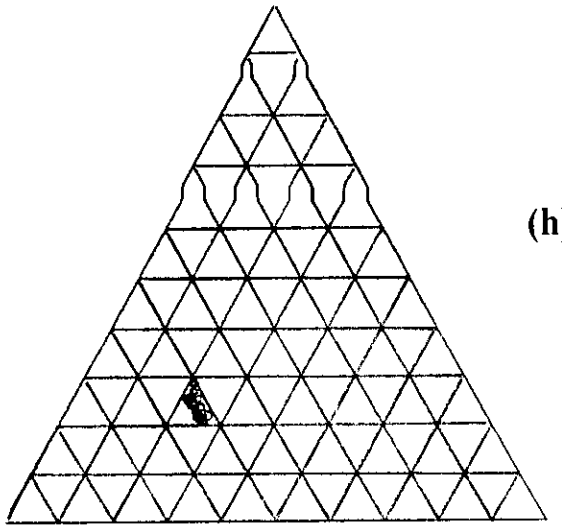


(g)

DA-DOUBLE Si-H-ZSM-5 (4h) CATALYST

SPACE VELOCITY = 1	×
SPACE VELOCITY = 2	•
AT EQUILIBRIUM	o

o-xylene

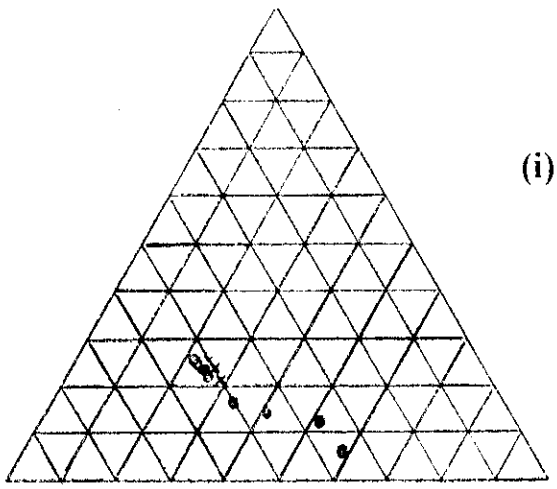


(h)

m-xylene p-xylene

H-MORDENITE CATALYST

o-xylene



(i)

m-xylene p-xylene

Si-H-MORDENITE CATALYST

SPACE VELOCITY = 1	×
SPACE VELOCITY = 2	•
AT EQUILIBRIUM	o

3.4. Kinetic study

The reaction rate has been evaluated as mole toluene converted per gm catalyst per hour.

For a space velocity of 1.0 g $g^{-1}h^{-1}$, molar rate = 3 x 10^{-6} mol toluene g^{-1}catalyst s^{-1}. Also for a space velocity of 2.0 g $g^{-1}h^{-1}$, molar rate = 6 x 10^{-6} mol toluene g^{-1}catalyst s^{-1}

The r-values obtained are given in Table 15, and the activation energy, E_a, has been calculated according to the Arrhenius equation.

$$r = A\ e^{-Ea/RT}$$

$$Lnr = LnA + \frac{Ea}{R} \bullet \frac{1}{T}$$

Where A is the preexponential factor.

R is the universal gas constant.

T is absolute reaction temperature.

Plots of Ln r vs. 1/T are given in Figs.38, 39, 40 and 41 whereby the E_a values are calculated and listed in Table 16.

The E_a value obtained for the overall reactivity of toluene at a space velocity of 2.0 g $g^{-1}h^{-1}$ using all catalysts containing H-ZSM-5 as well as its silicon incorporating version, whether primarily dealuminated or not, give almost the same

value (~ 11.0 k cal $mole^{-1}$). Only, catalyst 4** which has been siliconized twice gives a somewhat high E_a value (13,47 k cal $mole^{-1}$) indicating that excessive Si has been deposited in the zeolitic channels and significantly decreased the reaction rate at all temperatures, and in particular at lower temperatures.

At high severity (temperatures of 500 - 600°C and a WHSV of 1.0 g $g^{-1}h^{-1}$) much lower E_a values (approximately half the E_a values obtained at the lower severity) are obtained, indicating that physical factors are encountered during the process.

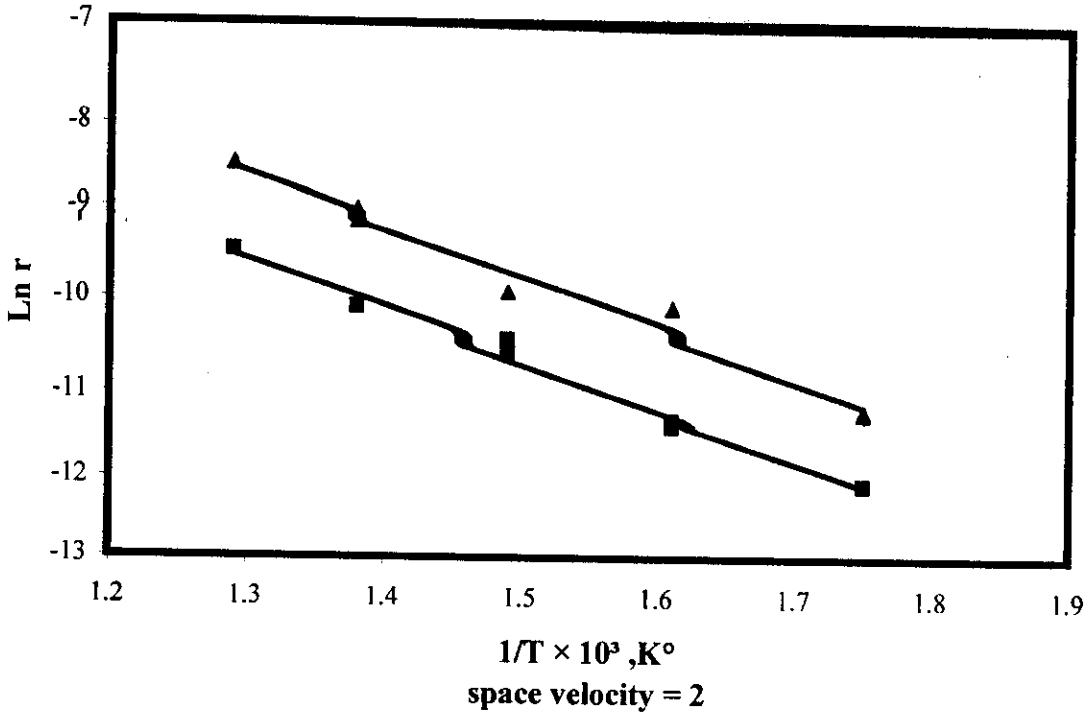
Diffusion limitation is the most predominant effective factor since the main products are of a large molecular weight (xylenes) than the feeding material (toluene). This is substantiated on comparing the E_a values obtained using the H-ZSM-5 versions as catalysts and those including H-MOR as catalysts. The latter zeolite is a large pore one and diffusion throughout these pores are not significantly restricted. Hence, on the mordenite catalysts, E_a is ~16.0 k cal $mole^{-1}$ at the high temperature and low space velocity conditions, which may be attributed to enhanced coke deposition in the pores of H-MOR. Silicon in H-MOR does not affect E_a values.

