

# The effect of temperature and cyclic alkoxy silane deposition procedures on the silanisation and subsequent catalytic and sorption properties of zeolites

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Received 23 January 2001; received in revised form 15 May 2001; accepted 22 June 2001

## Abstract

It has been shown that it is necessary to carefully control the reaction conditions when silanising a zeolite. It has previously been shown that using vapour or liquid deposition procedures and static or flow systems influences the properties of the silanised zeolite. Here it is shown that the deposition temperature and the number of silanisation/calcination cycles are of great importance. By careful control of the number of cycles it is possible to systematically modify the diffusional properties of the zeolite while at the same time inertising the external surface acidity. On the basis of the changes in adsorption properties of the silanised zeolite, it is suggested that diffusional changes are more likely due to blockage of pore entrances, resulting in a greater diffusion pathway, than due to a controlled narrowing of the pore openings. The amount of Si deposited/nm<sup>2</sup> is an indicator of the efficiency of the silanisation process. A reaction pathway for the silanisation process is proposed as well as the influence of this procedure on the selectivity of the zeolite for a variety of reactions. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Zeolites; Silanisation; Diffusional properties

## 1. Introduction

The structural characteristic of greatest interest for catalysis by zeolites is the channel system because of the well-known shape selective properties of zeolites. As it is well known, the size and dimensionality of these channel systems result in molecules being subjected to different diffusional resistances thus controlling ultimately the selectivity in catalytic reactions. Because the external surface is fully accessible to all molecules, it promotes non-shape selective reactions. It is therefore of great interest to study the effects of

passivating or inertising external acid sites in order to promote the shape selective reactions.

Inertisation of external surface sites can be achieved by a number of techniques [1,2]. Silanes, disilanes, etc. are inappropriate for this purpose since they enter the entire channel system of the zeolite and result in an inertising of internal and external acid sites. The focus of this paper is on the use of bulky alkoxy-silanes which are able to silanise and consequently inertise only the external acid sites [1,3–6]. This treatment has a most important secondary effect of narrowing or blocking entrances to pores thus modifying the diffusional properties of the zeolite and ultimately the shape selectivity of zeolites for catalytic reactions since the internal acid sites remain catalytically active. This silanisation procedure is generally carried out using

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chemical vapour deposition (CVD) methods. The silicon source is usually a bulky alkoxy-silane complex such as tetramethoxysilane (TMOS) or tetraethoxysilane (TEOS). TEOS with a kinetic diameter of about 0.96 nm is particularly suitable [4] in that it minimises the possibility of silanisation of the internal surface of zeolites such as ZSM-5, mordenite and beta.

This paper presents results which show that, by controlling the temperature and the number of silanisation cycles in the silanisation process, the amount of external surface acidity can be reduced in a controlled manner, and the diffusional and sorption properties of the treated zeolite modified in a way in which the selectivity of certain catalytic reactions are significantly changed. Proposals are made on the reactions occurring during the silanisation process.

## 2. Experimental

Modification of the external surface of zeolites was studied using the zeolites ZSM-5, mordenite and beta. Specific details on the modification procedures have been described previously [5,6]. Crystal sizes generally varied from 0.5 to 2  $\mu\text{m}$ , but in some cases, the size was almost 10  $\mu\text{m}$ . The Si/Al ratios are shown in Table 1. Using TEOS as the silica-source, modification was carried out in two different ways, viz. in a static vacuum system and a vapour phase flow system. After the deposition step, the catalysts were calcined in air. A typical deposition/calcination cycle for a vapour phase flow system is shown in Fig. 1. This shows the TEOS breakthrough curve during CVD at 50 °C indicating the deposition, flushing and heating and heating/calcination parts of the cycle.

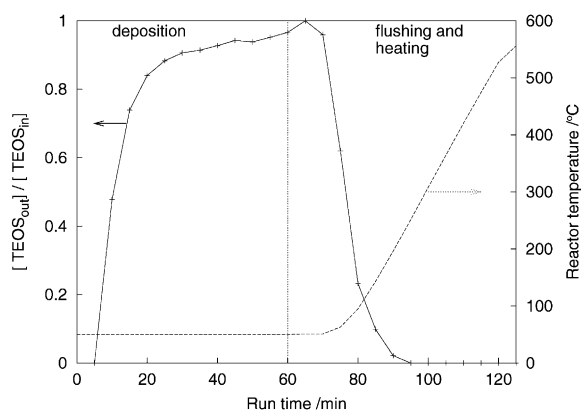


Fig. 1. Typical TEOS breakthrough curve during CVD of ZSM-5 at 50 °C showing deposition, flushing and heating parts of the cycle.

