The kinetics of silylation of hydroxylated silica 1: Aerosil

M. S. Nadiye-Tabbiruka and J. M. Haynes

School of Chemistry, University of Bristol, Bristol, United Kingdom

Abstract: The kinetics of the silylation of hydroxylated silica, the non-porous Aerosil using trimethylchlorosilane, under various reaction conditions has been investigated by a gravimetric technique and found to follow the law:

$$\frac{1 + b}{t} \ln \left( \frac{M_o}{M_o - M} \right) - \frac{M_o b}{M_o t} = k_a$$

which represents a first order reaction retarded by one of its products. From this analysis, the activation energy in the temperature range 598 K to 673 K, was found to be 155 kJ mol\(^{-1}\). The reaction is independent of pressure at values greater than 15 torr.

Key words: Aerosil – silylation kinetics – trimethylchlorosilane

Introduction

The silylation of silica, and many other hydroxylated adsorbents, has been used in the determination of the population of hydroxyl groups on the surfaces of the adsorbents. The resulting surfaces are hydrophobic, and show marked reduction in adsorption particularly of electron donor molecules. Because of their selective adsorption properties, these modified adsorbents are finding increasing applications in the field of chromatography, in industry and in reducing the fragility of optical fibres. A detailed study of the kinetics of silylation should reveal the mechanism and the optimum reaction conditions.

The kinetics of the silylation reaction depend, among other things, on the silane used [1, 2, 3], and on the type of silanol groups at the surface [4, 5, 6, 7, 8]. However, the mechanism of silylation using halosilanes is not yet clearly understood. In this case, the reaction is characterised by a fast initial part followed by a subsequent slow process. The fast reaction was attributed to “very active hydrogen bonded silanol groups” by Snyder and Ward [4], to part replacement of silanols by Chlorine atoms by Hertl and Hair [5], and to geminal and vicinal silanols by Van Venzelen [6]. The slow process was attributed to isolated silanol groups by some workers [4, 6], and to steric hindrance by others [2].

Chlorinated silanes are physisorbed around 303 K but chemisorbed at and above 523 K [7]. Under optimum reaction conditions, TMCS selectively reacts with isolated silanols on a one-to-one ratio in a first order reaction [7].

Attempts to fit the entire range of experimental data to a suitable rate law have not been quite successful. However, in the derivation of the kinetic law; the adsorption of the side products such as the halo acids (HX), has not been considered. These are likely to complicate the kinetics particularly when the gravimetric technique is used.

This paper provides the data for analysis, reviews the various analytical methods which have been used and investigates the unexplored possibility of the retardation of the reaction by the adsorption of HX.
Experimental

Apparatus and materials

A schematic diagram of the apparatus which was used for all the silylation reactions is given in Fig. 1. A mercury diffusion pump, backed by a rotary pump is used to achieve a vacuum of about \(10^{-5}\) torr, as checked with a McLeod gauge. The pressure in the system is followed using a calibrated pressure transducer (PT), the output of which is in units of mV. The output is assumed to remain linear, with respect to pressure in the pressure range 0 to 760 torr, 1 mV being approximately equivalent to 4.615 torr.

The silica sample used was Aerosil crush obtained from pellets prepared in a hand press. It was chosen because it is a nonporous silica sample. This was to minimise mass transfer problems which complicate the study of a porous sample.

Trimethylchlorosilane (TMCS) of BDH Chemicals Ltd of Poole and of purity 99.99% was chosen as the organosilane for the study. This was transferred directly to the sample reservoir and purified by the freeze-thaw process.

Table 1. Conditions of reaction for the silylation of silica (all Temp K)

<table>
<thead>
<tr>
<th>Run no</th>
<th>(T_{\text{pretreat}})</th>
<th>(T_{\text{react}})</th>
<th>extent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1((\times 2))</td>
<td>598</td>
<td>598</td>
<td>infinity</td>
</tr>
<tr>
<td>3((\times 3))</td>
<td>673</td>
<td>673</td>
<td>infinity</td>
</tr>
<tr>
<td>4((\times 3))</td>
<td>673</td>
<td>663</td>
<td>infinity</td>
</tr>
<tr>
<td>5((\times 3))</td>
<td>653</td>
<td>653</td>
<td>infinity</td>
</tr>
<tr>
<td>7((\times 4))</td>
<td>673</td>
<td>653</td>
<td>infinity</td>
</tr>
<tr>
<td>9((\times 2))</td>
<td>673</td>
<td>598</td>
<td>inf.(,1/4)</td>
</tr>
</tbody>
</table>

*) experiments performed at different pressures to check on the effect of pressure changes for pressures \(> 15\) torr.

Procedure

A sample of Aerosil, of mass about 200 mg, was loaded into a silica sample bucket and suspended from the microbalance. The balance had been calibrated prior to loading.

The system was pumped out at room temperature for 24 hours, by which time the samples had reached a constant weight. The stability of the vacuum was tested by isolating the system from the pumps for several hours and checking for leaks.

The adsorption line to tap 2 was flushed several times with oxygen, using tap 1 (see Fig. 1). An oxygen pressure of approximately 100 torr was then let into the system, between tap 1 and 2 (with tap 3 open), and the temperature of the sample raised to 473 K for several hours to oxidise any organic contaminants.