Thorough characterization of a silicon oxynitride coated silica gel synthesized *via* chemical surface coating

Nathalie R. E. N. Impens,[a] Koen Schrijnemakers,[a] Etienne F. Vansant,[a] Piet Grobet,[b] Joseph Riga[c] and Olivier Brouxhon[c]

[a]*University of Antwerpen (UIA), Laboratory of Inorganic Chemistry, Department of Chemistry, Universiteitsplein 1, B-2610 Wilrijk, Belgium*

[b]*Catholic University of Leuven, Department of Agricultural Sciences, Kardinaal Mercierlaan 92, B-3001 Leuven, Belgium*

[c]*University Notre-Dame de la Paix, Institute for Studies in Interface Sciences, Rue de Bruxelles 61, B-5000 Namur, Belgium*

Mesoporous silica gel coated with a preceramic polysilazane coating has been pyrolysed in order to obtain a nitride coating on the pore walls. The reactions involved were studied using a combination of thermogravimetry (TG) and IR spectroscopy (FTIR) of the solids and volatiles. The bulk and surface chemical compositions of the ceramic end products have been determined by FTIR, NMR and X-ray photoelectron spectroscopy (XPS). The morphology including the homogeneity of the coating was investigated using a combination of N_2 porosimetry and transmission electron microscopy.

Recently, the interest in ceramic coatings has increased enormously, due to their exceptional mechanical, electrical, thermal and chemical properties, which make them useful in several aspects of modern technology. In many cases, they are used as protective coatings for oxidizable materials or for electronic applications. Recently, the synthesis of inorganic polymers as precursors for ceramics has gained much interest.[1–12] Pyrolysis of the precursors gives rise to an alternative low-energy synthesis route, which permits more flexible handling and processing of the ceramic end product. The Si_3N_4 polymeric precursors are usually prepared in the liquid phase, using a mixture of a chlorosilane and ammonia, dissolved in an inert or a reaction-restraining solvent, such as toluene or pyridine. Seyferth[2,13] stated that preceramic polymers could have various applications *e.g.* as binders, or as infiltration or coating agents for ceramic bodies. For example, Coblenz *et al.*[14] demonstrated that, when carbon–carbon composites are coated with a silazane polymer and pyrolysed in an inert atmosphere, the resulting Si_3N_4 coated bodies have a noticeably improved oxidation resistance. However, in order to ensure a chemical bond between the substrate and the preceramic coating, an *in situ* synthesis of the polymer has to be preferred.

The *in situ* formation of thin homogeneous ceramic coatings, independent of substrate texture, can be obtained using chemical surface coating (CSC).[15] With this technique, the substrate is repeatedly reacted with pure, gaseous reactives in a cyclic manner, forming a polymeric preceramic coating, which is chemically bound to the substrate surface. Thermally treating this so-called coating precursor[15] yields the formation of a thin ceramic surface layer, which is covalently connected to the substrate.

Treating a mesoporous silica gel with pure gaseous $SiCl_4$ and NH_3 in a cyclic manner at room temperature results in the formation of a preceramic polysilazane coating. The first treatment of the silica gel with $SiCl_4$ performed at 663 K is responsible for the covalent bonds between the preceramic polysilazane layer and the substrate. As a function of the number of ($SiCl_4$–NH_3) reaction cycles, the pores are gradually filled with the preceramic polymer. The occurring reaction mechanisms, the final composition of the coating precursors and the porosity changes during the synthesis are described elsewhere.[16,17]

In the present work, the thermal conversion of the $[Si(NH)_2]_x$ coating precursor into a nitride-coated silica gel is investigated in detail. A qualitative study of the conversion mechanism is obtained by a combination of the thermogravimetric analysis of the coating precursor and IR analysis of the produced solids and volatiles. The chemical composition of the bulk and surface of the end products is determined using FTIR spectroscopy, ^{29}Si solid-state NMR with Si–H cross polarization and decoupling (^{29}Si CP and DEC MAS NMR) and X-ray photoelectron spectroscopy (XPS). The coated silica gel morphology and coating homogeneity are determined using transmission electron microscopy (TEM) and N_2 porosimetry. In this way, the use and perspectives of chemical surface coating as a new technique to coat very irregular surfaces with thin ceramic films is investigated in detail.