BLE. 13 RATE OF TOLUENE CONVERSION, r, USING THE H-ZSM-5 AND H-MORDENITE CATALYSTS AT VARIOUS REACTION TEMPERATURES.

catalysts	*space velocity =2*					*space velocity = 1*		
	Rate X 10^5					*Rate X 10^5*		
TEMPERATURE, K°	573	623	673	723	773	773	823	873
H-ZSM-5, cat. 1	1.37	4.07	4.91	11.99	20.49	12.32	16.02	18.48
*Siliconized H-ZSM-5, cat. 1**	0.58	1.2	2.76	4.06	8.23	5.83	7.4	8.74
*Siliconized DA-H-ZSM-5, (1h), cat. 2**	0.79	1.58	2.83	5.45	10.15	6.4	8.19	9.56
*Siliconized DA-H-ZSM-5, (2h), cat. 3**	1.31	2.48	4.12	10.63	15.06	9.62	11.97	14.02
*Siliconized DA-H-ZSM-5, (3h), cat. 4**	1.48	3.65	6.69	12.49	18.32	10.65	13.07	15.65
DA-H-ZSM-5, (3h), cat. 4	2.28	5.03	8.48	19.57	25.57	14.13	19.04	20.06
*Double siliconized DA-H-ZSM-5, (3h), cat 4***	0.38	0.88	1.84	4.4	8.44	5.43	6.52	8.06
H-Mordenite, cat.5	1.22	3.09	4.64	10.5	19.37	2.93	5.13	8.83
*Siliconized H-Mordenite, cat.5**	0.36	0.9	1.55	2.93	7.29	1.35	2.4	4.3

TABLE. 14 ACTIVATION ENERGY OF TOLUENE CONVERSION REACTION, E_a USING THE H-ZSM-5 AND H-MORDENITE CATALYSTS AT VARIOUS REACTION TEMPERATURES

CATALYSTS	***activation energy , kcal space velocity = 2***	***activation energy , kcal space velocity = 1***
H-ZSM-5, cat. 1	11.29	5.76
*Siliconized H-ZSM-5, cat. 1**	11.35	5.86
*Siliconized DA-H-ZSM-5, (1h), cat. 2**	10.98	5.73
*Siliconized DA-H-ZSM-5, (2h), cat. 3**	10.96	5.57
*Siliconized DA-H-ZSM-5, (3h), cat. 4**	10.92	5.41
DA-H-ZSM-5, (3h), cat. 4	10.81	5.12
*Double siliconized DA-H-ZSM-5, (3h), cat 4***	13.47	5.66
H-Mordenite,cat.5	11.68	16.2
*Siliconized H-Mordenite, cat.5**	12.4	16.31



