Determination of acidities of zeolites by photoacoustic spectroscopy*

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Photoacoustic spectroscopy is found to be a useful technique for determining the acidity of zeolites. The acidity so determined correlates well with temperature programmed desorption studies of ammonia and product distribution.

INTRODUCTION

Determination of surface acidity forms an important aspect of the characterization of catalysts[1]. Several semi-quantitative and quantitative methods have been employed to study the acidity of catalysts in the last several years[2]. These include ammonia desorption, pyridine adsorption and n-butylamine titration with visual indicators. The titration method using n-butylamine with Hammett indicators would become a simple quantitative method, provided one can obtain the relative intensities of the absorption bands in the electronic spectra. We pointed out recently that photoacoustic spectroscopy[3] (PAS) provides a reliable technique to quantitatively estimate the acid sites for oxide catalysts[4,5]. Since the estimation of acidity forms an important aspect of the characterization of zeolites[6,7], we have been interested in the use of PAS for the purpose[5]. In this communication we report the acidity distribution in several zeolite samples determined by PAS and have shown that acidities obtained by this technique compare satisfactorily with ammonia desorption studies. We also briefly comment on why the technique is successful although indicators used are likely to have molecular diameters larger than the diameters of the apertures in the dehydrated zeolites.

EXPERIMENTAL

The zeolites used in this study were evacuated *in vacuum* (10^{-3} Torr) for 12 h around 750 K. The samples were then transferred and stored in a dry box for further studies. We have observed that big particles took a longer time for equilibration than the smaller ones and indicators like dimethyl yellow took more time for equilibration. In order to obtain consistent and rapid equilibration we have chosen particle sizes 300–400 mesh.

The set of indicators used in this study with colour changes together with pK_a values are given in *Table 1*. The indicator solutions were prepared in dry benzene. The spectra were recorded with a home-built spectrometer[3] at a resolution of 20 nm. The scanning

Table 1 Set of indicators used, their colour changes together with their colour change intervals (pK_a)

Indicator	Colour change and pK_a			
Bromothymol blue	Red (pink)	− 1.5	Yellow	
	Yellow	+ 6.8	Bluish green	
Thymol blue	Red	+ 1.7	Yellow	
	Yellow	+ 8.9	Blue	
Methyl red	Pink	+ 5.0	Yellow	
Dimethyl yellow	Pink	+ 4.0	Yellow	

speed was 100 nm min^{-1} with a time constant of 1 s. The chopping frequency employed was 37 Hz. The procedure for n-butylamine titration is described elsewhere[3,5].

The zeolites studied are: HZSM-5, HZSM-11, HBZSM-5, HSAPO-5, silicalite-5, HALPO-5 and Linde-NaY, ZSM-5 and ZSM-11 both have intersecting channel systems with 10-membered ring opening with a free diameter intermediate to that in Linde A and faujasite. The known values of pore diameter, pore volume and number of tetrahedral atoms (Si, Al or P) that control the pore size for the various zeolites[8,9] are summarized in *Table 2*.

Certain caution is necessary before correlating the intensities of the conjugate acid-base pairs with concentration of such pairs. Recent experiments carried out in this laboratory have shown that the

Table 2 Values of pore size, ring size and intracrystalline volume for various zeolites[8,9]

Zeolite	Pore size[a] (nm)	Ring size[b]	Intracrystalline pore volume[c] (cm^3 g^{-1})	
			O_2	H_2O
SAPO-5	0.8	12	0.23	0.31
ALPO-5	0.8	12	0.18	0.3
Silicalite-5	0.52 × 0.58[d]	10	0.185	0.047
ZSM-5	0.54 × 0.56[d]	10	–	–

[a]Determined by standard method (Mc Bain-Bakr) after calcining at 500°–600°C
[b]Number of tetrahedral atoms (Si, Al or P) in ring that controls the pore size
[c]Pore volume near saturation, O_2 at −183°C, H_2O at ambient temperature
[d]Free aperture of channels