The catalytic activity of the external surface was determined using the cracking of 1,3,5-trisopropyl benzene (TiPB) as a probe reaction. TiPB has a kinetic diameter of 0.85 nm and is not expected to enter the channels of the zeolites. Disproportionation and aromatic alkylation reactions were used to investigate the influence of silanisation on the shape selective properties of the modified zeolites. These reactions were carried out in fixed bed reactors and the reaction conditions were chosen variously so as to ensure, as appropriate and desirable, differential operation, constant conversion, or indeed high conversion. Table 2 summarises the reaction conditions used for each reaction.

Methods used to characterise the samples with respect to relative percentage of crystallinity, external and total acidity, and sorption capacity have been described elsewhere [7]. Pyridine (Py) and 4-methylquinoline (MQ) were used to probe total

Table 1

Effect of various silanisation procedures on the Si/Al ratio, relative percentage of crystallinity and acidity of H-ZSM-5 using different deposition procedures

Deposition time (h)	Deposition procedure	Temperature (°C)	Si/Al	Crystallinity (%)	Py TPD (mmol/g)	MQ-TPD (relative percentage of MQ)
0 (ZSM-5)	–	–	34	100	0.46	100
60	Static vacuum	100	41	101	0.42	97
60	Static vacuum	200	37	99	0.41	55
60	Static vacuum	300	39	102	0.43	40
60	Static vacuum	400	36	105	0.43	35
8	Vapour flow	50	43	100	0.39	42
8	Vapour flow	400	42	94	0.41	20

Table 2  
Operating conditions used in the various reaction studies

Reaction	Zeolite	WHSV (h <sup>-1</sup> )	Temperature (°C)	Conversion (%)
TDP <sup>a</sup>	ZSM-5	2, 4	450	2
TDP	ZSM-5	1.8	550	9–2
TiPB <sup>b</sup>	ZSM-5	0.6	270	2–70
TiPB	ZSM-5	0.6	270	9–67
TiPB	MOR	0.6	200	13–80
TiPB	Beta	0.6	160	30–46
TiPB	ZSM-5	0.1	270	2–80

<sup>a</sup> TDP: toluene disproportionation.

<sup>b</sup> TiPB: tri-isopropyl benzene cracking.

and external surface acidity, respectively, using temperature programmed desorption (TPD) techniques. MQ has a kinetic diameter of  $\pm 0.73$  nm which would make it difficult to enter the pores of ZSM-5, but it is possible that it could enter the channels of mordenite (0.70 nm  $\times$  0.65 nm) and beta (0.76 nm  $\times$  0.64 nm) after long adsorption times (>24 h). A shorter adsorption time ( $\approx 3$  h), however, combined with the slow diffusion rate of MQ into the channel structure, resulted in MQ adsorption occurring mainly on the external surface. Therefore, when relatively shorter adsorption times ( $\approx 3$  h) were used, MQ-TPD spectra provided important information on the relative changes in the external surface acidity of mordenite and beta after modification.

The capacities of the samples to adsorb *n*-hexane, *p*- and *o*-xylene were used to estimate the extent of pore mouth narrowing and pore blocking. The compound *n*-hexane was adsorbed at 80 °C and *p*- and *o*-xylene were adsorbed at 150 °C. At these temperatures, the partial pressures for *n*-hexane, *p*- and *o*-xylene are 60.4, 2.36 and 1.72 mbar, respectively.

### 3. Results and discussion

#### 3.1. Characterisation of acidity and crystallinity

Initial studies of silanisation were carried out at different temperatures in a static vacuum and a vapour phase flow system. These systems have been previously described [8]. Although, these different procedures have different mechanisms of silanisation, the results are internally consistent and demonstrate clearly, for example, the relative effect of deposition

temperature, irrespective of the procedure. Table 1 shows these effects on the Si/Al ratio, crystallinity (%), total (Py TPD) and external (4-MQ-TPD) acidity of ZSM-5. It has previously been proposed that silanisation has no effect on the overall acidity of the zeolite, as determined by TPD using ammonia as the probe molecule [1,9]. However, it is clear from the results in Table 1 that, irrespective of silanisation procedure, even though the total acidity has decreased only marginally, the external surface acidity has decreased significantly. The amount of Si deposited was slightly greater when the flow system was used (even after lower deposition times and temperatures) as opposed to the static vacuum system. This has considerable significance for the use of a cyclic procedure. In the flow system, products of the silanisation reaction are constantly removed from the system and this seems to enhance silanisation, possibly by providing unhindered access to reactive sites for oncoming TEOS molecules. In the cyclic system, this is further enhanced by virtue of the calcination process which results in the formation of new reactive sites as will be discussed later. With respect to relative percentage of crystallinity, there are indications of significant decreases in the case of the flow system. It is possible that in the case of the static system a form of epitaxial growth occurs but that in the flow system amorphous silica layers are preferred as a result of the absence of products of reaction.