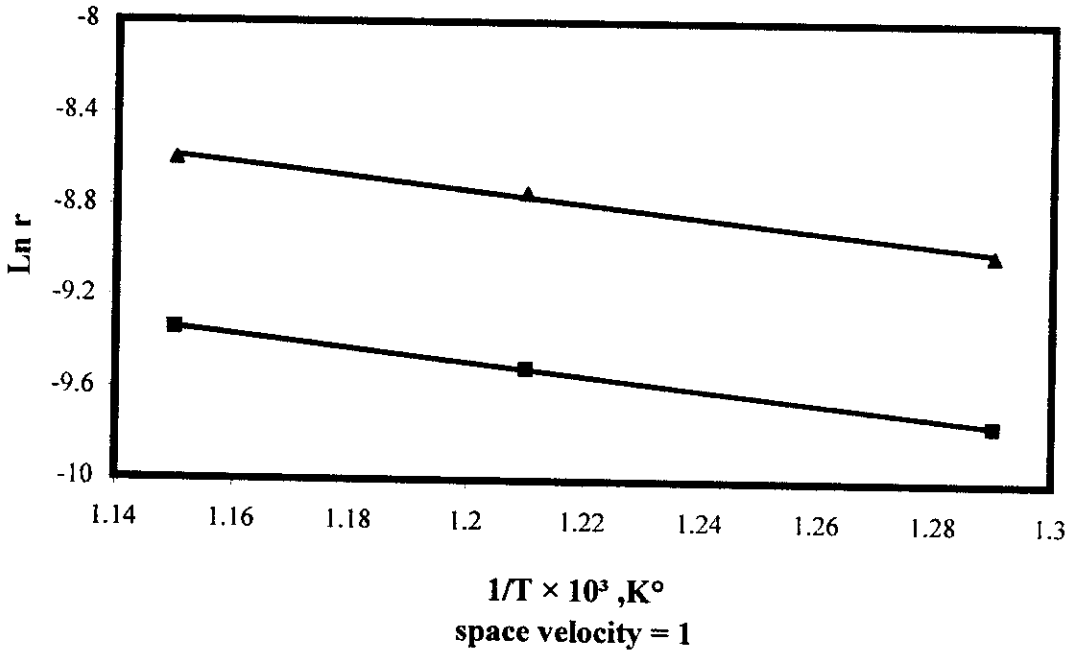


Fig. 38 ARRHENIUS PLOT FOR TOLUENE DISPROPORTIONATION ON H-ZSM-5 AND SILICONIZED H-ZSM-5 CATALYSTS

▲ H-ZSM-5, cat.1 ■ siliconized.H-ZSM-5, cat.1*

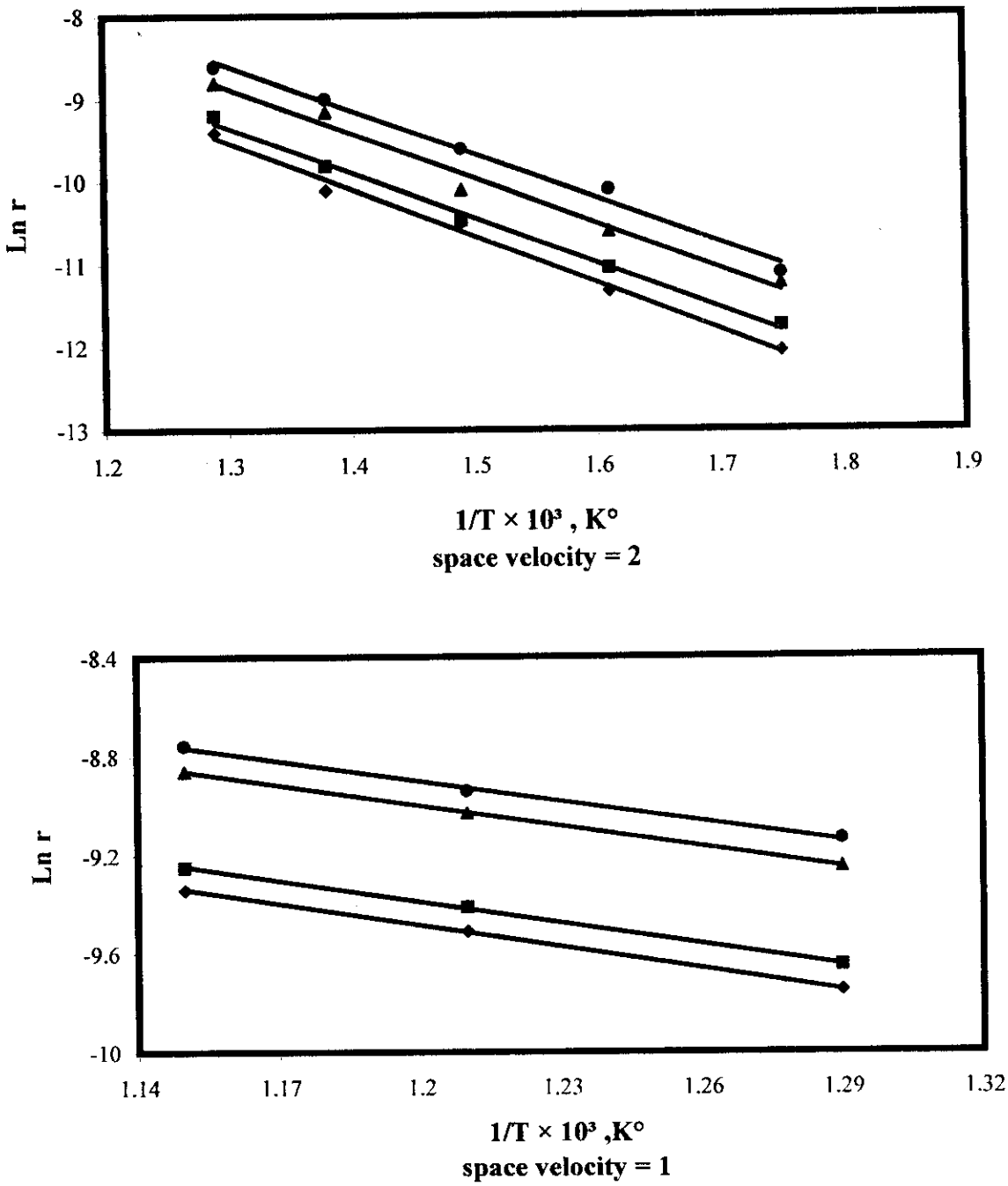


Fig. 39 ARRHENIUS PLOT FOR TOLUENE DISPROPORTIONATION ON SILICONIZED DEALUMINATED CATALYSTS

◆ siliconized H-ZSM-5, cat.1*
■ siliconized DA-H-ZSM-5, (1h), cat.2*
▲ siliconized DA-H-ZSM-5, (2h), cat. 3*
● siliconized DA-H-ZSM-5, (4h), cat.4*

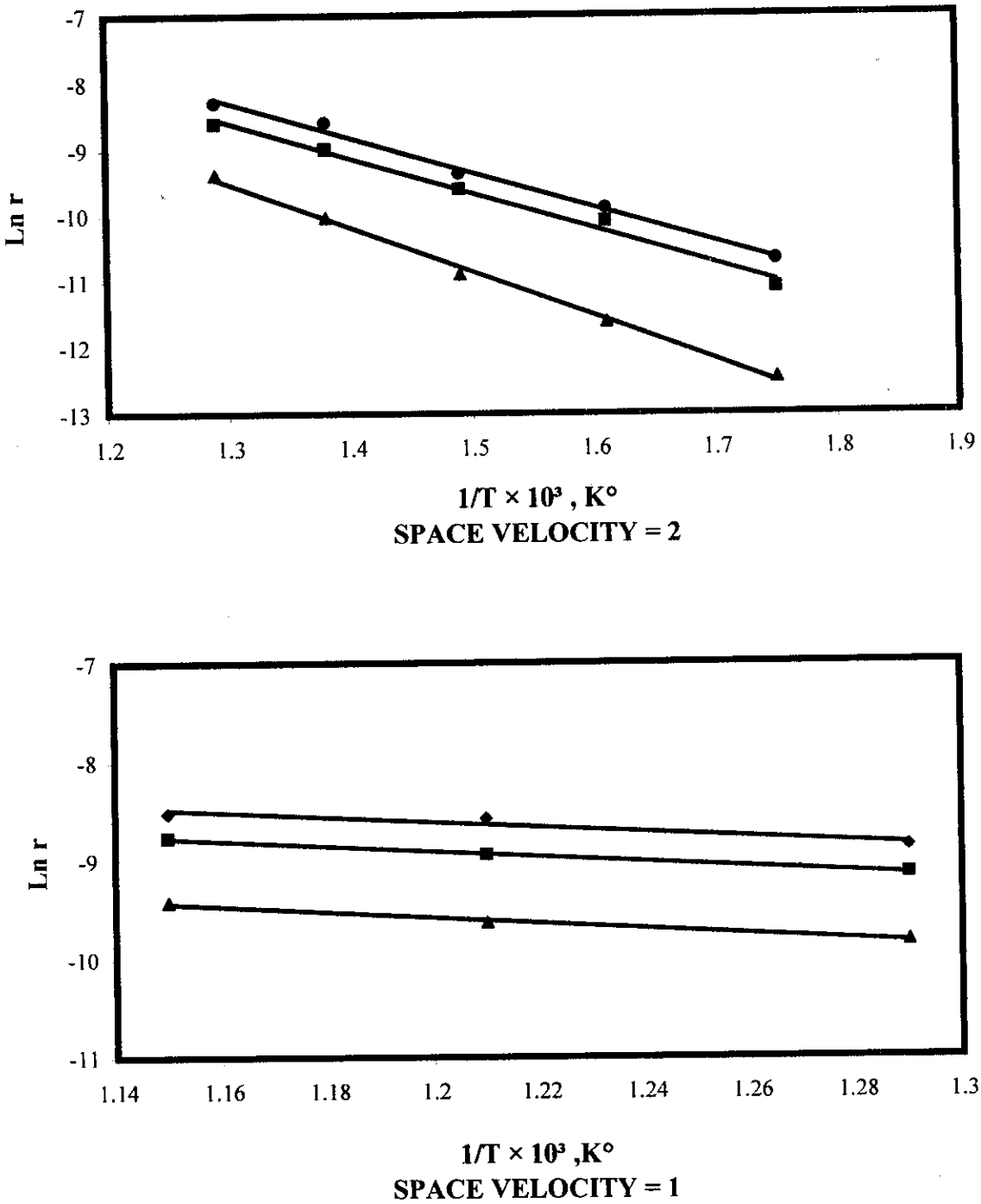


Fig. 40 ARRHENIUS PLOT FOR TOLUENE DISPROPORTIONATION ON DA-H-ZSM-5 (4h), (UNSILICONIZED, SILICONIZED AND DOUBLE SILICONIZED) CATALYSTS