Table 3 Comparison of activity of ferrisilicate with ZSM-5 zeolite

| | | Catalyst | |
| | | Ferrisilicate | ZSM-5 |
Hydrocarbons	Feed	Product	Product
Aliphatics	3.6	3.6	3.5
Benzene	0.1	4.0	4.8
Toluene	3.3	5.2	6.2
Ethylbenzene (EB)	23.1	16.1	15.0
p-Xylene	10.2	15.8	14.4
m-Xylene	54.0	41.0	41.6
o-Xylene	5.7	12.1	12.0
C_9^+	–	1.2	2.5
Xylene loss (%)	–	1.0	1.9
EB conversion (%)	–	30.3	35.0
Approach to equilibrium			
p-Xylene	–	89.0	73.0
m-Xylene	–	75.2	70.5
o-Xylene	–	66.2	68.6

Reaction temperature = 653 K; LHSV = 6.6 h^{-1} H$_2$/HC = Nil; pressure = one atmosphere

xylenes) are converted into unwanted toluene and C_9^+ aromatic products. Careful analysis of the results shows that over ferrisilicate conversion of ethylbenzene is low with low xylene loss and percent approach to equilibrium for p-xylene is higher as compared to ZSM-5 zeolite. There is also a decrease in concentration of benzene, toluene and C_9^+ aromatics in the product. The low catalytic activity and high p-xylene selectivity of ferrisilicate is attributed to the lower concentration of strong acid sites.

CONCLUSIONS

The results presented above demonstrate that Fe^{3+} ions in ferrisilicate are situated at the zeolite lattice sites. The acidity and catalytic activity measurements reveal that strength and concentration of strong structural Brönsted acid sites (TPD III peak) is lower than that of ZSM-5. Consequently, its catalytic property in the isomerization of xylenes is different from that of ZSM-5.

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intensities cannot be linearly related to the quantity of the dye absorbed due to scattering effects[10]. Thus the same wt% age of the indicator must be employed in a related series of experiments. Since the depth to which the indicator molecule penetrates into the pores is likely to be considerably smaller than the thermal diffusion length of the material (typically of the order of several microns), one may assume that all the indicator molecules contribute to the PA intensity. A more serious problem is to correlate the intensity with concentration. Because slurries are used in the study, it is difficult to reproduce the band intensities; however, since only the intensity ratios of the bands are required by us, we need to take into account only the changes in the relative intensities at the absorption maxima of the conjugate acid–base pairs. We require the relative ratios of the intensities at the wavelengths of interest for conjugate base and acid (with and without n-butylamine, respectively). From the changes in the ratios of intensities at these wavelengths, changes in their relative concentration of the conjugate acid base are obtained.

RESULTS AND DISCUSSION

In *Figures 1* and *2*, we show typical PA spectra of different indicators obtained for two zeolite samples. In *Figure 3*, we show the results of our acidity measurements on dehydrated zeolites. For convenience, we can describe the plots in terms of two regions. One near the highest acidity ($H_o \approx -1.5$) and the other for the lowest acidity ($H_o \approx +6.0$). We see that the equivalent number of sites decreases in the order HZSM-5 > HBZSM-5 > HZSM-11. HALPO-5 has no acid sites with $H_o \leqslant 0.0$. In the ammonia TPD studies (*Figure 4*), HZSM-5 is seen to have the highest proportion of γ-sites (See Topsoe *et al.*)[11] in terms of ammonia equivalents, while HALPO-5 has no γ- or β-ammonias. Since HSAPO-5 does not seem to have a well defined γ-peak, it must be assumed to have very few γ-sites compared to HZSM-11 or HZSM-5. We

