The Effect of Silanisation on the Catalytic and Sorption Properties of Zeolites

C.T. O'Connor*, K.P. Möller and H. Manstein
Centre for Catalysis Research, Department of Chemical Engineering, University of Cape Town

Abstract

Silanising zeolites can result in significant beneficial changes to their catalytic and sorptive properties. It is, however, necessary to carefully control the reaction conditions when silanising a zeolite. Apart from the different effects of using vapour or liquid deposition procedures and static or flow systems, the deposition temperature and the number of silanisation/calcination cycles are of great importance. By careful control of these conditions, it is possible to systematically modify the diffusional properties of the zeolite while at the same time inertizing the external surface acidity. The diffusional changes are more likely due to a blockage of pore entrances, resulting in a greater diffusion pathway, than to a controlled narrowing of the pore openings. By careful control of the number of silanisation/calcination cycles, it is possible to systematically change the diffusional properties. The amount of Si deposited/nm² is a good indicator of the process of silanisation. Silanised zeolites are able to significantly increase the yield of particular isomers as a result of the diffusional constraints.

Keywords: Zeolites, Silanization, Catalysis, Sorption

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. The size and dimensionality of these channel systems result in molecules being subjected to different diffusional resistances, thus ultimately controlling the selectivity of the reaction. Although the channel system has a large internal surface area, it has been shown that the external surface area of, for example, ZSM-5, is much greater than would be expected if it were assumed to be a perfectly spherical particle. Because the external surface is fully accessible to all molecules, it behaves catalytically in a non-shape-selective manner, and it is therefore of great interest to study the effects of passivating or inerting external acid sites in order to promote the shape-selective reactions. One way to achieve this is to silanise the zeolite. This treatment has the most important secondary effect of narrowing or blocking entrances to pores and thus modifying the diffusional resistances experienced by different molecules, either reducing the pore diameter or increasing the diffusional path length, respectively.

Although a wide range of zeolite structures is known, for reasons relating to properties such as physical and thermal stability, only relatively few have gained widespread industrial application as catalysts. Examples of these are Zeolite Y, Mordenite, ZSM-5 and Beta. For this reason, it is of great interest to develop methods to modify the channel system of these zeolites so as to produce the same diffusional properties of other more exotic but less stable zeolites.

Inertisation of external surface sites can be achieved by a number of techniques. One method passivates or poisons by sorbing bulky, strong base molecules such as methylquinoline onto the zeolite. The bulkiness ensures that the molecule does not enter into the pores of the zeolite, thus possibly poisoning the internal sites of the crystal. Another method of inerting external acid sites is to remove such sites

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1 Accepted: August 8, 2007
1 Rondebosch, 7700, South Africa
* Corresponding author
TEL: +27-21-650 2701, FAX: +27-21-650 3782
E-mail: Cyril.oconnor@uct.ac.za
by using chelating agents such as EDTA. It has also been extensively reported that treatment with molecules such as silanes, disilanes, SiCl₄ or diborane can result in a modification of the internal surface of a zeolite. However, passivation of exclusively external surface sites accompanied by modification of the pore opening is generally only achieved using an alkoxy-silane complex. This silanisation procedure is generally carried out using chemical vapour deposition (CVD) methods. The silicon source is usually a bulky alkoxy-silane complex such as tetramethoxysilane (TMOS) or tetraethoxysilane (TEOS). With respect to bulkiness, it is important to note that TMOS, for example, has a kinetic molecular diameter of about 0.89 nm which must be compared to the pore opening of H-ZSM-5, for example, which is 0.54-0.56 nm. TEOS has a kinetic diameter of about 0.96 nm, which makes it even more suitable with regard to minimising the possibility of silanisation of the internal surface.

There are many reports in the literature on the use of such methods and these have been reviewed elsewhere (e.g. 3-6). The zeolites most commonly investigated have been Mordenite and ZSM-5, and the silanising agents generally used have been TMOS and TEOS. In general, there is consensus that the most important effect of silanisation is not so much the inertisation of external surface acid sites, which occurs readily, but rather the changes in the diffusional properties of the zeolite by either narrowing or blocking the pore openings. In the latter case, the resultant greater diffusional path length mimics the effect of using a larger crystal size as far as catalytic shape selectivity of the zeolite is concerned. In this respect, the reactions most widely studied to date have been the disproportionation of alkyl aromatics (e.g. 6,7,10-12) since these reactions lead to the formation, respectively, of a variety of alkyl isomers with different diffusional coefficients and can thus be used to observe the effect of changes in diffusional properties.