◆ DA-H-ZSM-5, (4h), cat.4
■ siliconized DA-H-ZSM-5, (4h), cat.4*
▲ double siliconized DA-H-ZSM-5, (4h), cat.4**

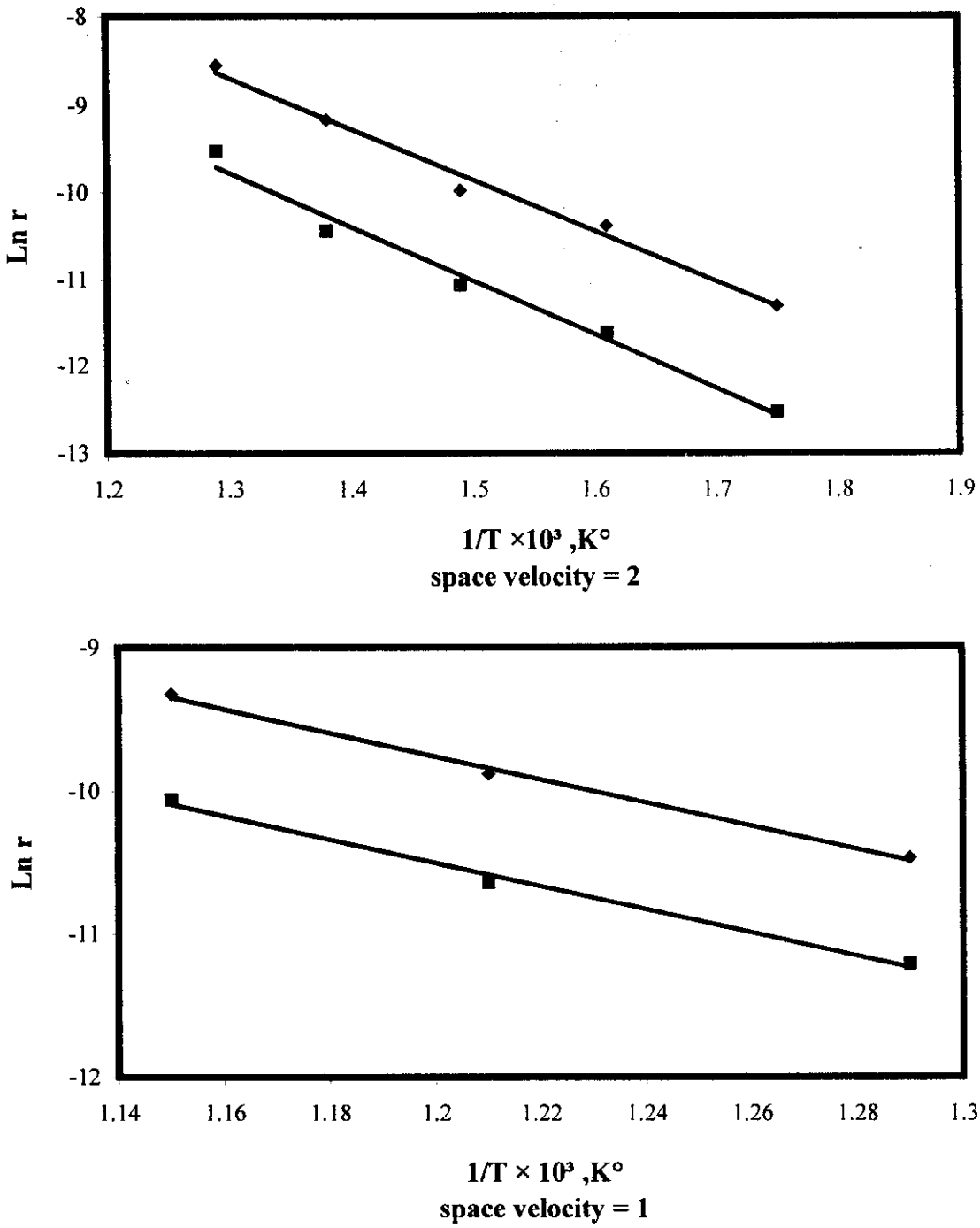


Fig. 41 ARRHENIUS PLOT FOR TOLUENE DISPROPORTIONATION ON H-MORDENITE AND SILICONIZED H-MORDENITE CATALYSTS

◆ H-Mordenite,cat.5 ■ siliconized H-Mordenite, cat.5*

3.5. COMPARISON BETWEEN H-ZSM-5 AND H-MORDENITE CATALYSTS:

In general, the ZSM-5 catalysts are more active than the corresponding mordenite catalysts. For instance, using H-ZSM-5 catalyst benzene produced via disproportionation is much higher than that produced via hydrocracking at all temperatures at low severity (300 - 500°C and WHSV of 2.0 g $g^{-1}h^{-1}$) (Fig.42X_a). However, at high severity (500 - 600°C and WHSV of 1.0 g $g^{-1}h^{-1}$), the benzene produced via hydrocracking is much higher than that produced via disproportionation at temperatures of 550 and 600°C (Fig. X_b).

Incorporation of Si in H-ZSM-5, (Fig.X_c and X_d) evidently decreases hydrocracking compared to disproportionation, particularly at the high severity. This can be attributed to masking some strong acid sites with Si, since hydrocracking is principally dependent on these acid sites, whereas disproportionation depends on catalyst geometry rather than acid sites strength.

On the other hand on H-MOR, at low severity (300 - 500°C and WHSV of 2.0 g $g^{-1}h^{-1}$) (Fig.43Y_a), the reactivity of toluene towards producing benzene via disproportionation and hydrocracking does not significantly differ from that on H-ZSM-5 (Fig.X_a). Nevertheless, at high severity (500 - 600°C and WHSV of 1.0 g $g^{-1}h^{-1}$) (Fig.Y_b) the hydrocracking activity is greatly suppressed compared to that of disproportionation which is attributed to enhanced coke deposition in the pores of H-MOR .

Incorporating Si in H-MOR (Figs.Y_c and Y_d) does not give significant reactivities compared to the reactivities in case of H-ZSM-5 catalysts. This is attributed to the wide pores of H-MOR zeolite which are not sensitive to silicon deposition as has taken place in the smaller pores of H-ZSM-5 which are highly sensitive to the incorporation of added materials.