Experimental

Silica gel (KG 60, Merck) was pretreated at 973 K for 17 h, in order to dehydrate and dehydroxylate the substrate, resulting in a surface carrying only isolated silanols (0.011 $\equiv$SiOH A^{-2}).[18,19] The silica was allowed to cool in an N_2-purged glove-box before starting the synthesis of the ($SiCl_4$–NH_3) coating precursor. The ($SiCl_4$–NH_3) preceramic polymer synthesis was performed in a gas adsorption apparatus at room temperature, except for the $SiCl_4$ treatment of the pure silica surface, which was performed at 633 K in order to ensure the formation of a chemical bond between the substrate and the preceramic polymer. The gas adsorption apparatus is described in detail elsewhere.[15,16] Extreme care was taken in order to prevent the samples from absorbing moisture, by handling them under N_2 or *in vacuo*. The coating precursors were heated in a N_2-purged Lenton tube furnace with different temperature programmes: after heating for 1 h at 673 K, the samples were heated at 10 K min^{-1} to 1173, 1373 or 1473 K. After 1 h at the maximum temperature (T_{max}) the samples were cooled to 673 K at 10 K min^{-1}. Finally, the samples were stored *in vacuo* at room temperature.

IR spectra were recorded on a Nicolet 5DXB FTIR spectrometer with photoacoustic detection (FTIR PAS). The PA detector is a prototype of the MTEC-100 cell, constructed by

J. F. McClelland. The photoacoustic cell was flushed with zeolite-dried helium in a glove box. The mirror velocity of the spectrophotometer was 16 cm s^{-1}.

XPS analyses were performed on a SSI-SSX 100 spectrometer equipped with an Al-Kα X-ray source ($h\nu$= 1486.6 eV). Charge referencing was performed using the C 1s line of the adventitious hydrocarbon (284.8 eV).

^{29}Si MAS NMR spectra were recorded at 298 K on a Bruker 400 MSL spectrometer, using a 4 kHz magic angle spinning. The magic angle was set prior to the insertion of the samples, by optimizing the response of the ^{79}Br signal of the spinning side band of KBr. Two types of experiments were performed: proton decoupling (DEC) and cross-polarization. The DEC experiments were performed using a 2 μs 90° ^{29}Si pulse and a 3600 s cycle time, whereas the CP analyses were obtained with a 2 μs 90° ^{29}Si pulse and a 5 s cycle time.

The N_2 adsorption–desorption isotherms at 77 K were measured with a Quantachrome Autosorb 1 instrument. The sample surface area was calculated using the BET model,[20] while the pore size distributions were obtained using the Barret–Joyner–Halenda (BJH) model.[21] The *t*-plot method of Lippens and de Boer[22] was used in order to measure the microporosity.

Results and Discussion

Conversion reactions

During the thermal conversion of the polysilazane-coated silica gel into ceramic, various condensation reactions yielding a stable, cross-linked coating structure are expected. In order to investigate the occurring reactions, the mass changes during the thermal treatment in combination with the IR spectra of the evolved gas and the solid end product are recorded. The thermogravimetric behaviour of the coating precursor synthesized with seven reaction cycles, performed in N_2 atmosphere at a heating rate of 10 K min^{-1} is shown in Fig. 1. Qualitatively, a similar thermogram was observed for a coating precursor synthesized with four reaction cycles.

At 563 K. A sudden mass decrease of 32 and 38% is observed for coating precursors synthesized with four and seven ($SiCl_4$–NH_3) reaction cycles, respectively (Fig. 1). Comparing the IR spectra of the solids treated at this temperature [Fig. 2(*b*)] and the coating precursor created at room temperature [Fig. 2(*a*)] shows a strong decrease of the NH_4^+ absorption bands at 3147, 3051, 2821, 1770 and 1440 cm^{-1}.

Elemental analysis showed that the NH_4Cl concentration falls down to <3 mass% after thermally treating a four- and seven-reaction cycle coating precursor at 563 K. Sublimation of ammonium chloride is expected to cause the majority of the mass loss at this temperature. However, a difference is observed between the analytically determined amount of initial NH_4Cl present at the coating precursors made with four and seven reactions cycles and the experimental mass loss at 563 K, *i.e.* 27 and 32% instead of 32 and 38%, respectively. Therefore, additional possible reactions have been studied.

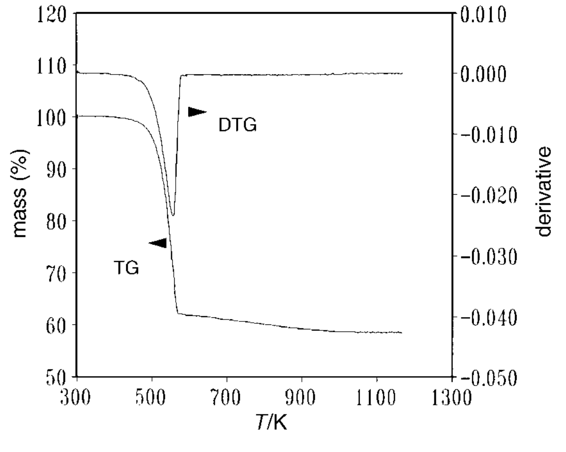

Fig. 1 TG and DTG analyses in a nitrogen atmosphere of the coating precursor after seven reaction cycles (heating rate 10 K min^{-1})

