The Preparation of Silicon Oxynitride, Si_2N_2O, as a High Surface Area Powder by Reaction of Silica with Ammonia at 1100 °C

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The title reaction is found to occur with an amorphous, non-porous but high surface area form of silica; other silica phases, differing in crystallinity and porosity, give substantially lower degrees of nitrogen incorporation on reaction with ammonia.

We describe a convenient synthesis of silicon oxynitride, Si_2N_2O, as a high surface area powder, from the reaction of a particular silica phase with ammonia. Thermally stable inorganic materials in high surface area forms can be of interest in the fields of ceramics, as precursors to consolidated, fully dense bodies, and heterogeneous catalysis, as catalysts or catalyst supports. In the specific case of silicon oxynitride it has recently been noted that this compound has attractive material properties but that a suitable synthesis is lacking.[1]

The literature on the reaction of silica with ammonia shows surprisingly large differences in the degree of nitrogen incorporation. Thus Brinker and Haaland[2] found only 0.5 %w N in a pure silica gel treated in flowing ammonia up to 1090 °C. Kamiya *et al.* have found[3] up to 6 %w N in fibrous silica gels on treatment with ammonia up to 1000 °C. In contrast, Brow and Pantano[4] have reported the formation of dense silicon oxynitride films with 40 atom % N by treating thin (100 nm) microporous silica films with ammonia at about 1100 °C. In earlier work it had been shown[5] that a silica obtained from hydrolysis of silicon diimide gave Si_2N_2O on treatment with ammonia for four days at 900 °C; this reaction has incorrectly been cited, in a reference work on silica,[6] as taking place at 550 °C.

We have investigated the reaction of various silica phases with ammonia, with the idea that porosity and crystallinity could be important factors: porosity, since this determines access of ammonia to the bulk structure (and here it should be noted that the kinetic diameter of ammonia is 0.26 nm, which is less than the value of 0.36 nm for nitrogen;[7] thus solids with a large specific surface area measured by nitrogen adsorption are suitable for reaction with ammonia), and crystallinity, since it will presumably be more difficult to replace two-co-ordinate oxygen by three-co-ordinate nitrogen in a crystalline structure than in an amorphous one. Silica phases with various combinations of porosity and crystallinity are readily available, and the samples used in this work are shown in Table 1.

The results of treating these phases with ammonia at 1100 °C are shown in Table 2. It can be seen that (i) amorphous forms of silica give rise to higher bulk nitrogen contents than the crystalline ones, (ii) Aerosil silica gives a material with a surface composition corresponding to that calculated for Si_2N_2O, *i.e.* 28 %w N, (iii) extending the reaction time for Aerosil results in a similar value for the bulk, and (iv) the loss of surface area in the treated silica gel is proportionally much higher than for the Aerosil samples. The form of the Brunauer–Emmett–Teller (BET) isotherm for the Aerosil-derived products is the same as that for the starting Aerosil; in both cases the surface area is derived from small particles, *i.e.* these are non-porous materials.

Spectroscopic characterisation has provided some further information on the silicon oxynitride materials derived from Aerosil. Firstly, solid-state ^{29}Si n.m.r. showed no signal, even with a pulse delay of 3000 s. This is attributed to an extremely long relaxation time (>2 h) and/or a very broad signal due to a variety of local environments in the material, which is amorphous by *X*-ray diffraction. The absence of a signal at *ca.* δ −110, however, excludes the presence of silica, indicating that the sample is not a mixture of SiO_2 and Si_3N_4. Secondly, from *X*-ray photoelectron spectroscopy we can determine an Si 2p binding energy of 102.1 eV, intermediate between the values of 101.7 and 102.2 eV reported and cited for Si_2N_2O by Brow and Pantano;[4] our value of 103.6 eV for the starting Aerosil is identical with that reported by these authors for silica. Thirdly, Fourier-transform i.r. spectroscopy shows that the strong band with a peak maximum at 1109 cm^{-1} (Si–O vibration) in Aerosil silica progressively shifts to lower wavenumbers, and also broadens, with increasing nitrogen content, reaching a value of about 1040 cm^{-1} in the product with 25%w nitrogen. This has provided us with a rapid impression of the degree of nitrogen incorporation in these Aerosil-derived oxynitrides, and these i.r. data are being further interpreted by Professor Quintard and his co-workers at the University of Limoges, France, who have already analysed the infrared spectrum of crystalline Si_2N_2O.[8]

This work has thus provided a convenient synthesis of a high surface area form of silicon oxynitride, Si_2N_2O, in which the high surface area is derived from the external surface of small

Table 1. Types of silica used for reaction with ammonia.

	Porous	Non-porous
Crystalline	Silicalite[a]	Quartz wool, Quartz powder
Amorphous	Silica gel[b]	Aerosil-300[b,c]

[a] Silicalite is an aluminium-free structural analogue of zeolite ZSM-5. [b] *Ca.* 300 m^2 g^{-1}. [c] Aerosil is the trade name for a silica manufactured by Degussa.

Table 2. Reaction of various types of SiO_2 with flowing NH_3 (30 l h^{-1}) at 1100 °C.[a]

SiO_2	Bulk N, %w[b]	Surface N, %w[c]	Surface N, % at.[c]	Surface area/ m^2 g^{-1} [d]
Quartz wool	<1	14	20	
Quartz powder	2	10	14	
Silicalite/15 h	2	7	10	
Silicalite	4	7	11	
Silica gel[e]	10	13	19	34
Aerosil	22	24	34	
Aerosil/12 h	25	28	40	132
Aerosil/24 h	27	28	40	150

[a] All reactions carried out for 4 h unless otherwise stated, using 1—5 g silica. The products obtained from Aerosil and silica gel are amorphous, as determined by *X*-ray powder diffraction. [b] Determined by chemical analysis at the Technical University, Eindhoven. [c] Determined by *X*-ray photo-electron spectroscopy. [d] Determined by nitrogen adsorption (B.E.T. method). [e] 10 g used.

particles which in themselves are non-porous. In related work we have described approaches to similar materials using low temperature solution chemistry.[9]

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