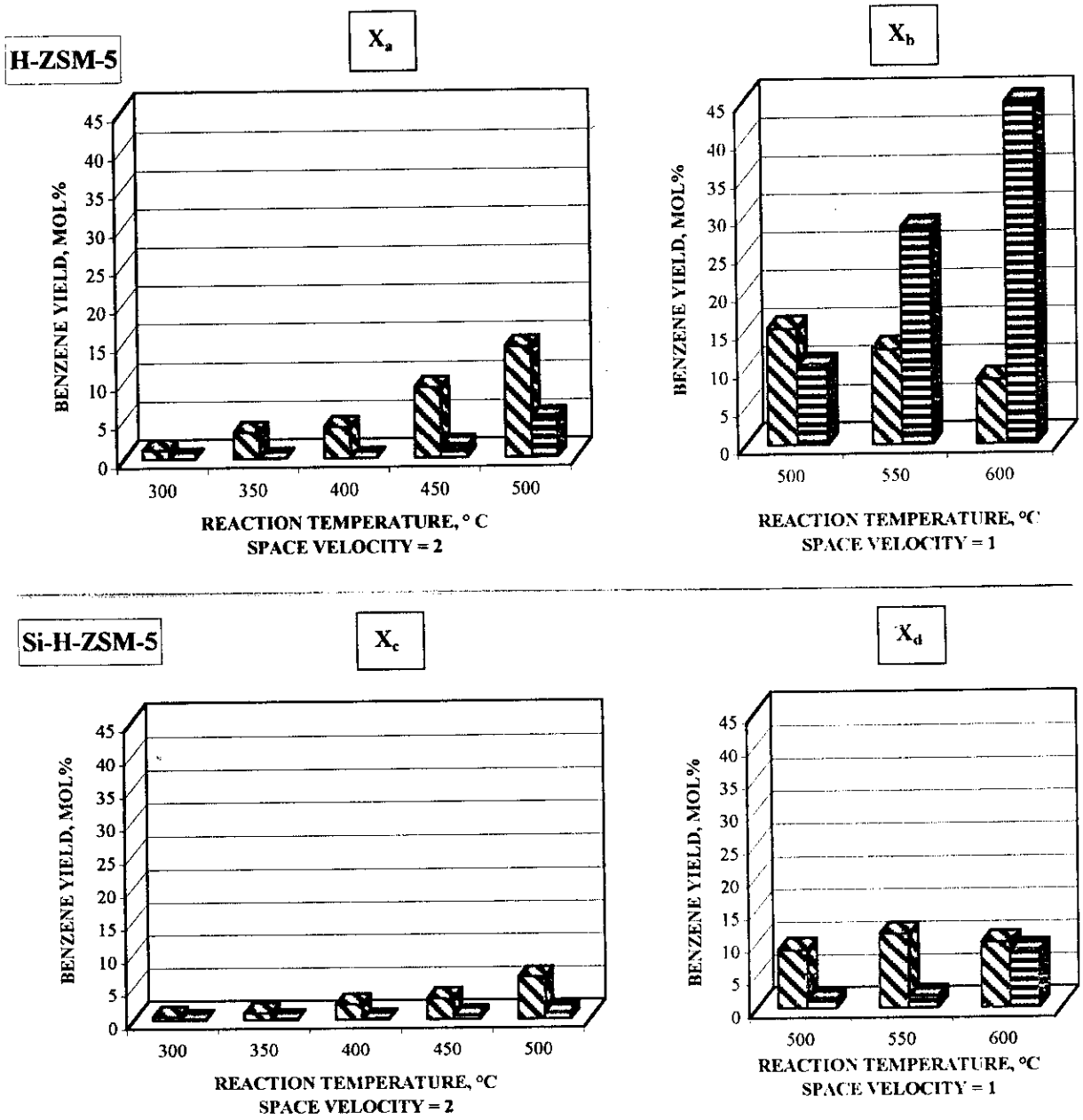


Fig .42 BENZENE PRODUCED VIA DISPROPORTIONATION VS. BENZENE PRODUCED VIA HYDROCRACKING AT LOW AND HIGH REACTION SEVERITIES USING H-ZSM-5 & Si-H-ZSM-5 CATALYSTS.

▨ benzene via disproportionation ▤ benzene via hydrocracking

TABLE. 15 COKE FORMATION (g. COKE g. $^{-1}$CATALYST h^{-1}) ON UNSILICONIZED AND SILICONIZED H-ZSM-5 AND H-MORDENITE CATALYSTS.

CATALYST	COKE FORMATION gm coke / gm catalyst. hr
H-ZSM-5	0.055
Si-H-ZSM-5 (3% Si)	0.04
H-MORDENITE	0.115
Si-H-MORDENITE (3% Si)	0.07

ABLE. 16 EFFECT OF SPACE VELOCITY ON TOTAL TOLUENE CONVERSION ON TOLUENE DISPROPORTIONATION REACTION AT 500°C USING H-ZSM-5 AND H-MORDENITE CATALYSTS.

TYPE OF CATALYSTS	LOW SEVERITY*	HIGH SEVERITY**
H-ZSM-5, cat. 1	34.15	41.06
*Siliconized H-ZSM-5, cat. 1**	13.83	19.43
*Siliconized DA-H-ZSM-5, (1h), cat. 2**	16.92	20.93
*Siliconized DA-H-ZSM-5, (2h), cat. 3**	25.11	32.07
*Siliconized DA-H-ZSM-5, (3h), cat. 4**	30.53	35.5
DA-H-ZSM-5, (3h), cat. 4	42.93	47.09
*Double siliconized DA-H-ZSM-5, (3h), cat 4***	14.06	18.09
H-Mordenite,cat.5	32.28	9.76
*Siliconized H-Mordenite, cat.5**	12.15	4.51