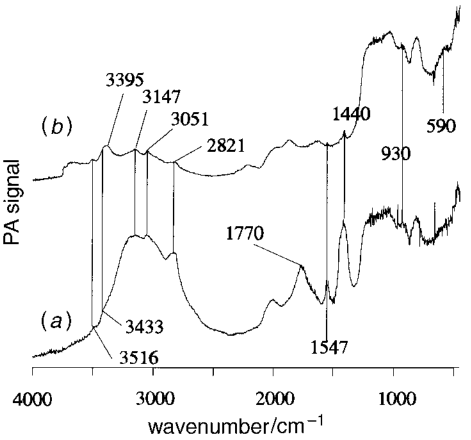

Fig. 2 FTIR PA spectra of the silica gel with preceramic coating after four reaction cycles: (*a*) at 298 K; (*b*) after heating to 563 K

First, FTIR gas analysis showed the liberation of NH_3 during thermal treatment up to 563 K, while a marked decrease of the NH_2 bending (1547 cm^{-1}) and the reappearance of the SiCl band at 590 cm^{-1} [Fig. 2(*b*)] are observed. These results indicate the reversed ammoniation reaction (1) as proposed by Low *et al.*[23]

$$\equiv SiCl + 2NH_3 \leftrightharpoons \equiv SiNH_2 \cdots NH_4Cl \qquad (1)$$

Secondly, the condensation of amino groups to silazanes, according to a reaction proposed by Fink *et al.*[24] [reaction (2)] may not be excluded:

$$2\equiv SiNH_2 \rightarrow \equiv SiNHSi\equiv + NH_3 \qquad (2)$$

However, they observed this reaction at temperatures >873 K *in vacuo*. A difference in reaction temperature can be expected due to the different amino group separations in both studies: Fink *et al.*[24] synthesized amino groups on an Aerosil surface thermally pretreated at 1073 K, *via* NH_3 treatment at 873 K. As the replacement of the hydroxy groups by $-NH_2$ was almost complete, the separation between the amino groups and the original hydroxy groups is similar, being approximately 1 nm according to the silanol number of Zhuravlev.[18,19] In the present study, the major portion of the amino groups of the preceramic precursor are geminal[16] and therefore much closer to each other, with a N···N distance of 0.3 nm.

Therefore, interaction between these amino groups can occur at lower temperatures. Finally, the presence of both SiCl and $SiNH_2$ groups also makes reaction (3) possible:[25]

$$\equiv SiCl + H_2NSi\equiv \rightarrow \equiv Si-NH-Si\equiv + HCl \qquad (3)$$

As no HCl liberation is detected, reactions (1) and (2) are quantitatively more important than reaction (3): if HCl is liberated, it should react immediately with the liberated NH_3 from the reversed ammoniation reaction (1) and reaction (2) producing NH_4Cl, which immediately sublimes from the sample surface. Additionally, the presence of the SiCl band shows that reaction (3) occurs only to a small extent at 563 K in comparison with reaction (1). Fig. 3(*b*) shows that the Si—N band at 930 cm^{-1} remains qualitatively unchanged after the thermal treatment, whereas the Si_2N-H band at 3359 cm^{-1} becomes visible after the sublimation of most of the NH_4Cl, indicating the presence of the polysilazane coating at the silica surface.

Summarizing, these data show that the major part of

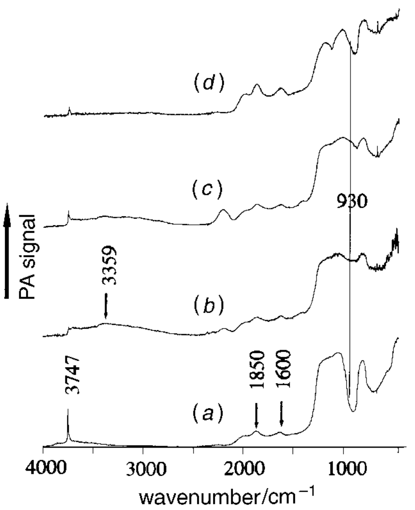

Fig. 3 FTIR PA spectra of (*a*) silica gel thermally treated at 973 K; coated silica gel after heating at (*b*) 1173 K; (*c*) 1373 K and (*d*) 1473 K

the mass loss is caused by the sublimation of NH_4Cl, but that also condensation reactions (2) and (3) and the reversed ammoniation reaction (1) of the primary amines are responsible for the mass decrease at 563 K.