Figure 2 Normalized PA spectra of dyes adsorbed on silicalite-5. (a) Bromothymol blue; (b) dimethyl yellow, and (c) methyl red. (——), (---) and (·····) represent progressive addition of n-butylamine starting from a value of zero
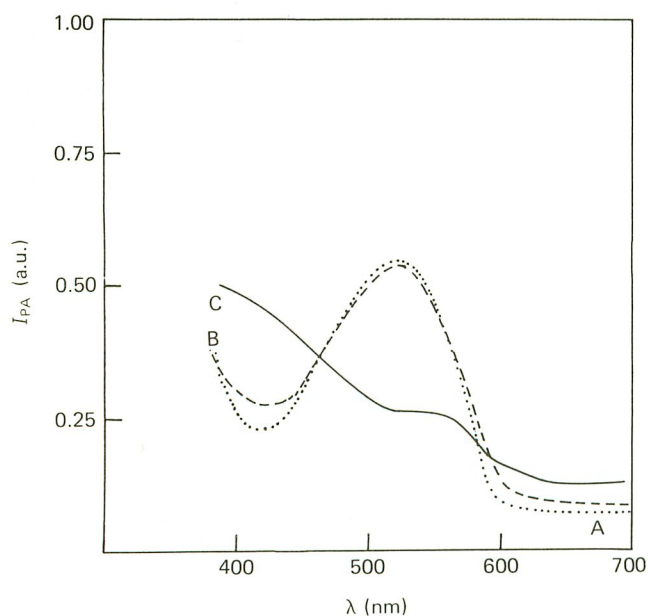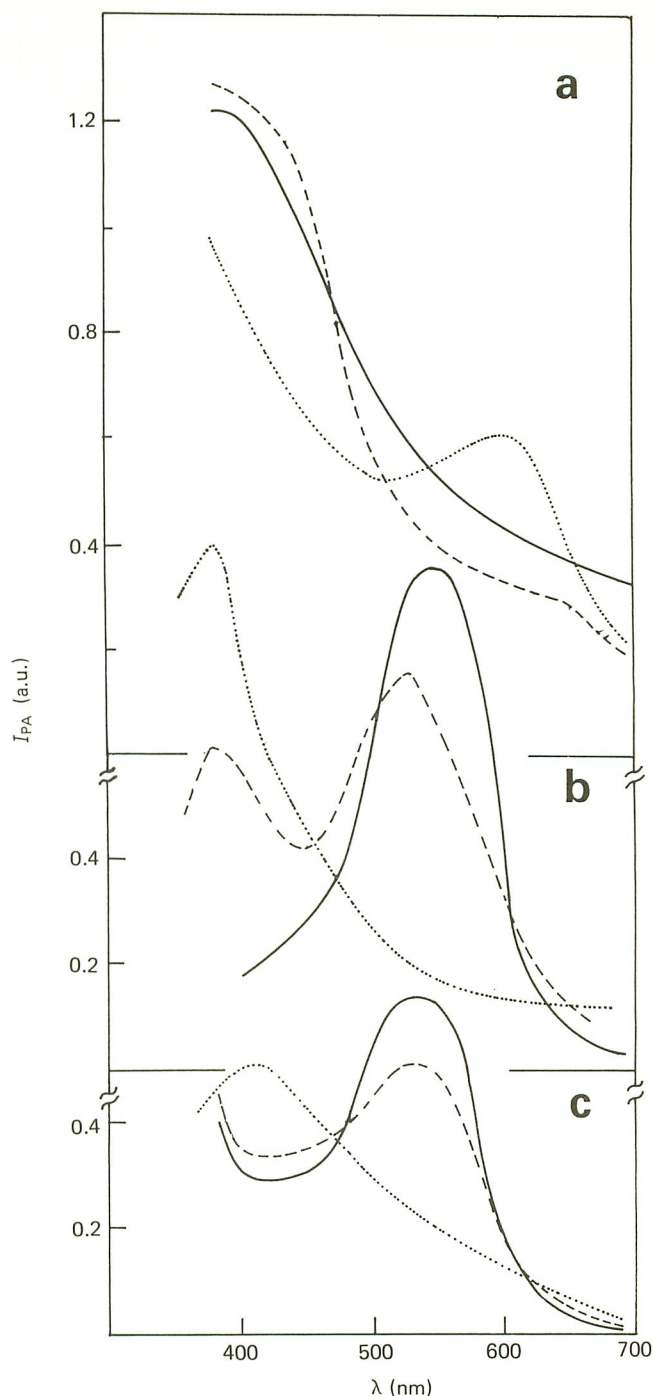
Figure 1 Normalized PA spectra of dyes adsorbed on HZSM-5: (A) dimethyl yellow (B) methyl red and (C) bromothymol blue