*Low severity; temperatures between 300 - 500°C, and WHSV of 2.0 g g^{-1} h^{-1}

**High severity; temperatures between 500 - 600°C, and WHSV of 1.0 g g^{-1} h^{-1}

6. X-RAY DIFFRACTION ANALYSIS:

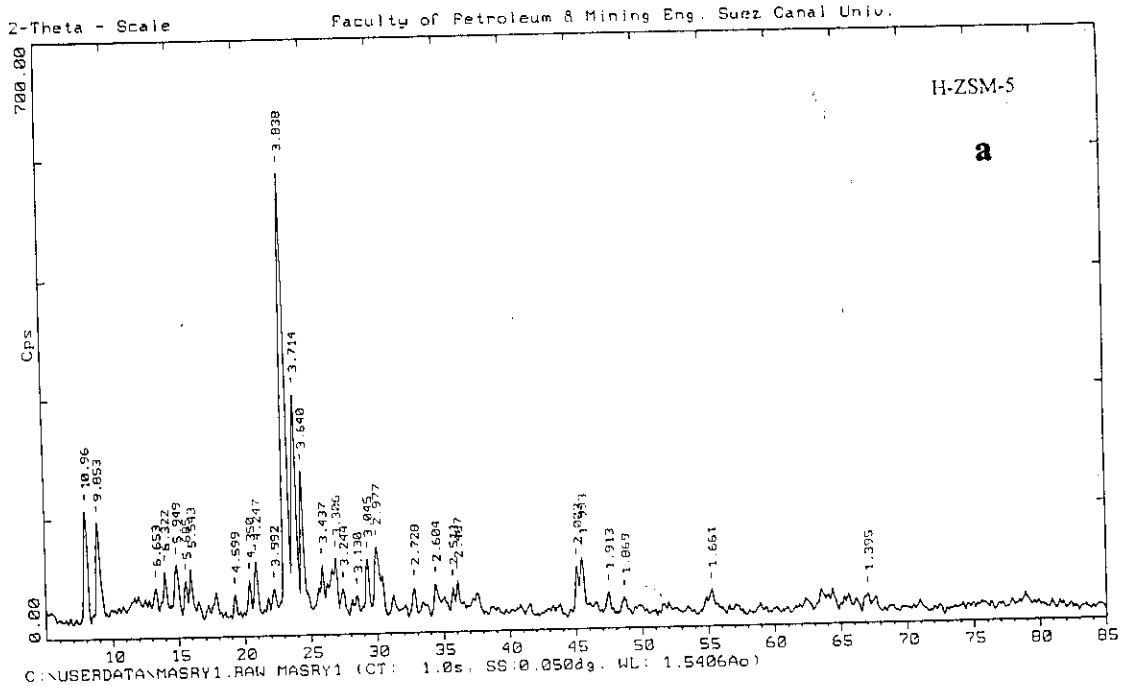
The XRD patterns (Figs. 44 a-d) obtained for the as-synthesized and :id dealuminated H-ZSM-5, under study, show a progressive decrease of ıe lowest 2θ peak to lower and lower 2θ values via progressive ealumination. However, such shift to lower 2θ values is so small that it is isually unrecognized. Even though the d-values of each peak is printed in ıe obtained patterns at the apex of each peak. Although these values show ery slight diffrences, yet they are meaningful.

For the as-synthesized H-ZSM-5, the d-value of the lowest 2θ peak is 0.96 A° compared to 11.00, 11.01 and 11.04 for the progressively .ealuminated samples, i.e., using 0.5N HCl for 1, 2 and 4h, respectively. \nother evidence for the progressive dealumination is the enlargement of he lowest 2θ peak relative to the 100% peak appearing at d value = 3.838 \°. The ratio of these two peaks is found to be 0.272 for the as-synthesized .ample and increases to obtain 0.356, 0.439 and 0.497 for the samples lealuminated for 1, 2 and 4h, respectively. However the XRD pattern Fig. 44-e) for the siliconized H-ZSM-5 sample shows that the ratio of hese two peaks amounts to 1.119 indicating that the lowest 2θ peaks ɔecame the largest peak, exceeding that of the 100% peak at 2θ = 23.0

Moreover, all peaks in this pattern get a shift to higher 2θ values, i.e., .ower d-values. The enrichment of the siliconized sample with silicon atoms caused an abundance of the Si-O-Si bonds relative to the Si-O-Al bonds originally present in the as-synthesized sample. The Si-O bond is

shorter than the Al-O bond, thus the siliconized H-ZSM-5 has attained a significant shrinkage of the crystals of this zeolite. This shrinkage should have decreased the channels dimension that resulted in more selective production of para-xylene (Table 4).

Similarly, the lowest 2θ peak in the XRD pattern (Fig. 45 a-b) obtained for H-MOR has significantly enlarged relative to the peak at 2θ = 3.447. The ratio of the 13.40 d-value peak to the 3.45 d-value peak is 0.74 for the as-synthesis H-MOR compared to 1.05 for the siliconized H-MOR. However, a shift of all peaks to higher d-values has taken place via siliconization of H-MOR.