Between 563 and 973 K. Only a small mass loss is observed (Fig. 1), arising from the production of NH_3. Comparing the IR spectra of the precursor treated at 563 and 1173 K [Fig. 2(*b*) and 3(*b*), respectively] shows a complete disappearance of the primary amines (3516, 3433, 1547 cm^{-1}), a decrease in the secondary amines signal (3359 cm^{-1}), and the presence of the Si—N band at 930 cm^{-1}. These data imply further condensation towards a nitride-like structure with increasing temperature. The reappearance of a small OH absorption band at 3747 cm^{-1} is due to bond breaking of some siloxanes, indicating a reaction with the silica bulk. The liberated ammonia originating from reaction (1) and reversed reaction (2) means that Morrow's reaction[26] can be expected:

$$\equiv SiOSi\equiv + NH_3 \rightarrow \equiv SiOH + \equiv SiNH_2 \qquad (4)$$

In this way, nitrogen can diffuse into the bulk silica by attack of ammonia on the bulk siloxanes.

Evolution of the chemical composition during synthesis

Bulk FTIR study. The chemical composition of the coating precursor (298 K) and the coated silica gel heated at 1173, 1373 and 1473 K were determined by a combination of FTIR PAS, XPS and NMR techniques. Fig. 3 shows IR spectra of the untreated and coated substrate heated at different temperatures. Comparing Fig. 3(*b*) and (*c*) shows the growth of the silanol absorption band (3747 cm^{-1}) relative to the reference band at 1850 cm^{-1} with increasing conversion temperature. This indicates that the SiO_2 bulk modification increases according to reaction (4). However, all the end products possess relatively low OH concentrations in comparison with the untreated silica gel [Fig. 3(*a*)], indicating the presence of chemical bonds between the coating and the silica substrate. At 1373 K, the silazane band totally disappeared [Fig. 3(*c*)], indicating a total conversion of the polysilazane preceramic coating into a nitride coating. A further raising of the temperature to 1473 K [Fig. 3(*d*)] leads to drastic change in the total silica vibration pattern: a splitting of the 1250–1050 cm^{-1} asymmetric SiOSi stretch has occurred, whereas the relative areas of the 1850 and 1600 cm^{-1} SiOSi combination and overtone vibrations have changed. The same phenomenon was observed in the IR spectrum of pure silica gel thermally treated at 1473 K, and was due to sintering, leading to a totally collapsed, non-porous structure. Therefore, the changes in Fig. 3(*d*) may also indicate a structure deformation, but a morphological study is necessary to confirm this statement. With increasing temperature, the Si—N band seems to shift towards higher absorption frequencies. At 1473 K, the SiOSi absorption band at 1250–1000 cm^{-1} has merged with the Si–N band. This may indicate a conversion of the silicon nitride into silicon oxynitride,[27] but a more detailed compositional investigation using XPS and NMR spectroscopy is required.

Bulk NMR study. More information about the chemical composition of the bulk samples can be obtained using CP and DEC ^{29}Si MAS NMR. Whereas the CP technique amplifies the signals of hydrogen-containing Si species, the decoupling technique provides a quantitative picture of the occurrence of the different tetrahedral silicon arrangements. Fig. 4 shows ^{29}Si CP and DEC MAS NMR spectra for pure silica, the coating precursor and the end products obtained at 1173 and 1373 K.

Relative to the pure substrate [Fig. 4(*a*)], the formation of the coating precursor at room temperature leads to the disappearance of the −91.8, −101.3 and the decrease of the −110 ppm bands in the CP and DEC spectra, assigned to the $O_2Si(OH)_2$,[28] O_3SiOH[29] and SiO_4[29] species, respectively [Fig. 4(*b*)]. Whereas the disappearance of the SiOH species is due to the presence of the chemical bonds between the substrate and the preceramic coating, the SiO_4 band reduces to 50% in the decoupling spectrum due to the doubling of mass during the precursor formation: whereas the untreated silica gel contains 100% SiO_2, the coating precursor contains 50% SiO_2 and 50% polysilazane structure together with NH_4Cl. An additional band positioned at −39.8 ppm is observed in both the CP and DEC MAS NMR spectra. Some other bands between −50 and −90 ppm are only observed in the CP spectrum arising from the presence of hydrogen, but are

