General method of preparation of mesoporous M/Si_3N_4 nano-composites *via* a non-aqueous sol–gel route

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Received (in Cambridge, UK) 19th August 2005, Accepted 28th September 2005
First published as an Advance Article on the web 14th October 2005
DOI: 10.1039/b511790a

We report a general method for the preparation of transition-metal silicon nitride nanocomposites; for example, mesoporous Pd–Si_3N_4 nanocomposite materials with high surface area were prepared by pyrolysis of a silicon palladium imide–chloride complex which was synthesized by reaction of silicon diimide gel with palladium chloride. These porous nanocomposites catalyse organic reactions.

There has been considerable interest in the preparation of transition-metal loaded porous materials due to their potential applications in heterogeneous catalysis, catalytic gas filters and other fields.[1–3] The porous materials, which are used as supports of the active phases, are generally oxides such as SiO_2, Al_2O_3 and zeolites.[1,2,4] These materials show a rather low thermal conductivity, which makes them unstable at high temperature, mainly due to the sintering reaction of the active metals with the supports. Silicon nitride exhibits high thermal conductivity, good mechanical properties and low chemical reactivity, even at high temperature, and has been widely studied in recent years for use in dense high temperature ceramics.[5–7] However, there are few reports of using silicon nitride as a support of catalytically active phases.[8,9]

We have reported the preparation of a high surface area mesoporous silicon diimide gel, $Si(NH)_x(NH_2)_y(NMe_2)_z$ Me=CH_3, by acid-catalyzed ammonolysis of tris(dimethylamino)silylamine, $(Me_2N)_3SiNH_2$, TDSA.[10] Pyrolysis of the silicon diimide gel at 1000 °C gave a mesoporous amorphous silicon nitride with high surface area and narrow pore size distribution.[11] These properties suggest that our silicon nitride is a potentially useful catalyst support.

In this paper we report the preparation of mesoporous palladium-loaded silicon nitride composites by a non-aqueous sol–gel chemical route (Fig. 1). This research will open up a new chemical route to prepare porous transition metal/Si_3N_4 nano-composite materials.

Silicon diimide gel was prepared by a modification of our previously reported method.†[10] IR, ^{29}Si and ^{13}C CP-MAS NMR analyses indicated that the gel contained a considerable amount of residual dimethylamino groups $Si(NH)_x(NH_2)_y(NMe_2)_z$. Physisorption analysis showed that the gel exhibited a mesoporous structure with high surface area (1032 m^2 g^{-1}) and narrow pore size distribution (50–120 Å).

Reaction of this silicon diimide gel with palladium(II) chloride $PdCl_2$ in THF at room temperature gave a yellow powder, **1**.‡ Pd K-edge EXAFS shows that in **1** palladium is connected to both chlorine (Pd–Cl 2.30(3) Å) and nitrogen (Pd–N 2.05 Å). There is no evidence for Pd···Pd distances at *ca.* 3.4 Å observed in both $PdCl_2(NH_3)_2$ and $PdCl_2(en)$, indicating that the Pd is most likely dispersed throughout the gel rather than being in localised aggregates. The best fit to coordination numbers for **1** was for a "$PdClN_3$" type complex, indicating the reaction of a surface ≡$SiNH_2$ group with the $PdCl_2$ to form ≡SiNH–Pd–Cl type species (eqn (1)).

$$\equiv \mathrm{Si{-}NH_2} + \mathrm{PdCl_2} \rightarrow \equiv \mathrm{SiNH{-}}\underset{|}{\overset{|}{\mathrm{Pd}}}\mathrm{Cl} + \mathrm{HCl} \qquad (1)$$

The Pd in ≡SiNH–Pd–Cl was then most likely coordinated with two further N containing groups to give a four-coordinate square planar geometry expected for Pd(II), as the surface of the gel has many functional groups such as Si–NH_2, Si–NH and Si–NMe_2. Whilst this gives the best explanation of the EXAFS data, it must be remembered that it is an averaging structural technique, so that there is probably a distribution of species with two, one and no chlorine atoms attached to the Pd, with the gel surface N functional groups providing both the atoms and charge balance to maintain square-planar Pd(II). The detailed structure of **1** is still under investigation and will be published separately. Physiosorption analysis shows that the complex also exhibits a mesoporous structure with a type IV physiosorption isotherm. The pore size distribution of **1** is very similar to that of the silicon diimide gel, but the BET surface area was 187 m^2 g^{-1} lower than