In Table 1, a sample was treated at 400 °C using the vapour flow method for 8 h. Table 3 shows results at the same silanisation temperature for a sample treated for 6 cycles of 10 h each. The Si/Al ratios for these two samples are 42 and 41 respectively which are essentially equivalent and total acidities were found to be 0.41 mmol/g for both samples. The external acidity of the first sample however is reduced by 80% and that of the second by 100%. From this, it is deduced that the cyclic method is more efficient in utilising the TEOS to inertise external acid sites and that the vapour flow method results in a build up of silica in a non-uniform manner on selected sites.

#### 3.2. Effect of number of silanisation cycles on the acidity and the sorption properties of zeolites

As indicated above, to date, there have been few reported detailed investigations into the effect of

Table 3

Effect of cyclic versus single silanisation procedure on Si/Al ratio, total acidity (mmol Py/g), external surface acidity (relative measure of 4-MQ adsorption), percentage of crystallinity and adsorption of *n*-hexane and *p*-xylene of H-ZSM-5, mordenite and beta<sup>a</sup>

Zeolite	Si/Al	Total acidity (mmol/g)	Relative external acidity	Crystallinity (%)	Adsorption wt.% change	
					<i>n</i> -Hexane	<i>p</i> -Xylene
H-ZSM-5 (pure)	34	0.46	100	100	10.3	3
H-ZSM-5 (400/6 × 10) <sup>b</sup>	41	0.41	0	98	10.4	2.7
H-ZSM-5 (400/60) <sup>c</sup>	36	0.43	35	105	10.2	3.0
Mordenite (pure)	10	1.03	100	100	5.7	1.7
Mordenite (400/6 × 10)	11	0.94	0	95	2.6 <sup>a</sup>	1.0 <sup>a</sup>
Mordenite (400/60)	12	1.03	1	95	5.5	1.2
Beta (pure)	18	0.72	100	100	11.1	3.2
Beta (400/6 × 10)	22	0.67	3	95	10.0	2.5
Beta (400/60)	19	0.75	1	101	10.7	2.5

<sup>a</sup> Adsorption was still far removed from equilibrium after 3 h.

<sup>b</sup> Implies silanization at 400 °C of 6 cycles of 10 h each.

<sup>c</sup> Implies silanization at 400 °C of 1 cycle of 60 h.

using cyclical methods of silanisation, i.e. cycles of silanisation followed by calcination [4]. Fig. 1 shows a typical deposition–silanisation/calcination sequence and Table 3 shows the effect of cyclic silanisation of three different zeolites in a static vacuum system. It compares the properties of the fresh zeolite with those of a sample silanised, firstly, in a single step of 60 h, and, secondly, in six sequential steps of 10 h each. In the case of H-ZSM-5, the cyclic procedure leads to a greater deposition of silicon and at the same time to a lower total acidity. In the cyclic process when freshly silanised zeolite is calcined, the reaction products are removed and new sites exposed for further silanisation. This may lead to a more uniform silanisation and explain the greater deposition of silicon. At the same time, there will be a greater possibility of silanisation blocking pores since the reaction will be occurring throughout the external surface and not only on selected high energy sites. The lower relative percentage of crystallinity in the case of the cyclic process compared to the single step process is indicative of a tendency to produce an amorphous silica coating in the former case. In the case of the single step process in which there is no change in adsorption capacity for hexane or *p*-xylene, and only 65% loss of external acidity, the main silanisation reactions do not seem to be occurring at the pore entrances. On the other hand, the entire loss of external acidity in the case of the cyclic process with no change in hexane adsorption capacity but a decrease in *p*-xylene adsorption

capacity indicates that this method favours the development of a more uniform silica coating, including the narrowing and blockage of some pores, but that the three dimensional nature of the structure minimises the effect of this on diffusion of molecules. In the case of the one-dimensional mordenite, the pore blockage phenomenon associated with cyclic deposition is emphasised by observing that the only major difference between the two procedures is the significant decrease in hexane adsorption capacity. It must however be mentioned that in the case of cyclic deposition, the adsorption was so slow that equilibrium was not reached even after 3 h adsorption time. The three-dimensional beta behaved similarly to H-ZSM-5. Interestingly, in each case, after the cyclic process, at the stage when there is a total loss of external acidity, the total acidity is about 90–93% of the initial amount. This equates approximately with the external fraction of the surface area of the particles consistent with the loss of external surface acidity. In the single step process, the total acidity is very similar to that of the pure sample. This is probably due to the Py not being able to access some internal acid sites. This again is consistent with the cyclic process causing a more significant amount of pore mouth narrowing/blocking.