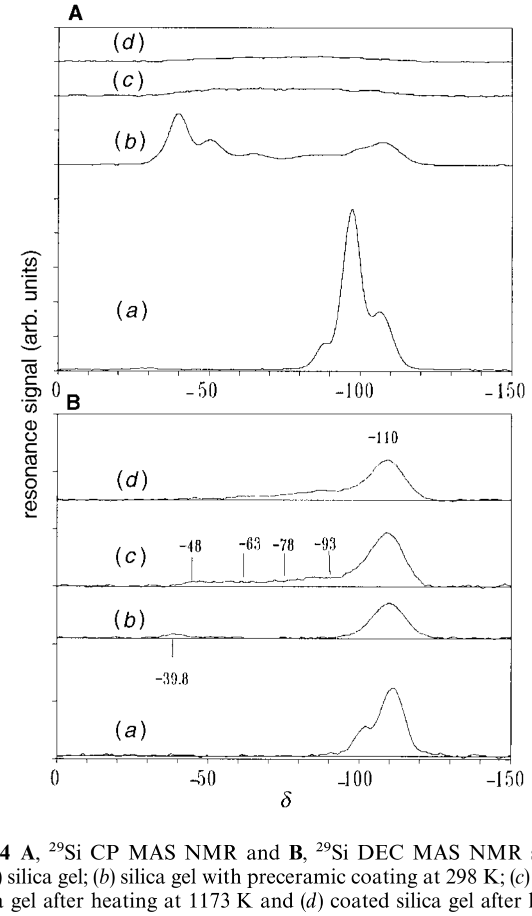

Fig. 4 **A**, ^{29}Si CP MAS NMR and **B**, ^{29}Si DEC MAS NMR spectra of (*a*) silica gel; (*b*) silica gel with preceramic coating at 298 K; (*c*) coated silica gel after heating at 1173 K and (*d*) coated silica gel after heating at 1373 K. The spectra are plotted on the same scale.

quantitatively too weak to be observed with the DEC technique. These bands represent the different tetrahedral Si arrangements in the preceramic coating. By analogy with silicon nitride and oxynitride assignments by NMR, the resonance frequency of Si bound by N and O is expected to decrease with increasing number of bound oxygens. Therefore, the bands close to -90 ppm are assigned to preceramic species near the silica bulk formed during the first reaction cycle, whereas the bands near -40 ppm are expected to represent the nitrogen-rich tetrahedral Si arrangements in the preceramic polymeric coating.

Fig. 4(*c*) and (*d*) show that very weak CP spectra are obtained from the heated samples. This indicates the absence of hydrogen, which confirms the FTIR conclusions [Fig. 3(*b*) and (*c*)]. However, some trends are observed in the DEC spectra of the converted samples with increasing temperature: the absolute intensity of the SiO_2 bulk resonance band (-110 ppm) and the SiN_4 band at -48 ppm decrease with increasing conversion temperature, in favour of the SiN_3O, SiN_2O_2 and $SiNO_3$ oxynitride species, with band positions at -63, -78 and -93 ppm, respectively[30] [Fig. 4(*c*) and (*d*)]. This indicates that the pure Si_3N_4 and SiO_2 phases diffuse into each other, leading to the formation of a mixed silicon oxynitride coating.

Surface XPS study. Whereas IR and NMR have given a general bulk picture of the conversion reactions and the chemical composition of the samples, XPS provides a more detailed picture of the chemical composition of the coatings. Fig. 5 shows Si 2p XP spectra of the untreated silica gel, the coating precursor and the converted samples prepared at 1173 and 1373 K. In order to investigate the evolution of the Si 2p binding energies as a function of the synthesis steps, some simulations were made and semi-quantitative data are provided in Table 1.

The Si 2p binding energy level of the untreated silica gel (Si_{SiO_2}) is at 104.2 eV with a full width at half maximum (FWHM) of 1.88 eV [Fig. 5(*a*), Table 1]. In order to find the binding energy of the Si 2p electron in a polysilazane environment (Si_{SiNH_x}), the simulation of the spectrum of Fig. 5(*b*) was initiated by positioning one band at 104.2 eV, representing the bulk Si_{SiO_2}. Another band was found by iteration at 103.2 eV, with a normal FWHM of 1.84 eV, representing 80% of the total amount of Si detected. This band is assigned to the various $Si_{[Si(NH)_2]_x}$ species. As some photoelectrons are able to escape from part of the silica bulk underneath the polysilazane structure, the measuring depth can be roughly estimated as follows: as a 20:80% ratio was found between the Si_{SiO_2} and Si_{NH_x} band intensities [Fig. 5(*b*)], and taking into account that 75% of the XPS signal is due to electrons coming from a depth equal to the attenuation length ($\lambda_{Si} \approx 20$ A), the coating thickness can be estimated as between 30 and 35 A. Porosity measurements showed that after seven reaction cycles cylindrical pores of 60 A diameter are filled, indicating a preceramic coating thickness of *ca.* 30 A. Therefore good agreement is found between both preceramic coating thickness estimations.