To date, few authors have investigated in detail the importance of the careful control of the experimental procedures used in the silanisation process, particularly with respect to temperature and the number of silanisation cycles. Roeger et al. 7 have shown in a study of silanisation of HZSM-5 using TEOS that the cyclic silanisation/calcination procedure is critical in ensuring a controlled change in diffusional properties. Similarly few if any authors have taken care to measure the internal and external acidity after the silanisation process.

This paper presents results which show that a carefully controlled silanisation procedure using the alkoxy-silane, TEOS, can result in subtle but important changes in the amount of external surface acidity, in the diffusional properties of the zeolite and, consequently, in the catalytic and sorption properties of the treated zeolite.

### Experimental Procedures

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 8-12. Crystal sizes were approximately log-normally distributed around the mean values indicated in Tables 1 and 2. The Si/Al ratios are shown in Table 1. Using tetraethoxysilane (TEOS) as the silica source, modification was carried out in three different ways, viz. in a static

### Table 1: Effect of various silanisation procedures on the Si/Al ratio, relative % crystallinity and acidity of H-ZSM-5 using different deposition procedures

<table>
<thead>
<tr>
<th>Deposition Time (h)</th>
<th>Deposition Procedure</th>
<th>Temp. (°C)</th>
<th>Si/Al</th>
<th>% Crystallinity</th>
<th>Pyridine TPD (mmol/g)</th>
<th>MQ TPD (Rel. % MQ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (ZSM-5)</td>
<td>—</td>
<td>—</td>
<td>34</td>
<td>100</td>
<td>0.46</td>
<td>100</td>
</tr>
<tr>
<td>60</td>
<td>Static Vacuum</td>
<td>100</td>
<td>41</td>
<td>101</td>
<td>0.42</td>
<td>97</td>
</tr>
<tr>
<td>60</td>
<td>Static Vacuum</td>
<td>200</td>
<td>37</td>
<td>99</td>
<td>0.41</td>
<td>55</td>
</tr>
<tr>
<td>60</td>
<td>Static Vacuum</td>
<td>300</td>
<td>39</td>
<td>102</td>
<td>0.43</td>
<td>40</td>
</tr>
<tr>
<td>60</td>
<td>Static Vacuum</td>
<td>400</td>
<td>36</td>
<td>105</td>
<td>0.43</td>
<td>35</td>
</tr>
<tr>
<td>8</td>
<td>Vapour Flow</td>
<td>50</td>
<td>43</td>
<td>100</td>
<td>0.39</td>
<td>42</td>
</tr>
<tr>
<td>8</td>
<td>Vapour Flow</td>
<td>400</td>
<td>42</td>
<td>94</td>
<td>0.41</td>
<td>20</td>
</tr>
<tr>
<td>21</td>
<td>Liquid (water) a</td>
<td>25</td>
<td>39</td>
<td>104</td>
<td>0.40</td>
<td>53</td>
</tr>
<tr>
<td>21</td>
<td>Liquid (C₆H₁₄) b</td>
<td>25</td>
<td>37</td>
<td>96</td>
<td>0.44</td>
<td>29</td>
</tr>
</tbody>
</table>

a. Water and hexane, respectively, were diluents; 5 vol% TEOS.
b. Parent material had a crystal size of 1.5 μm and was used in powdered form.
vacuum system, vapour phase flow system and in the liquid phase. 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/calcination parts of the cycle. The results in Table 3 were generated using this procedure. The crystal diameter of the H-ZSM-5 was approximately 150 nm. 0.5 g of powder was supported on 4.5 g of inert sand of approx. 200 μm diameter.

The catalytic activity of the external surface was determined using the cracking of 1,3,5-triisopropyl benzene (TiPB) as a probe reaction\(^{11}\). TiPB has a kinetic diameter of 0.85 nm and is not expected to enter the channels of the zeolites. Disproportionation\(^{11,12}\) 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. TiPB conversions were carried out in the temperature range of 270°C and toluene disproportionation at temperatures in the region of 500°C.