may thus associate the γ-sites with H_o close to or less than zero. Silicalite-5 will have some γ-sites as there are sites which have H_o nearly equal to zero, although none could be detected at lower values of H_o. There seems to be no apparent correlation between the number of α-sites (ammonia desorbed near 330 K) and the milliequivalent of n-butylamine at lower H_o values. The number of β-sites (ammonia desorbing $\sim$ 460 K) seems to be related to the milliequivalents of n-butylamine for $H_o \sim 6.0$. In this case, the weaker α-sites could actually have H_o greater than 7.0.

We suggest that the sites with $H_o = -1.5$, 6.0 and > 6.0 possess acidities equivalent to H_2SO_4, acetic acid
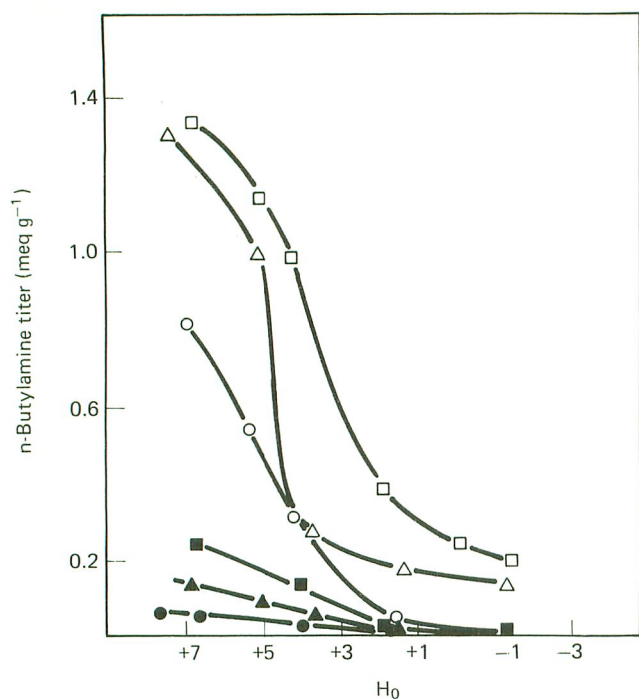
Figure 3 Plot of n-butylamine titre against the Hammett acidity function (H_o) for various zeolite samples: (□), HZSM-5; (△), HBZSM-5; (○), HZSM-11; (■), HASPO-5; (▲), silicalite-5; (●) HALPO-5

Table 3 Variation of acidity of zeolite (Linde NaY) with calcination temperature

Temperature (°C)	Acidity measured by NH$_3$ TPD (mmol g^{-1})	Acidity measured at $H_o = -1.5$ (mmol g^{-1})
350	1.01	0.140
450	1.05	0.170
550	2.90	0.378
650	1.70	0.283
750	1.54	0.210

acetate and ammonium hydroxide are associated with heats of formation of ~ 167.44, 87.91 and 33.49 kJ mole^{-1}. Interestingly, the experimental adsorption activation energies of ammonia on the γ-, β- and α-sites are reported to be 162.42, 96.70 and 84.56 kJ mole^{-1} respectively. The heats of adsorption for ammonia range from 160.33 to 100.6 kJ mole^{-1} (Ref. 12). This lends credibility to the suggestion that the β-sites may be considered to have H_o ~ 6.0.

In order to test the PA method further, we have heated a zeolite (Linde NaY) to different temperatures and measured the end point of the titration corresponding to $H_o = -1.5$. The titration values compare well with the results of irreversibily adsorbed ammonia (*Table 3*).