When the same difference in binding energy is accepted between the 2p electrons of Si_{SiO_2} and $Si_{Si_3N_4}$ as observed by Brow and Pantano,[31] the $Si_{Si_3N_4}$ band should be positioned at 102 eV. In order to simulate the Si 2p spectra of the converted samples, two bands were positioned at 104.2 and 102 eV, assigned to Si_{SiO_2} and $Si_{Si_3N_4}$ respectively, as the formation of silicon nitride was expected (IR and NMR). By iteration, an intermediate band was found at 103 eV, having the same energy as $Si_{[Si(NH)_2]_x}$. However, IR and NMR studies showed the practical absence of silazanes and H-containing species, respectively. Therefore, this band can be assigned to a species with a composition intermediate between SiO_2 and Si_3N_4, *i.e.* silicon oxynitride. These results indicate that Si 2p XPS can not distinguish silazanes from silicium oxynitride. Comparing the simulations of the spectra of Fig. 5(*c*) and (*d*), Si_{SiO_2} and $Si_{Si_3N_4}$ disappear in favour of silicon oxynitride formation with increasing pyrolysis temperature. Assuming a similar measuring depth for both samples, these results confirm the NMR conclusions, that diffusion of nitrogen into the silica bulk occurs, resulting in a thicker coating of silicon oxynitride.

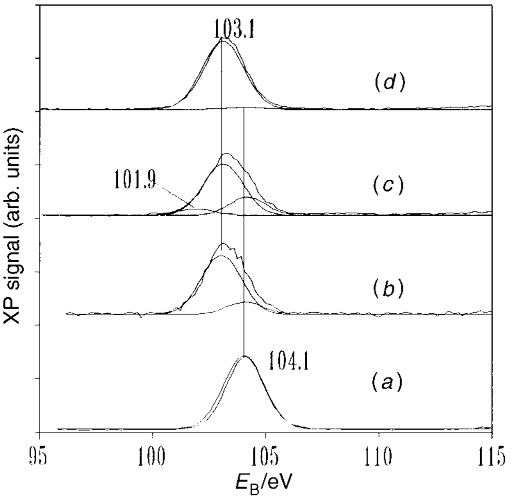

Fig. 5 XP spectra of (*a*) silica gel; (*b*) silica gel with preceramic coating at 298 K; (*c*) coated silica gel after heating at 1173 K; (*d*) coated silica gel after heating at 1373 K

Morphology of the coated silica gel after pyrolysis

The overall morphology of the coated silica gel has been studied using transmission electron microscopy (Fig. 6). Photographs of untreated and coated silica gel heated at 1173 K indicate that the original morphology is unchanged after the thermal treatment. A similar TEM picture was found for the coated silica gel up to 1373 K. This shows, in combination with the chemical data, that ultrathin films can be created in a very controlled way on an irregular substrate.

A more detailed picture of the coated silica gel morphology is obtained using N_2 porosimetry. The isotherms and pore size distributions (Fig. 7) of the coated silica gel heated at 1373 K is compared to the pure substrate which was similarly thermally treated. The coated silica gel created at 1173 and 1373 K exhibited a similar hysteresis type as the pure substrate, indicating that the presence of the coating does not affect the pore shape up to 1373 K (Fig. 7). For the coated silica gel

Table 1 Band assignments and percentages of different species in silica gel, the preceramic material and the coated silica gel according to the Si 2p XPS signal

E_B/eV	assignment	SiO_2 gel	coating precursor	end product (1173 K)	end product (1373 K)
104.1	SiO_4	100	20	22	2
103.1	$Si(NH)_4$	—	80	—	—
103.1	SiO_xN_{4-x}	—	—	70	98
101.9	SiN_4	—	—	8	—

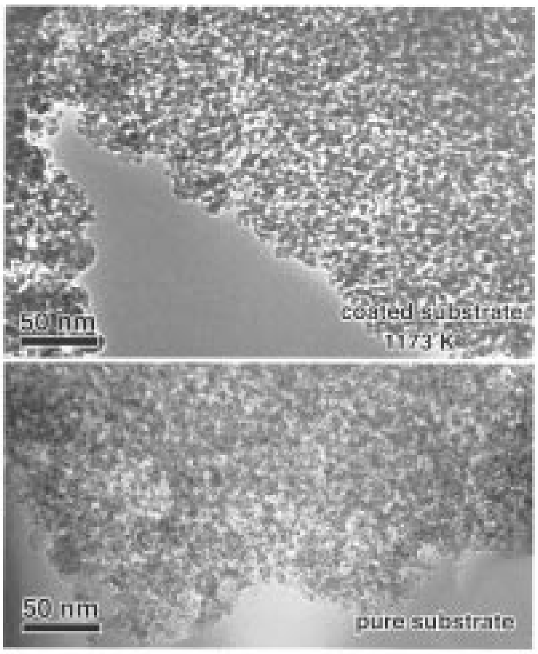

Fig. 6 Transmission electron micrographs of silica gel as the pure substrate (top) and the coated silica gel after heating at 1173 K (bottom)