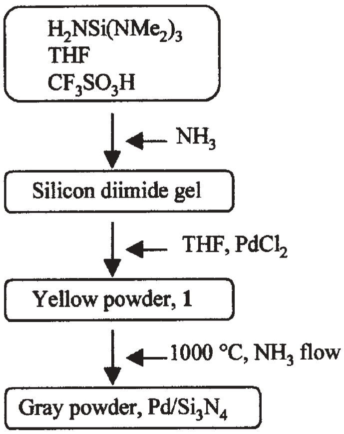

Fig. 1 The synthetic procedure for Pd/Si_3N_4 composites.

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that of silicon diimide gel, suggesting that palladium has been inserted in the pores of the gel.

When **1** was pyrolyzed in a tube furnace at 1000 °C under NH_3 flow, a gray powder with a ceramic yield of 66.5% was obtained.§ The XRD pattern of the pyrolyzed product indicates the formation of crystallized α-Si_3N_4 and metallic palladium, but a significant quantity of amorphous material is also present (Fig. 2).[12] The IR spectrum shows two broad bands. One broad band from 854 to 1060 cm^{-1} is consistent with the presence of amorphous Si_3N_4.[13] Another broad band from 3320 to 3450 cm^{-1} suggested that a considerable amount of $(NH)_x$ groups are present in the pyrolyzed product. ^{29}Si NMR CP-MAS NMR showed a single broad resonance at −48 ppm ascribable to the presence of Si_3N_4.[14] The conversion of palladium to metallic particles was confirmed by Pd K-edge EXAFS. The transmission electron microscopy shows that very small metal particles (5–20 nm) are dispersed in the Si_3N_4 matrix (Fig. 3).

It should be noted that pyrolysis of the silicon diimide gel without insertion of palladium under the same pyrolysis conditions gave only an *amorphous* silicon nitride.[11] Although palladium-induced crystallization of amorphous silicon has been reported,[15] to our knowledge this is the first example of palladium-induced crystallization of amorphous silicon nitride.

Pyrolysis of **1** at 2 °C min^{-1} gave a product with only one pore size distribution at 50–120 Å which is very similar to that of **1** (Fig. 4). However, pyrolysis of **1** at 5 °C min^{-1} led to the formation of a product with two pore size distributions at 50–120 and 150–250 Å (Fig. 4), although both products display similar type IV nitrogen adsorption isotherms typical of mesoporous materials (Fig. 5). The BET surface area of the product produced at 2 °C min^{-1} is 552 m^2 g^{-1}, 144 m^2 g^{-1} higher than that of product pyrolyzed at 5 °C min^{-1}. In order to investigate the effect of the pyrolysis heating rate on the pore size distribution and surface area of the products **1** was also pyrolyzed at 600 °C with a heating rate of 5 °C min^{-1}. Nitrogen physisorption analysis shows that the product pyrolyzed at 600 °C with a heating rate of 5 °C min^{-1} has a very similar pore size distribution to that of **1** (Fig. 4) The surface area is 677 m^2 g^{-1}. The decrease in the surface area is caused mainly by the shrinkage of some pores during the condensation and/or during some rearrangement steps of silicon diimide gel network.[11] The limited change in the pore size distribution at this temperature is due to the relatively stable cross-linked network of the gel. It is clear that the effect of the heating rate on the pore size distribution should occur at temperature from 600 to 1000 °C. The inorganic intermediate converts into a crystalline material at this temperature range. The higher heating rate (5 °C min^{-1}) may destroy the network of intermediates and lead to the formation of a second pore size distribution and greater decrease of surface area.