As already indicated, a major objective of the silanisation of zeolites is to inertise the external surface acidity and to modify the diffusional properties of the zeolite in a controlled manner so as ultimately to modify the resistance to diffusion for the

molecules of interest. In this way, the shape selective properties of the zeolites can be modified. Changes in diffusional resistance can occur either as a result of increased diffusional path lengths resulting from blockage of some pore openings or of pore narrowing which will inhibit the diffusion of larger molecules through pore mouths. Decoupling these two effects is not simple. For example, it is well known that crystal size of a zeolite, and thus diffusional path length, can significantly influence selectivity in a reaction [10]. Table 3 has shown that there is little difference between the sorption properties of the various zeolites for the different silanisation methods although for the one-dimensional mordenite there is a significantly lower rate of adsorption of hexane in the case of cyclic deposition. This may be indicative of pore blockage which would have a more significant effect for this dimensionality. Beta also shows a lower hexane adsorption rate for the cyclic deposition sample whereas there is little difference in the case of H-ZSM-5.

### 3.3. Effect of temperature on silanisation

Fig. 2 shows that the higher the silanisation temperature, the higher the initial TEOS conversion, thus resulting in a higher deposition of silica on the surface

at each cycle. As the number of modification cycles increases, it can be seen that the apparent TEOS conversions converge to a steady-state value. This is indicative of a change of reaction mechanism with temperature. In order to investigate the extent of deposition and to quantify the effects on the catalytic properties, the number of Si atoms deposited per surface area ( $\text{Si}/\text{nm}^2$ ) per cycle was calculated, based on TEOS conversion and the BET adsorption area. Fig. 3 shows that similar Si coatings of, for example,  $20 \text{ Si}/\text{nm}^2$ , can be achieved by using a combination of temperatures of 400, 300, 200 and  $50^\circ\text{C}$  and 2, 4, 13 and 16 cycles, respectively. Therefore, both temperature and number of cycles are important parameters. Although, the amount of silicon deposited is roughly the same in each case, this gives no indication of the physical characteristics of the deposited layer required to provide the desired reaction behaviour. These characteristics are best determined by carrying out appropriate probe reactions.

The above results allow a preliminary proposal to be made regarding the mechanism for the silanisation process. A mechanism for the reaction of TMOS with the zeolite surface was first proposed by Niwa et al. [11] with reference to mordenite. It is generally accepted that the alkoxysilane (TMOS and TEOS) interacts with the surface silanols forming the respective

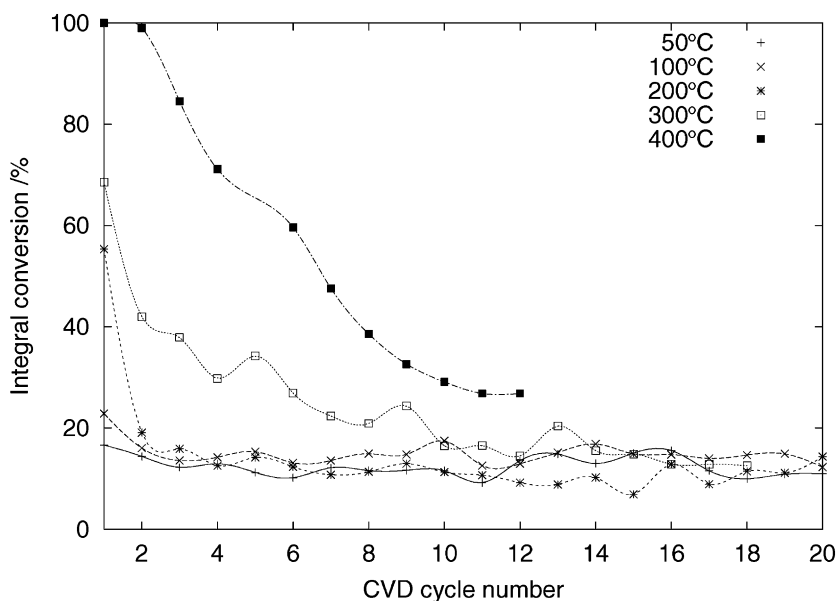


Fig. 2. Integral TEOS conversion at different deposition temperatures versus cycle number using ZSM-5.