pyrolysed at 1173 and 1373 K a shift of the pore size distribution was observed towards smaller pore sizes indicating pore narrowing (Fig. 7). As the pore shape remains unchanged while pore narrowing is observed, it can be concluded that the silica substrate is regularly coated after heating to 1373 K.

Table 2 lists the total pore volume and the BET surface area of the end products and pure silica gel after identical thermal treatment. Upon increasing the temperature from 1173 to 1373 K, the effect of the pore volume decrease due to the presence of the coating becomes smaller, indicating shrinkage of the coating due to condensation reactions and sintering. At 1473 K, no practical difference in porosity is observed between the pure substrate and the end product, as both samples are totally sintered, leading to the formation of non-porous structures, which confirms that the IR spectral changes of the 1473 K treated end product [Fig. 3(*d*)] indeed originate from drastic morphological changes.

Conclusions

A silicon oxynitride coating on mesoporous silica gel has been synthesised *via* chemical surface coating. The reaction mechanisms of the thermal conversion of the preceramic coating into a chemically bound nitride coating have been determined qualitatively by a combination of FTIR analysis of the solids and volatiles. The surface as well as the bulk composition of the coated silica gel was determined as a function of the pyrolysis temperature. With increasing temperature, both nitrogen diffusion into the silica bulk and the disappearance of the Si_3N_4 phase were observed, leaving a mixture of different silicon oxynitride phases on the pore walls. Comparison of TEM images, N_2 adsorption–desorption isotherms and pore size distributions of the untreated and coated silica gel showed that a very regular coating was formed at the pore walls.

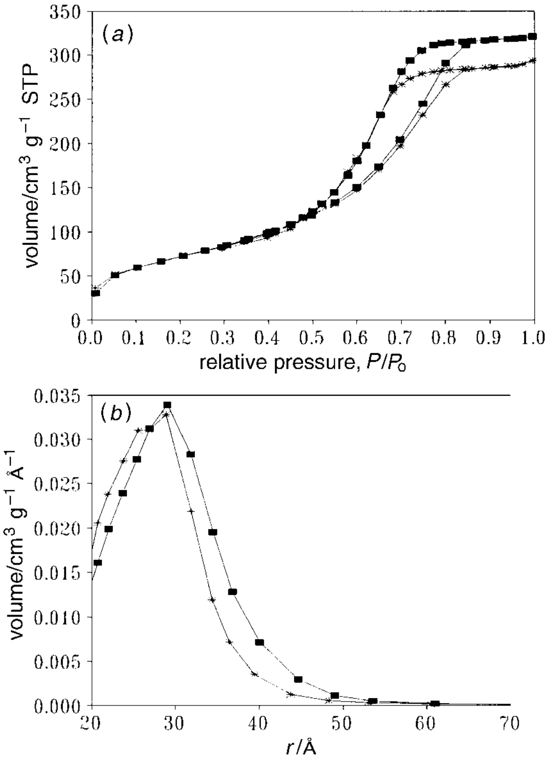

Fig. 7 (*a*) N_2 adsorption–desorption isotherms at 77 K and (*b*) desorption pore size distributions of (■) silica gel and (✳) coated silica gel after identical thermal treatments, with a maximum temperature of 1373 K

Ultimately, it is shown that the oxynitride coatings are chemically bound to the silica substrate, and the coated silica gel texture approaches the original substrate texture. This implies the applicability of chemical surface coating in the synthesis of a ceramic coating on a very irregular substrate, with a minimal impact on the materials morphology.

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References

1 Y. Yokoyama, T. Nanba, I. Yasui, H. Kaya, T. Maeshima and T. Isoda, *J. Am. Ceram. Soc.*, 1991, **74**, 654.
2 D. Seyferth, in *Advances in Chemistry Series 224*, ed. J. M. Zeigler and F. W. G. Fearon, American Chemical Society, 1990, p. 565.
3 M. Birot, J. P. Pillot and J. Dunogues, *Chem. Rev.*, 1995, **95**, 1443.