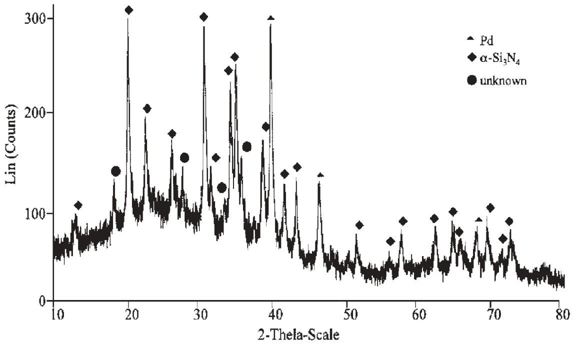

Fig. 2 XRD spectrum of the pyrolyzed product from complex **1**.

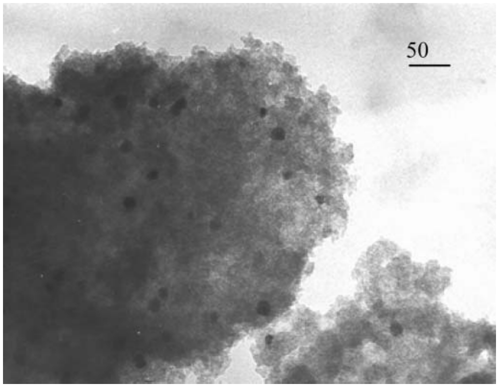

Fig. 3 TEM of the pyrolyzed product from complex **1**.

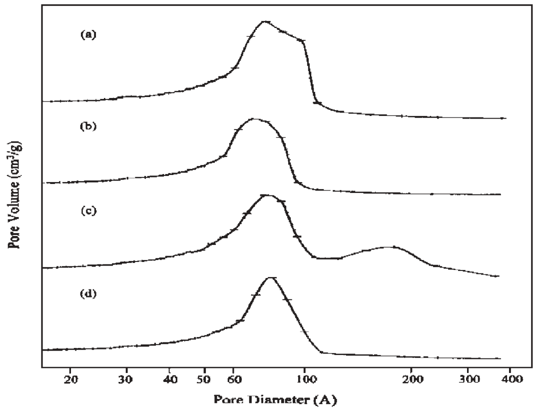

Fig. 4 Pore size distribution of (a) reaction product of silicon diimide gel with $PdCl_2$ and the products pyrolyzed at (b) 600 °C at 5 °C min^{-1}; (c) 1000 °C at 5 °C min^{-1} and (d) 1000 °C at 2 °C min^{-1}.

Preliminary results indicate that these new mesoporous Pd/Si_3N_4 nanocomposites can indeed be used to catalyse organic reactions, *e.g.*, we have used Si_3N_4 incorporating 2 wt% of Pd to catalyse the hydrogenation of hex-1-ene to hexane and also to isomerise terminal alkenes to more useful internal alkenes. This

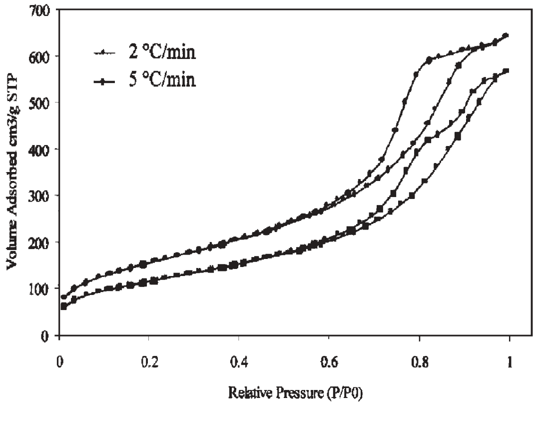

Fig. 5 Nitrogen adsorption and desorption isotherms of the products pyrolyzed at 1000 °C with heating rate of 2 and 5 °C min^{-1}.

general method has been used to prepare, with some minor modifications, other mesoporous M/Si_3N_4 nanocomposites, where M = Ni, Co, Zr and Ru. These M/Si_3N_4 composites have been used in solid-state gas sensors as selective gas filters that increase their sensitivity and selectivity.[16] Their catalytic properties are currently being investigated.

We thank the EPSRC of United Kingdom and the EU project NANOSENSOFLEX for financial support. We also thank the Council for the Central Laboratory of the Research Councils (CCLRC) for access to synchrotron radiation and computing facilities at Daresbury Laboratory.