Methods used to characterise the samples with respect to relative % crystallinity, external and total acidity, and sorption capacity have been described elsewhere\(^{10}\). Pyridine (Py) and 4-methylquinoline (MQ) were used to probe total and external surface acidity, respectively, using temperature-programmed desorption (TPD) techniques. MQ has a kinetic diameter of ± 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 × 0.65 nm) and Beta (0.76 × 0.64 nm) after long adsorption times (>24 h). A shorter adsorption time (≈3h), however, combined with the slow diffusion rate of MQ into the channel structure, resulted in MQ adsorption

### Table 3

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Si/Al</th>
<th>Total Acidity (mmol/g)</th>
<th>Rel. Ext. acidity</th>
<th>% Cryst.</th>
<th>Adsorption Wt. % change</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZSM-5 (pure)(^{3})</td>
<td>34</td>
<td>0.46</td>
<td>100</td>
<td>100</td>
<td>10.3</td>
</tr>
<tr>
<td>ZSM-5 (400/6×10)</td>
<td>41</td>
<td>0.41</td>
<td>0</td>
<td>98</td>
<td>10.4</td>
</tr>
<tr>
<td>ZSM-5 (400/60)</td>
<td>36</td>
<td>0.43</td>
<td>35</td>
<td>105</td>
<td>10.2</td>
</tr>
<tr>
<td>H-M (pure)(^{5})</td>
<td>10</td>
<td>1.03</td>
<td>100</td>
<td>100</td>
<td>5.7</td>
</tr>
<tr>
<td>H-M(400/6×10)</td>
<td>11</td>
<td>0.94</td>
<td>0</td>
<td>95</td>
<td>2.6(^{7})</td>
</tr>
<tr>
<td>H-M(400/60)</td>
<td>12</td>
<td>1.03</td>
<td>1</td>
<td>95</td>
<td>5.5</td>
</tr>
<tr>
<td>H-Beta (pure)(^{3})</td>
<td>18</td>
<td>0.72</td>
<td>100</td>
<td>100</td>
<td>11.1</td>
</tr>
<tr>
<td>H-Beta (400/6×10)</td>
<td>22</td>
<td>0.67</td>
<td>3</td>
<td>95</td>
<td>10.0</td>
</tr>
<tr>
<td>H-Beta (400/60)</td>
<td>19</td>
<td>0.75</td>
<td>1</td>
<td>101</td>
<td>10.7</td>
</tr>
</tbody>
</table>

a. Adsorption was still far removed from equilibrium after 3 hours
b. Samples were used in powder form. The nominal particle diameter (μm) was: ZSM-5 = 1.5, H-M = 0.8 (agglomerates of 0.2 μm), H-Beta =1.7 (agglomerates of 0.2 μm)

Fig. 1 Typical TEOS breakthrough curve during CVD of ZSM-5 at 50°C showing deposition, flushing and heating parts of the cycle.
occurred mainly on the external surface. Therefore, when relatively shorter adsorption times (≈3h) 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. 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. Sorption and diffusion studies were also carried out using cyclohexane and 1,2,4-trimethylbenzene.

Results and Discussion

Initial studies of silanisation were carried out in a static vacuum system, a vapour phase flow system and in a liquid phase system. 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 (pyridine TPD) and external (4-methylquinoline TPD) acidity of ZSM-5. However, it is clear from the results in Table 1 that, irrespective of the 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. Liquid phase deposition in a hexane solvent resulted in significant external surface silanisation at ambient conditions, similar to that achieved at 400°C in either of the vapour systems. This was an exploratory study and was not investigated further in this work. However, the liquid phase procedure clearly appears to have considerable attraction. With respect to relative % crystallinity, there are indications of significant decreases in the case of the flow system and in the liquid (hexane) 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.