The activities of the zeolite catalysts for the conversion of methanol and formation of various products are summarized in *Table 4*. As expected, the catalyst with the highest proportion of strong acid sites (H_o ~ < 0.0) are effective for the conversion of methanol
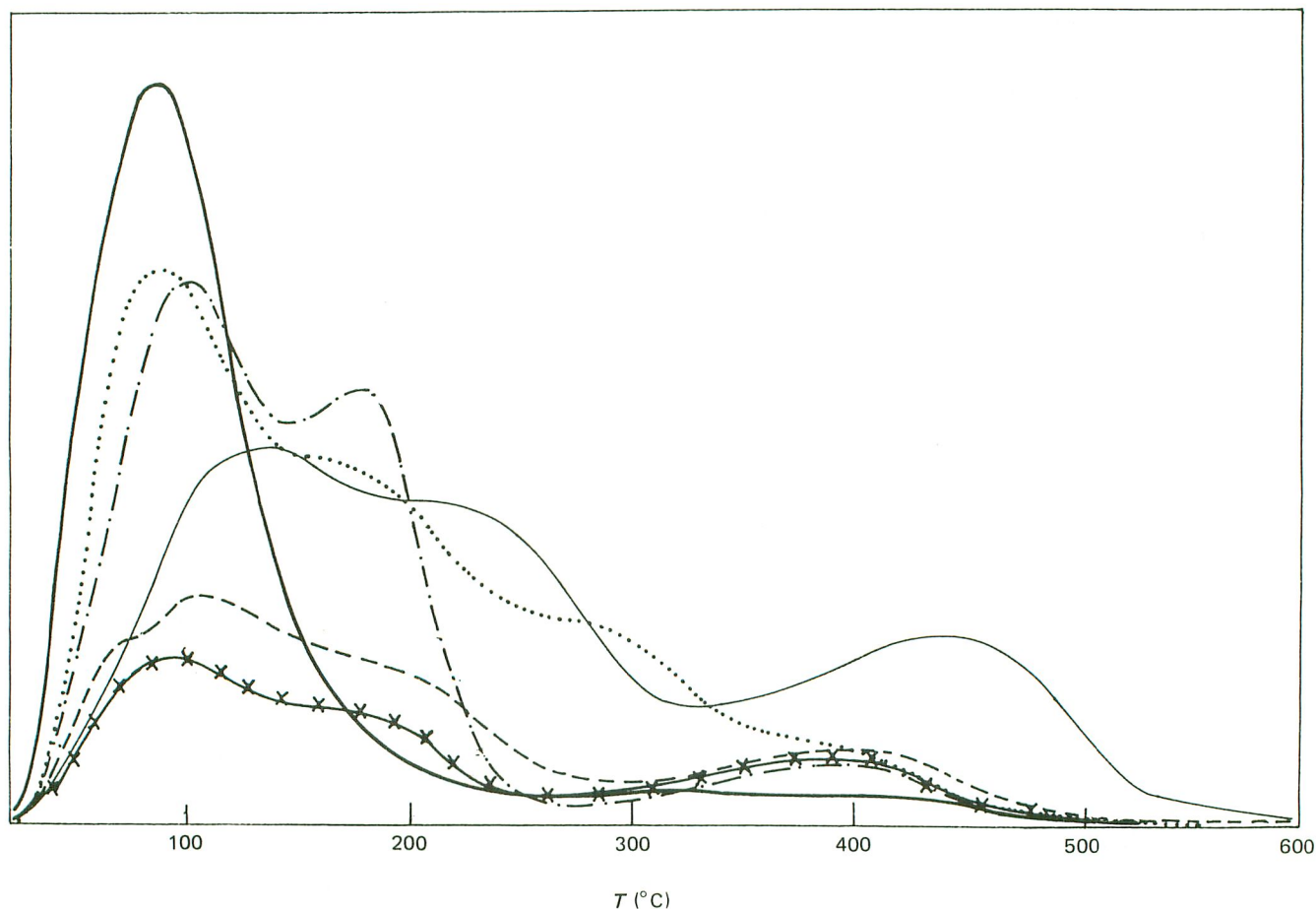
and water respectively (see Benesi and Winquist[2]). Reactions of ammonia with sulphuric acid, acetic acid and water to yield ammonium bisulphate, ammonium