Notes and references

† All procedures were performed under a protective nitrogen atmosphere using standard Schlenk techniques or in a nitrogen filled glove-box. To a solution of TDSA (17.09 g, 97 mmol) in dry THF (700 mL) in a 2000 mL round-bottomed three-necked flask was added trifluoromethanesulfonic acid (86 μl, 97 mmol). After heating at 50 °C for 16 h, the solution was allowed to cool to room temperature. A solution of ammonia (0.39 g, 22.8 mmol) in cold THF (6 mL) was added. After being left quiescent at room temperature for 18 h, ammonia gas was bubbled through for 10 min. The resulting mixture was left standing at room temperature for another 18 h to give a rigid gel. Evaporation of the solvent and evolved dimethylamine in a stream of nitrogen followed by drying under reduced pressure at 50 °C for 5 h yielded a translucent white solid.

‡ To a mixture of $PdCl_2$ (0.027 g) and silicon diimide gel (0.64 g) was added 20 mL dry THF followed by stirring at room temperature for 72 h. Evaporation of THF by a stream of nitrogen and then drying under reduced pressure at 50 °C for 6 h yielded a yellow powder.

§ The complex **1** was pyrolyzed in a tube furnace. About 0.5 g of complex **1** was placed in a BN boat, which was then introduced into a quartz tube in a glove-box. The quartz tube was removed from the glove-box and connected with NH_3 flow. The complex **1** was heated to 200 °C and held at 200 °C for 2 h, and then heated at 1000 °C for 2 h under a NH_3 flow.

1 M. Che, O. Clause and Ch. Marcilly, in *Handbook of Heterogeneous Catalysis*, ed. G. Ertl, H. Knözinger and J. Weitkamp, Wiley VCH, Weinheim, 1997, vol. 1.

2 F. S. Nicholas and K. D. Prabir, *Sens. Actuators, B*, 2003, **88**, 168.

3 S. Kolyma, H. Nakashima, Y. Sugahara and K. Kuroda, *Chem. Lett.*, 1998, 191.

4 L. T. Marjolein, A. D. Jos and P. J. Krijn, *J. Mol. Catal. A: Chem.*, 2001, **173**, 75.

5 C. Boberski, R. Hamminger, M. Peuckert, F. Aldinger, R. Dillinger, J. Heinrich and J. Huber, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1560.

6 H. P. Baldus and M. Jansen, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 329.

7 E. Kroke, Y. L. Li, C. Konetschny, E. Lecomte, C. Fasel and R. Riedel, *Mater. Sci. Eng., R*, 2000, **26**, 97.

8 C. Méthivier, J. Massardier and J. C. Bertolini, *Appl. Catal., A*, 1999, **182**, 337.

9 F. Monnet, Y. Schuurman, F. Cadete Santos Aires, J. C. Bertolini and C. Mirodatos, *Catal. Today*, 2001, **64**, 51.

10 R. Rovai, C. W. Lehmann and J. S. Bradley, *Angew. Chem., Int. Ed.*, 1999, **38**, 2036.

11 F. Cheng, S. Clark, S. M. Kelly, J. S. Bradley and F. Lefebvre, *J. Am. Ceram. Soc.*, 2004, **87**, 1413.

12 Powder diffraction data file, 01-076-1407 (for α-Si_3N_4) and 03-065-2867 (for Pd metal), JCPDS International Center for Diffraction Data, Swathmore, PA, 2003.

13 (*a*) K. Nakamoto, *Infrared and Roman Spectra of Inorganic and Coordination Compounds, Part B: Application in Coordination, Organometric, and Bioinorganic Chemistry*, John Wiley & Sons, Inc., New York, 1997; (*b*) N. Wada, S. A. Solin, J. Wong and S. Prochazka, *J. Non-Cryst. Solids*, 1981, **43**, 7.

14 K. R. Carduner, C. S. Blackwell, W. B. Hammond, F. Reidinger and G. R. Hatfield, *J. Am. Chem. Soc.*, 1990, **112**, 4676.

15 F. A. Quli and J. Singh, *Mater. Sci. Eng., B*, 1999, **67**, 139.

16 M. Baumbach, A. Schütze, F. Cheng, S. M. Kelly, H. Delprat, F. Parret, P. Menini, K. Soulantica, B. Chaudret and A. Maisonnat, *Proc. IEEE Sensors*, Vienna, 2004.