As indicated above, there have to date been few reported detailed investigations into the effect of using cyclical methods of silanisation, i.e. cycles of silanisation followed by calcination. Table 2 shows the effect of cyclic silanisation on 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 60h, and, secondly, in 6 sequential steps of 10h each. In the case of HZSM-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 % 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 1-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 hours adsorption time. The 3-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% of the initial amount. In the single-step process, the total acidity is very similar to that of the pure sample. This is probably due to the pyridine 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 inert 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 resistances can occur either as the 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. It is, for example, well known that the crystal size of a zeolite, and thus the diffusional path length, can significantly influence selectivity in a reaction.\textsuperscript{13} Table 2 shows that there is little difference between the sorption properties of the various zeolites for the different silanisation methods, although for the 1-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. In a study of the effect of temperature on silanisation, it was found 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.

The influence of the silanisation of zeolites on their ability to change selectivities in various catalytic reactions has already been alluded to earlier in this paper. Commonly studied reactions have been toluene and ethylbenzene disproportionation. In the present study, the cracking of tri-isopropylbenzene (TiPB) probed the extent of inertisation of external surface acidity, and disproportionation and alkylation of toluene probed changes of diffusivity by monitoring the selectivities to specific product isomers. Fig. 2 shows the cracking activity of 1,3,5-TiPB as a function of Si deposited/nm\textsuperscript{2}. It is clear than once a Si loading of approximately 10 - 15 atoms/nm\textsuperscript{2} was achieved, the external acidity had essentially been removed. It has been reported that the number of external hydroxyls in H-ZSM-5 is in the range of 1 - 5.5 OH/nm\textsuperscript{2} and that the number of external cationic sites is about 8.9 sites/nm\textsuperscript{2}. These values agree broadly with the number of Si atoms deposited on the external surface which result in the total passivation or inertisation of the external surface catalytic activity. It is of interest to compare these results to those presented in Fig. 3 which shows the number of Si atoms deposited per nm\textsuperscript{2} of external surface area as a function of the CVD cycle number for different deposition temperatures using ZSM-5. Complete inertisation had virtually been reached after about 5 cycles at 50°C 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\textsuperscript{2}. However, at 400°C, as illustrated in Fig. 2, total inertisation of the external surface sites was only achieved at a coverage of ± 40 Si/nm\textsuperscript{2}. In every case, the performance of the sample silanised at 400°C showed 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. 4** shows the selectivity to p-xylene (given as a fraction of total xylene isomers) as a function of Si deposited/nm$^2$. At the very stage that the 1,3,5-TiPB activity has almost terminated, viz. at a coverage of about 10-15 Si/nm$^2$, the p-xylene selectivity increased most rapidly, ultimately reaching a selectivity of > 80% at a Si loading of about 35 Si/nm$^2$. **Fig. 5** shows the selectivity among the xylenes as a function of the number of CVD cycles using a CVD temperature of 200$^\circ$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 3** shows the number of cycles and the amount of Si deposited/nm$^2$ required to produce approximately 50% p-xylene selectivity for different deposition temperatures. These results show clearly that Si deposited/nm$^2$ 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 the number of CVD cycles.

**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 vapour or liquid deposition procedures and static or flow systems, on which the authors have previously reported, it is also most important to carefully 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$^2$ is a good indicator of the process of silanisation. 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. Although not discussed here, the authors have also demonstrated that silanisation is a powerful technique to favourably modify the sieving properties of a number of zeolites.

**References**


Author's short biography

C.T. O'Connor

Cyril O'Connor is the Dean of the Faculty of Engineering and the Built Environment at the University of Cape Town. He is a chemical engineer with a Ph.D. from the University of Cape Town and a D.Eng. from the University of Stellenbosch. He is the founding Director of the Centre for Catalysis Research and present Director of the Centre for Minerals Research both of which are based in the Department of Chemical Engineering. His main area of interest in catalysis is the synthesis and catalytic properties of zeolites. He is a former Vice-President of the International Zeolite Association and is presently Vice-Chairman of the Catalysis Commission of the IZA. He was Chairman of the Organizing Committee for the 14th International Zeolite Conference which was held in Cape Town in 2004. He is presently Chairman of the Council of the International Mineral Processing Congresses. He has published over 150 papers in international journals and has numerous publications in the proceedings of international conferences. He is a Fellow of the Royal Society of South Africa, of the South African Academy of Engineering, is an Hon. Fellow of the South African Institute of Mining and Metallurgy and of the South African Institution of Chemical Engineering.