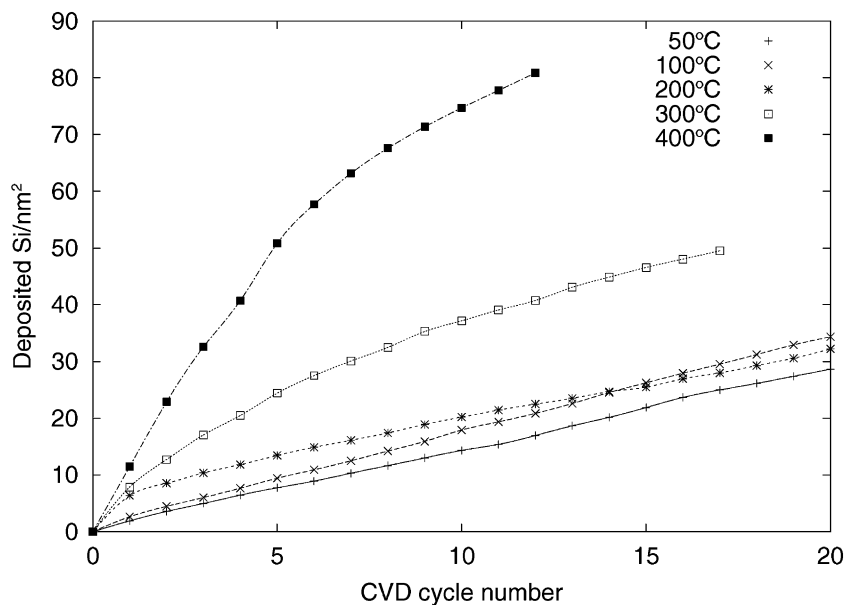
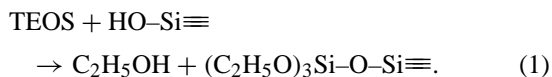


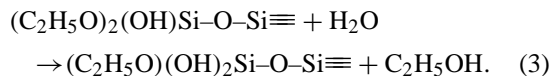
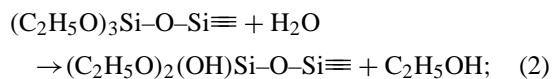
Fig. 3. Si atoms deposited/nm<sup>2</sup> of external surface area as a function of CVD cycle number for different deposition temperatures using ZSM-5.

alcohols. The silanisation process can be divided into the following reaction steps. Each sequential step in the following proposed mechanism is enhanced as the temperature increases.

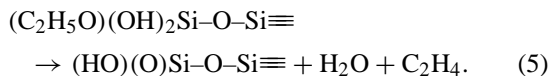
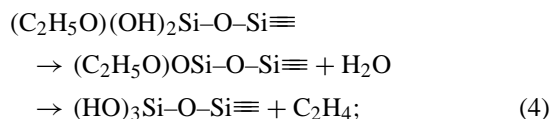
1. Adsorption: fully reversible adsorption of TEOS on the zeolite surface.
2. Deposition of TEOS:



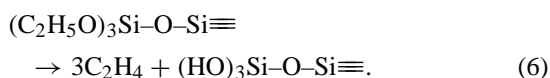
3. Water-induced series decomposition of TEOS:



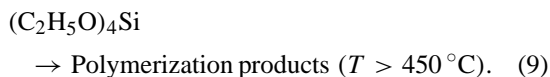
4. Termination reactions:



Overall:



5. Side reactions:



In the low temperature range, viz. up to 100 °C, physisorption is predominant. Only highly active sites on the external surface—those on the pore mouth close to the Al-sites in the secondary building layer—promote the surface reaction of the alkoxy silane, viz. the bonding of an alkoxy silane molecule accompanied by the formation of the corresponding alcohol (Rxn 1) and the deposition of a small amount of silica in a

highly selective manner. When increasing the deposition temperature to 200–300 °C chemisorption begins to dominate. Additionally, alcohol-dehydration (Rxn 7) takes place over the acid catalyst from about 200 °C thus resulting in the introduction of in-situ produced water into the reaction [12]. Water is known to hydrolyse the alkoxy groups of the alkoxy silanes, which decompose to the respective alcohol and silanols. The water-induced decomposition of chemisorbed alkoxy silane (Rxns 2 and 3) thus creates additional attachment sites. Furthermore, it is proposed that the shielding effect of the bulky ethoxy-groups is diminished to the size of small silanols and previously covered attachment sites are re-exposed for further reaction. Each additional layer of inert silica further reduces the acidity of the external surface. The alcohol dehydration reaction over the zeolite is thus ultimately inhibited and the water-catalysed decomposition reaction terminates since there is no more water formed (Rxn 4). At higher temperatures, however the tri-silanol species will readily dehydrate to form the siloxane (Si=O) and silanol (Si-OH) groups (Rxn 5) thus facilitating the next sequence of TEOS deposition.