T (°C)

Figure 4 Temperature programmed desorption (TPD) curves for ammonia on various zeolite samples. (——), HZSM-5; (---), HZSM-11; (·····), HSAPO-5; (—·—·), HBZSM-5; (–×–×), silicalite-5; (——), HALPO-5

Table 4 Catalytic activity of the various zeolite samples for the conversion of methanol and formation of various products (temperature, 350°C)

Product	HZSM-5	HZSM-11	HSAPO-5	HBZSM-5	Silicalite-5	HALPO-5
Methanol converted	99.4	98.0	84.2	96.15	90.0	50.0
Dimethyl ether	0.2	0.394	62.6	0.90	1.54	93.0
Hydrocarbons C_2	1.02	6.09	3.61	6.6	4.27	1.5
C_3	1.48	12.09	4.23	3.26	8.08	0.4
C_4	2.29	7.55	11.01	4.23	7.52	0.5
$\Sigma\ C_2{-}C_4$ Olefins	4.6	25.70	18.55	14.09	20.0	4.4
$\Sigma\ C_1{-}C_4$ Olefins	37.5	31.63	14.66	16.88	30.0	–
C_5^+ Aliphatics	25.99	6.53	3.89	40.0	23.55	–
C_6^+ Aromatics	32.1	26.99	–	29.05	24.89	–

and for the formation of hydrocarbons. HALPO-5 is the least active for the conversion of methanol and the almost exclusive formation of dimethyl ether indicates that α-sites (which in our opinion, is not seen in the titration range) are responsible for the reaction. Only these broad indications can be obtained from the present data and further studies would be required for a fuller interpretation.

On the use of Hammett indicators

Because of the wide belief that Hammett indicators do not enter zeolite cavities, such indicators have not been used for the study of acidities on the internal surfaces of zeolites. Recently, Anderson and Klinowski[13] have suggested that with the right choice of an indicator (molecular diameter less than the pore diameter), one could study the acidity of the surface of the wider pores. They believe, however, that the surface of the sodalite cages, for example, which could be reached only through rings of 2.2 Å diameter, cannot be studied by this technique. The present study suggests that the acidity distribution on the surfaces of all the pores in the zeolites may be nearly the same. However, it may as well be that this method probes the surfaces of the smaller pores as long as the smallest diameter of the rings (through which there is access to cages) is larger than the lateral diameter of n-butylamine molecule. When this condition is satisfied, n-butylamine molecules would be adsorbed on all the acid sites with H_o lower than that of the indicator used. Only when these are exhausted, the acid sites on which the indicator molecules are attached would be neutralized by n-butylamine and cause a colour change. Errors could arise if the indicator molecule, for example, physically blocks the access of amine molecules to the pores. The process could also be dominated by the kinetics of the process. Thus, on addition of the amine, the indicator on the surface may be neutralized and show a colour change; n-butylamine molecules may then diffuse into the pores (during equilibration) so that at equilibrium conditions, the amine molecule is adsorbed on the most acidic sites, again causing a change in the colour of the indicator. Such a behaviour has been noticed with certain indicators, the effect being marked as the particle size is increased. It is interesting that the titration values also do not correlate with the known values of pore size and pore volume.