Table 2 Total pore volume and surface area of substrates and end products identically thermally treated

	pore volume/cm^3 g^{-1}			surface area/m^2 g^{-1}		
T_{max}/K	substrate	end product	% diff.	substrate	end product	% diff.
1173	0.677	0.464	31	327	281	14
1373	0.492	0.444	10	265	263	1
1473	0.001	0.008	—[a]	1	5	—[a]

[a] Differences in pore volume and surface area are not calculated due to the extremely low porosity of both substrate and end product.

4 D. Seyferth and H. Plenio, *J. Am. Ceram. Soc.*, 1990, **73**, 2131.

5 N. R. Dando and A. J. Perotta, *Chem. Mater.*, 1993, **5**, 1624.

6 D. Seyferth and C. Strohmann, *Chem. Mater.*, 1995, **7**, 2058.

7 D. Bahloul, Pereira and P. Goursat, *J. Am. Ceram. Soc.*, 1993, **76**, 1156.

8 O. Funayama, M. Arai, Y. Tashiro, H. Aoki, T. Suzuki, K. Tamura, H. Kaya, H. Nishii and T. Isoda, *Nippon Seramikkusu Kyokai Gakujutsu Ronbunshi*, 1990, **98**, 104.

9 G. T. Burns, T. P. Angelotti, L. F. Hanneman, G. Chandra and J. A. Moore, *J. Mater. Sci.*, 1987, **22**, 2609.

10 D. Seyferth, G. H. Wiseman and C. Prud'homme, *Mater. Sci. Res.*, 1984, **17**, 263.

11 P. W. Lednor and R. De Ruiter, *Mater. Res. Soc. Symp. Proc.*, 1988, **121**, 497.

12 O. Funayama, H. Nakahara, M. Oroda, M. Okumura and T. Isoda, *J. Mater. Sci.*, 1995, **30**, 410.

13 D. Seyferth and G. Wiseman, *Polym. Preprints*, 1984, **25**, 10.

14 W. S. Coblenz, G. H. Wiseman, P. B. Davis and R. W. Rice, in *Proceedings of the Nineteenth University Conference on Ceramic Science*, North Carolina State University, Nov. 9, 1982.

15 E. F. Vansant, P. Van Der Voort and K. C. Vrancken, *Characterization and Chemical Modification of the Silica Surface*, Elsevier, Amsterdam, 1995.

16 N. R. E. N. Impens, K. Possemiers and E. F. Vansant, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, 4285.

17 N. R. E. N. Impens, K. Possemiers, K. Schrijnemakers, N. Maes and E. F. Vansant, *J. Porous Mater.*, in press.

18 L. T. Zhuravlev, *Colloids Surf. A: Physiocochem. Eng.*, 1993, **74**, 71.

19 L. T. Zhuravlev, *Langmuir*, 1987, **3**, 316.

20 S. Brunauer, P. H. Emmet and E. Teller, *J. Am. Chem. Soc.*, 1938, **60**, 309.

21 E. P. Barret, L. G. Joyner and P. P. Halenda, *J. Am. Chem. Soc.*, 1951, **73**, 373.

22 B. C. Lippens and J. H. de Boer, *J. Catal.*, 1965, **4**, 319.

23 M. J. D. Low, A. G. Severdia and J. Chan, *J. Catal.*, 1981, **71**, 144.

24 P. Fink, I. Plotzki and G. Rudakoff, *Wiss. Zeitschr. Friedrich-Schiller Univ. Naturwiss.*, 1990, **39**, 217.

25 P. Van Der Voort, K. C. Vrancken and E. F. Vansant, *J. Chem. Soc., Faraday Trans.*, 1993, **89**, 63.

26 B. A. Morrow and I. A. Cody, *J. Phys. Chem.*, 1975, **79**, 2405.

27 P. S. Peercy, H. J. Stein, B. L. Doyle and V. A. Wells, in *Proc. 7th Int. Conf. Chemical Vapour Deposition*, ed. T. O. Sedgwick and H. Lydtin, The Electrochemic Society, Princeton, New York, 1979, vol. 79, p. 199.

28 A. P. Legrand, *J. Chim. Phys. Physichim. Biol.*, 1987, **84**, 1203.

29 E. Lippmaa, M. Magi, A. Samoson, G. Engelhardt and A-R. Grimmer, *J. Am. Chem. Soc.*, 1980, **102**, 4889.

30 R. S. Aujla, G. Leng-Ward, M. H. Lewis, E. F. Seymour, G. A. Steyles and G. W. West, *Philos. Mag. B*, 1986, **54**, L51.

31 R. K. Brow and C. G. Pantano, *J. Am. Ceram. Soc.*, 1987, **70**, 9.

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