At higher temperatures, an increased amount of alkoxide is deposited onto the external surface but in a less selective way than at the low temperature. At temperatures such as 400 °C, there was a high weight gain due to silica deposition but also a rapid deactivation with respect to TEOS conversion. In addition to the deposition via chemisorption and the water-catalysed decomposition, uncontrolled polymerisation of the alkoxide in the gas-phase occurs at these high temperatures, thus increasing the probability of the TEOS to undergo reactions not only on the zeolite surface but also in the gas phase (Rxn 8). As a consequence, a high degree of non-specific silica deposition occurs. A parallel ethene oligomerisation reaction also occurs. Although, this will not happen to a great extent, it can contribute to pore mouth blockage. In the cyclic procedure, these oligomerisation products will be removed in the calcination step.

### 3.4. Catalytic activity of the silanised zeolites

The results presented here have shown the effect of silanisation temperature and number of silanisation cycles on the Si loading/nm<sup>2</sup> which is indicative of

the overall process. The importance of silanisation of zeolites on their selectivities in various catalytic reactions has already been alluded to earlier in this paper and the results of the present study are presented here. The results reported here refer to the ZSM-5 sample. Similar results were observed in the case of beta and mordenite in the case of TiPB cracking. The effect of the silanisation process were investigated by studying the performance of the modified zeolites using the cracking of TiPB, which probes the extent of inertisation of external surface acidity, and disproportionation and alkylation of toluene which probes changes to diffusivity by monitoring the selectivities to specific product isomers. Fig. 4 shows the cracking activity of 1,3,5-TiPB as a function of Si deposited/nm<sup>2</sup>. It is clear that once a Si loading of approximately 10–15 atoms/nm<sup>2</sup> was achieved, the external acidity had essentially been removed. A small residual cracking activity was observed and this is ascribed to the activity of external surface silanol sites. It has been reported that the number of external hydroxyls in H-ZSM-5 is in the range of 1–5.5 OH/nm<sup>2</sup> [13] and that the number of external cationic sites is about 8.9 sites/nm<sup>2</sup> [14]. These values agree broadly with the number of Si atoms deposited on the external surface which result in the total passivation or inertization of the external surface catalytic activity. It is of interest to compare these results to those presented in Fig. 3. Complete inertisation had virtually been reached after about 5 cycles at 50 and 100 °C, after 3 cycles at 200 °C and after about 1 cycle at 300 °C; all of which equate to ±10–15 Si/nm<sup>2</sup>. However at 400 °C, as illustrated in Fig. 4, total inertisation of external surface sites was only achieved at a coverage of ±40 Si/nm<sup>2</sup>. In every case, the performance of the sample silanised at 400 °C show this sample to behave quite differently. As mentioned earlier, this is most likely due to the fact that at this high temperature, there is a significant degree of homogeneous decomposition of the TEOS resulting in a much higher conversion of the TEOS and a much greater but less uniform deposition of Si.

Toluene disproportionation is a useful probe reaction since the selectivity to *p*-xylene is a good indicator of changes in diffusional properties. Fig. 5 shows the selectivity to *p*-xylene (given as a fraction of total xylene isomers) as a function of Si deposited/nm<sup>2</sup>. At the very stage that the 1,3,5-TiPB activity has almost terminated, viz. at a coverage of about 10–15 Si/nm<sup>2</sup>,

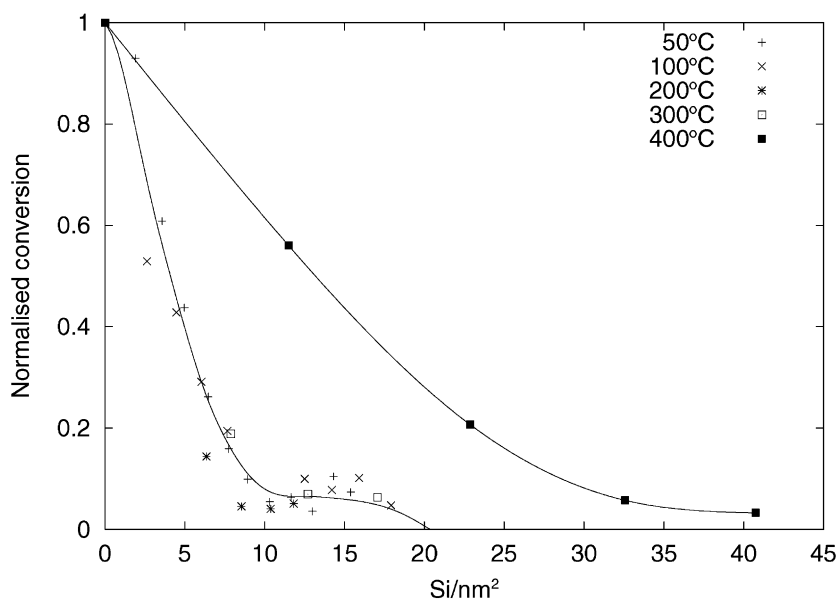


Fig. 4. Normalised conversion of 1,3,5-TiPB over ZSM-5 as a function of Si atoms deposited/nm<sup>2</sup> of external surface area for different deposition temperatures.