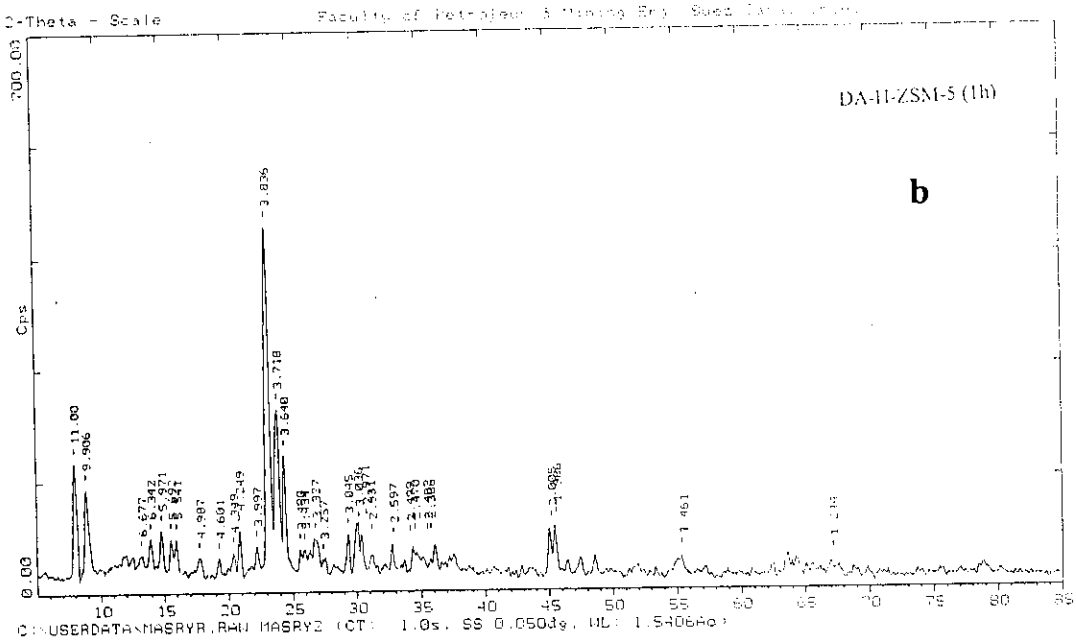
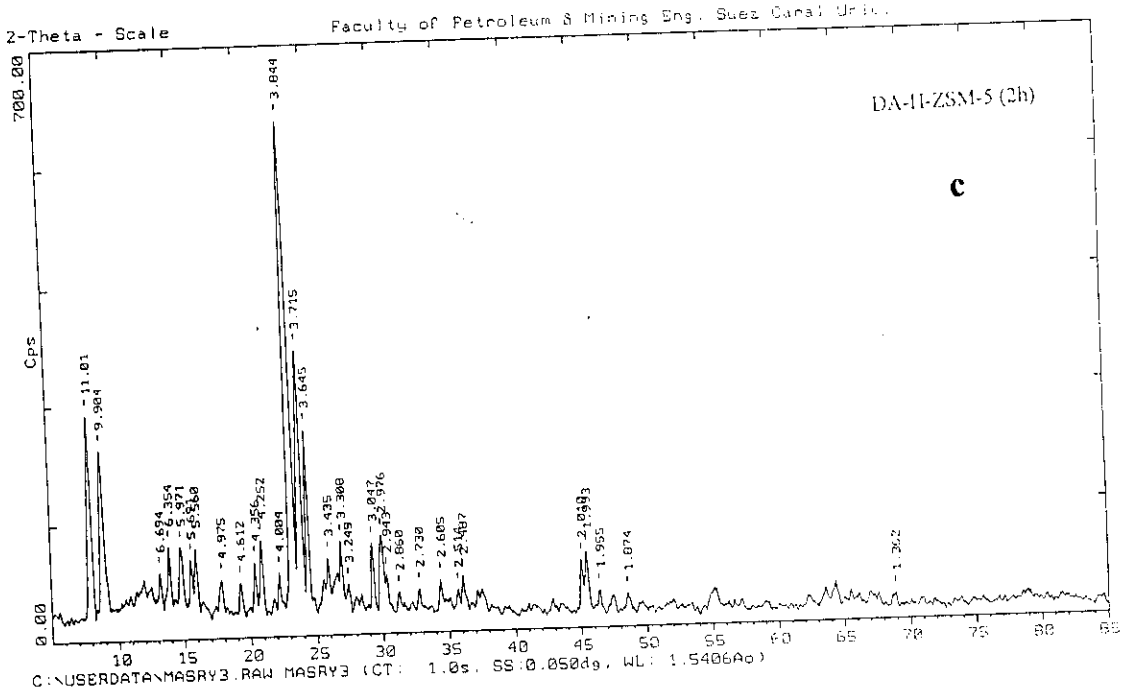
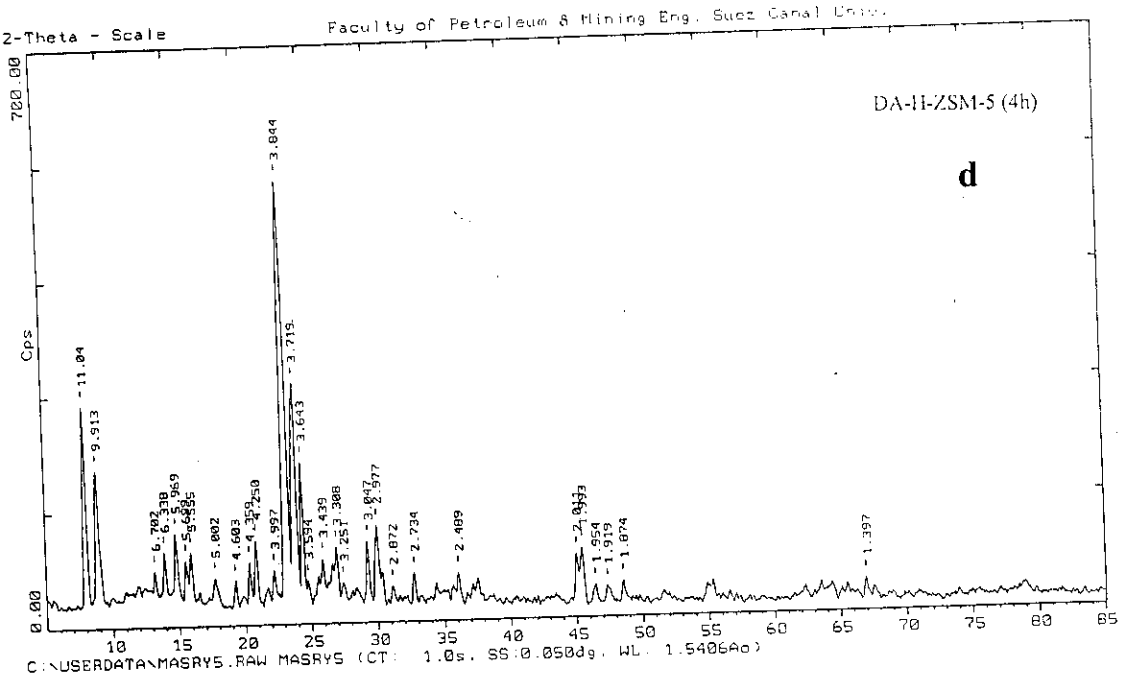
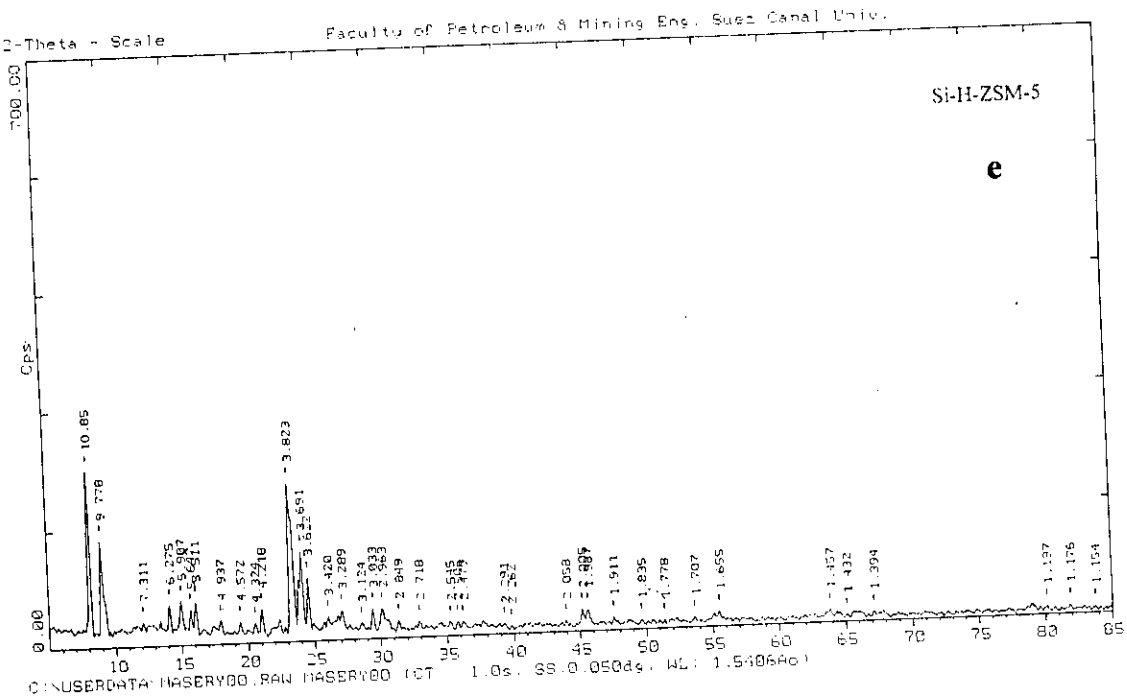