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Alkylation of toluene with methanol III:*Para*-selectivity on modified ZSM-5 zeolites

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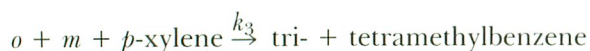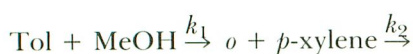*(Received 17 March 1986; revised 1 September 1986)*

Selectivity factors $\bar{S}$ have been derived for three xylene isomers obtained by methylation of toluene over ZSM-5 zeolites modified by the introduction of Fe, B and P ions. In the experimental conditions the reaction proceeds with formation of $o+p$ xylene up to onset of isomerization. Our results and previously published independent data show a close correlation of $\bar{S}$ and the guest electronegativity, indicating a role of the acidity in the reaction mechanism. The *para*-selectivity is attributed to the selective adsorption of $o+m$ xylenes on the acidic reaction site; the less polar *p*-isomer is rapidly desorbed.
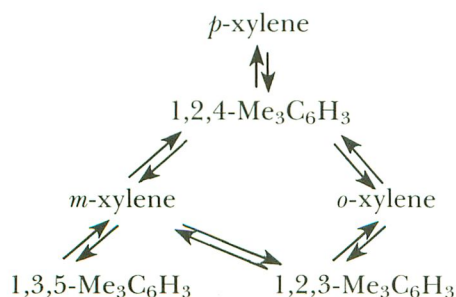
INTRODUCTION

Alkylation of toluene with methanol over zeolites may lead either to ethylbenzene/styrene or xylenes as a result of insertion of the methyl-group in the chain or in the ring[1]. The selectivity varies from basic zeolites (e.g. potassium-exchanged A and Y zeolites[2]) to acidic zeolites (H-zeolites, ZSM-5, etc.[3-6]), as discussed in previous work[7]. In particular, methylation of toluene over acidic catalysts with xylene formation has extensively been investigated[3-6]. The reaction proceeds in three consecutive steps according to:

$$\text{Tol} + \text{MeOH} \xrightarrow{k_1} o + p\text{-xylene} \xrightarrow{k_2}$$

$$o + m + p\text{-xylene} \xrightarrow{k_3} \text{tri-} + \text{tetramethylbenzene}$$

At high MeOH concentrations it is possible that isomerization of *o*- and *p*-xylenes formed in the first reaction step proceeds with a bimolecular mechanism according to the following scheme of parallel reactions[8]:

$$p\text{-xylene}$$
$$\Updownarrow$$
$$1,2,4\text{-Me}_3\text{C}_6\text{H}_3$$

m-xylene   *o*-xylene

$$1,3,5\text{-Me}_3\text{C}_6\text{H}_3 \qquad 1,2,3\text{-Me}_3\text{C}_6\text{H}_3$$

In this way formation of 1,2,4- and 1,2,3,-trimethylbenzene (TMB) is rationalized. In turn, *m*-xylene is formed by dealkylation of TMB up to equilibrium conditions. At low CH_3OH concentrations (with respect to toluene) and at relatively low contact times, both the bimolecular mechanism and the last step of the consecutive mechanism are blocked, and methylation over ZSM-5 catalysts no longer forms polyalkylates (TMB). According to Kaeding *et al.*[3] the reaction proceeds selectively to the commercially more interesting *p*-xylene isomer using ZSM-5 catalysts modified by B, P, etc. In this case the thermodynamic equilibrium conditions[9] (*meta* $\cong$ 50%, *ortho-* $\cong$ *para-* $\cong$ 25%) are overcome, and leading to an excess of the *para-* isomer. The result has been explained by the different steric encumbrance of the three isomers ($m > o > p$) and the microporosity of the modified catalysts[3]. However, diffusion in the micropores may not be the only reason for the high *para*-selectivity of shape-selective zeolites. Bhat[10] suggests that chemisorption of various isomers and/or toluene can also play a significant role in the performance of the catalyst. It is reasoned that ions such as P and B in the micropores of the ZSM-5 decrease the free diameter of the catalyst and favour diffusion of the sterically less requiring *p*-isomer. The rapid release of *p*-xylene shifts the thermodynamic equilibrium towards this isomer and enhances the *para*-selectivity.

In order to evaluate the effect of chemical adsorption of the reaction products on toluene methylation, we have investigated the correlation between selectivity and electronegativity of the ions by modifying the ZSM-5 lattice. In fact, as the catalytic reaction occurs