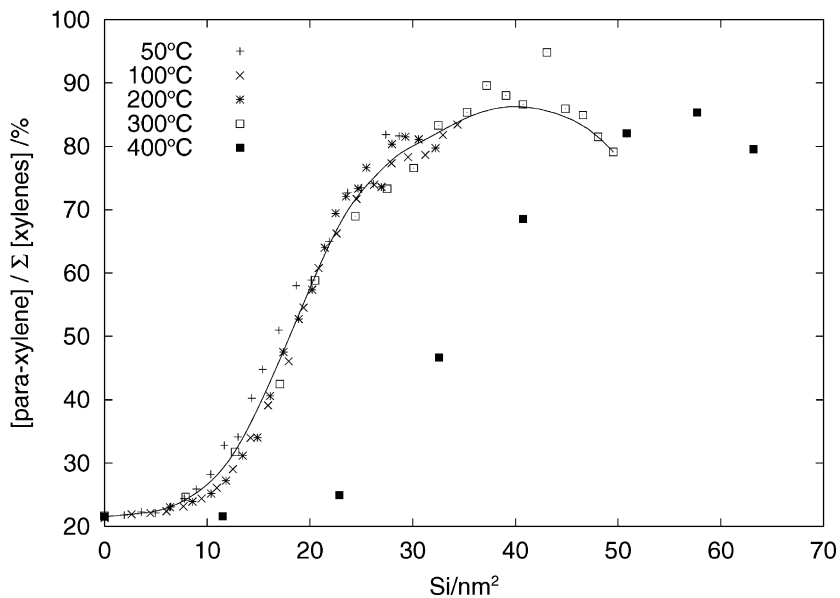


Fig. 5. The selectivity of *p*-xylene in the disproportionation of toluene over ZSM-5 as a function of Si atoms deposited/nm<sup>2</sup> of external surface area for different deposition temperatures.



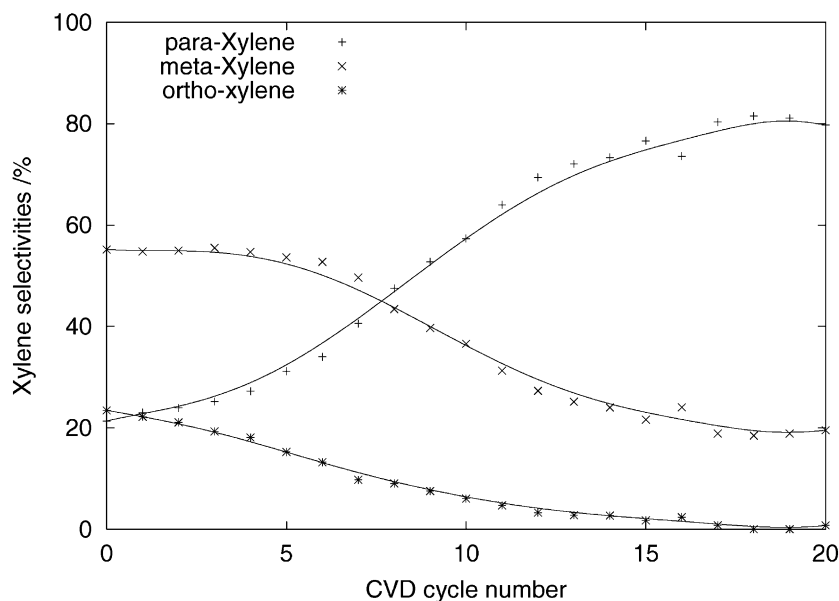


Fig. 6. Xylene selectivities in the disproportionation of toluene over ZSM-5 (deposition temperature = 200 °C) as a function of number of CVD cycles.

the *p*-xylene selectivity increased most rapidly, ultimately reaching a selectivity of >80% at a Si loading of about 35 Si/nm<sup>2</sup>. Fig. 6 shows the selectivity among the xylenes as a function of number of CVD cycles at a CVD temperature of 200 °C. Even though at this temperature, the TEOS conversion had reached a steady-state value of almost 15% after 3 cycles, it was only after about 7 cycles that the rate of increase of *p*-xylene relative to the other xylene isomers reached a maximum. Table 4 shows the number of cycles and the amount of Si deposited/nm<sup>2</sup> required to produce approximately 50% *p*-xylene selectivity for different deposition temperatures. These results

Table 4

Number of cycles and number of Si atoms deposited/nm<sup>2</sup> to obtain approximately 50% xylene selectivity for various deposition temperatures using ZSM-5

Deposition temperature (°C)	Number of cycles	Si/nm <sup>2</sup> (approximately)
50	12	16.1
100	10–11	18.6
200	8–9	18.1
300	3–4	18.8
400	3–4	33.0

show clearly that Si deposited/nm<sup>2</sup> is the parameter which probably best indicates the effect of silanisation, and is a key indicator of the combined effect of silanisation temperature and number of cycles. It is also significant to observe that the loading of Si occurred in such a continuous manner as illustrated by the uniformly continuous increase in *p*-xylene selectivity with number of CVD cycles.