Fig.44 X-RAY DIFFRACTION PATTERNS FOR H-ZSM-5 AND ITS VERSIONS


2-Theta - Scale
Faculty of Petroleum & Mining Eng. Suez Canal Univ.
DA-H-ZSM-5 (2h)
c
Cps
C:\USERDATA\MASRY3.RAW MASRY3 (CT: 1.0s, SS:0.050dg, WL: 1.5406Ao)


2-Theta - Scale
Faculty of Petroleum & Mining Eng. Suez Canal Univ.
DA-H-ZSM-5 (4h)
d
Cps
C:\USERDATA\MASRY5.RAW MASRY5 (CT: 1.0s, SS:0.050dg, WL: 1.5406Ao)


2-Theta - Scale
Faculty of Petroleum & Mining Eng., Suez Canal Univ.
Si-H-ZSM-5
e
Cps
700.00
0.00
10.85
9.778
7.311
6.275
5.607
5.411
4.937
4.572
4.324
4.218
3.823
3.691
3.420
3.289
3.124
3.033
2.963
2.849
2.718
2.645
2.591
2.262
2.058
1.911
1.835
1.778
1.707
1.655
1.457
1.432
1.394
1.197
1.176
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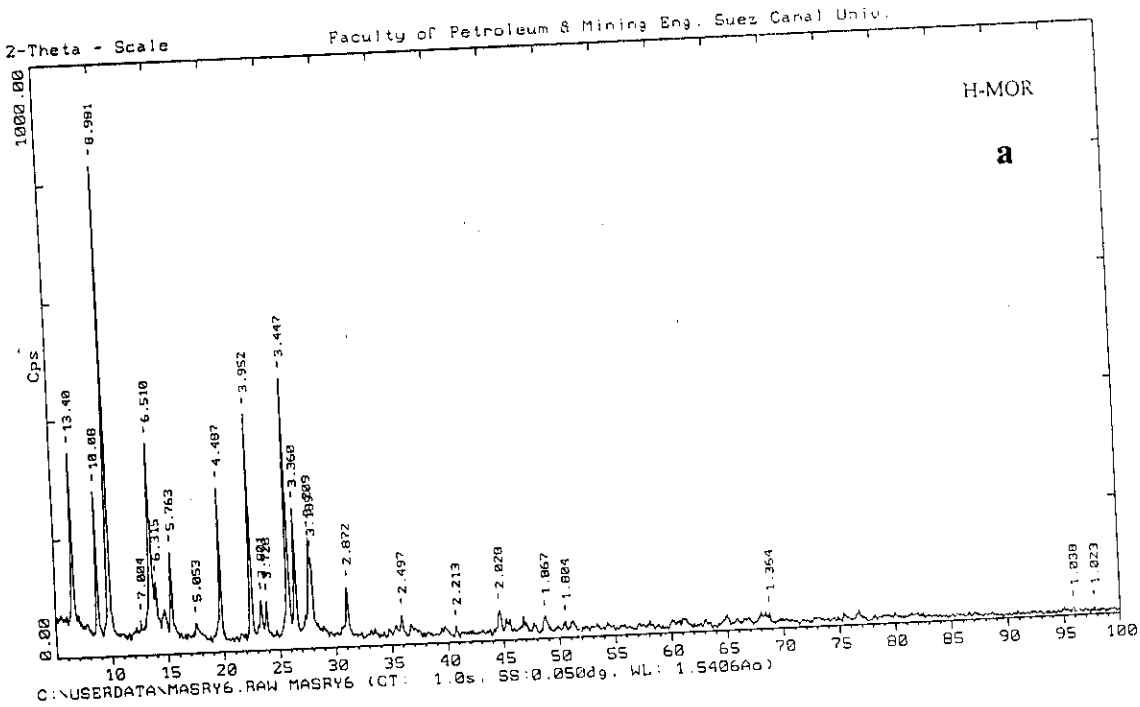
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
C:\USERDATA\MASERY00.RAW MASERY00 (DT 1.0s, SS:0.050deg, WL: 1.54060Ao)



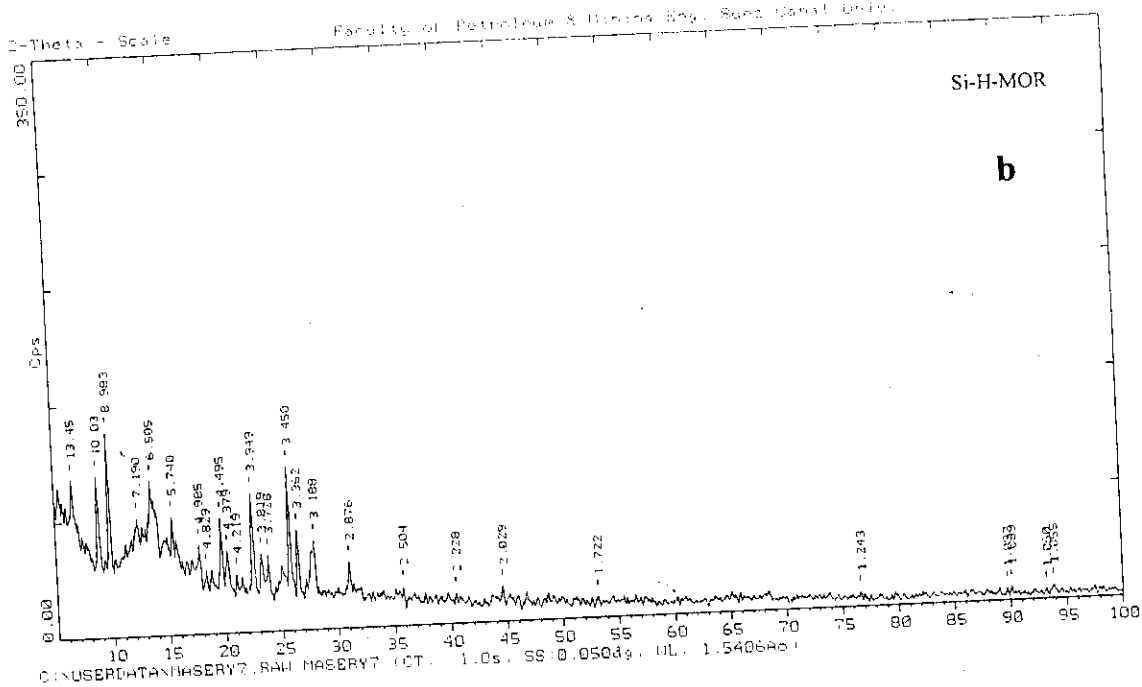


Fig. 45 X-RAY DIFFRACTION PATTERNS FOR H-MOR AND Si-H-MOR CATALYSTS