Finally, it should be noted that in all the samples used the total acidity as reported in Tables 1 and 3 are not significantly changed by the silanisation procedure, whereas the external surface acidity is significantly affected. Hence the changes in selectivity of samples can be ascribed to the diffusional changes resulting from the silanisation process rather than to any changes in the total number or strength of acid sites Table 4.

#### 4. Conclusions

It has been shown that it is necessary to carefully control the reaction conditions when silanising a zeolite. Apart from considerations such as using static or flow systems [8], it is also critical to consider the

effect of deposition temperature and the number of deposition/calcination cycles. By careful control of the number of cycles, it is possible to systematically reduce the diffusional properties of the zeolite to whatever extent is desired. It has been shown that the amount of Si deposited/nm<sup>2</sup> is a good indicator of the process of silanisation. The conversion of TEOS and the products of the silanisation reaction at different temperatures have been used to propose a reaction pathway. Results shown for a variety of reactions indicate that silanised zeolites are able to significantly increase the yield of particular isomers as a result of the changes in diffusional constraints resulting from the silanisation process and the inertisation of the external surface acid sites.

### Acknowledgements

The authors wish to acknowledge the financial support of the National Research Foundation.

### References

- [1] A. Choplin, Surface organometallic chemistry on zeolites: a tool for modifying the sorption properties of zeolites, *J. Mol. Catal.* 86 (1994) 501.
- [2] N.R.E.N. Impens, P. Van der Voort, E.F. Vansant, Silylation of micro-, meso- and non-porous oxides: a review, *Microporous Mesoporous Mater.* 28 (1999) 217.
- [3] Y. Murakami, Super selective catalysis by CVD zeolite, *Stud. Surf. Sci. Catal.* 44 (1989) 177.
- [4] I. Wang, C.-L. Ay, B.-J. Lee, M.-H. Chen, Selectivation of *p*-dialkylbenzene with in situ vapour phase deposition modification of H-ZSM-5, *Appl. Catal.* 54 (1989) 257.
- [5] H.P. Röger, M. Krämer, K.P. Möller, C.T. O'Connor, Effects of in situ chemical vapour deposition using tetraethoxysilane on the catalytic and sorption properties of ZSM-5, *Microporous Mesoporous Mater.* 21 (1998) 607.
- [6] R.W. Weber, J.C.Q. Fletcher, K.P. Möller, C.T. O'Connor, The characterisation and elimination of the external acidity of ZSM-5, *Microporous Mater.* 7 (1996) 15.
- [7] R.W. Weber, K.P. Möller, C.T. O'Connor, The chemical vapour and liquid deposition of tetraethoxysilane on the external surface of ZSM-5, *Microporous Mesoporous Mater.* 23 (1998) 179.
- [8] R.W. Weber, K.P. Möller, C.T. O'Connor, The chemical vapour and liquid deposition of tetraethoxysilane on ZSM-5, *Microporous Mesoporous Mater.* 35-36 (2000) 533.
- [9] Y.S. Bhat, J. Das, K.V. Rao, A.B. Halgeri, Inactivation of external surface of ZSM-5: zeolite morphology, crystal size, and catalytic activity, *J. Catal.* 159 (1996) 368.
- [10] W. Kaeding, Shape selective reactions with zeolite catalysts, *J. Catal.* 95 (1985) 582.
- [11] M. Niwa, S. Kato, T. Hattori, Y. Murakami, Fine control of the pore-opening of the zeolite mordenite by chemical vapour deposition of silicon alkoxide, *J. Chem. Soc. Farad. Trans. 1* (80) (1984) 3135.
- [12] M.T. Aronson, R.J. Gorte, W.E. Farneth, The influence of oxonium ion and carbenium ion stabilities on the alcohol/H-ZSM-5 interaction, *J. Catal.* 98 (1986) 434.
- [13] I.F. Vankelecom, S. van den Broeck, E. Merckx, H. Geerts, P. Grobet, J.B. Uytterhoeven, Silylation to improve incorporation of zeolites in polyimide films, *J. Phys. Chem.* 100 (1996) 3753.
- [14] D.H. Olson, G.T. Kokotailo, S.L. Lawson, W.M. Meier, Crystal structure-related properties of ZSM-5, *J. Phys. Chem.* 85 (1981) 2238.