

Tailored palladium containing silica spheres

Lubomira Tosheva and Johan Sterte*

Division of Chemical Technology, Luleå University of Technology, S-971 87 Luleå, Sweden.
E-mail: jost@km.luth.se

Received (in Cambridge, UK) 2nd March 2001, Accepted 4th May 2001
First published as an Advance Article on the web 31st May 2001

Palladium containing silica spheres are tailored by a multi-step procedure consisting of: (i) preparation of ion exchange resin–silica composites, (ii) Pd ion exchange, and (iii) calcination.

Controlled preparation of porous materials is of great technological interest for areas such as heterogeneous catalysis and molecular sieving.^{1,2} Advanced porous structures *e.g.* metallic macrostructures, have attracted special attention due to their unique properties. By colloidal crystal templating porous gold flakes have been produced with the size of the pores corresponding to the size of the latex microspheres used as templates.³ A number of macroporous, free-standing metal films have been prepared employing colloidal silica crystals as pore-size determining templates.⁴ Silica sol has been used as a nanoglue to synthesise composite aerogels containing different guest components *e.g.* Pt and Au.⁵ Recently, we reported a method for the preparation of silica-based macrostructures using anion exchange resins as templates.^{6,7} This method involves treatment of resin beads with silica solutions followed by calcination. The resin bead templates determine the final shape of the macrostructures whereas the combustion of the resin provides the materials with high and controlled porosity. Here, we report the synthesis of palladium containing silica spheres prepared by resin templating. The procedure is based on the fact that the resin–silica composites obtained after the ion exchange of silica species retain a high anion exchange capacity facilitating introduction of negatively charged ions such as PdCl_4^{2-} in a second step. Upon calcination the resin bead templates are removed and the palladium is obtained in an oxide form.

Macroporous strongly basic Dowex MSA-1 resin beads (mesh size 20–50, chloride form) were used as received from Sigma. In a typical synthesis batch, 30 g of resin were mixed with 150 g of sodium water glass solution (21.4 wt% SiO_2 , 6.7 wt% Na_2O , Akzo Nobel) in a polyethylene reactor. The synthesis mixture was treated in an oil bath preheated to 100 °C under reflux until the initially floating resin particles sank, after 4 h. The resin–silica composites obtained were separated by decanting, rinsed repeatedly with distilled water and dried at 105 °C. Palladium was subsequently introduced into the composites by ion exchange using a solution of 0.01 M palladium chloride (PdCl_2 , Aldrich) dissolved in 1 M hydrochloric acid. Composites and palladium solutions were mixed in different weight ratios (*e.g.* 1 g composite mixed with 5, 10 or 20 g of Pd solution and the corresponding samples were designated as Pd5, Pd10 and Pd20) in a beaker and placed on a shaker overnight. After this procedure the initially brownish color of the Pd solutions turned colorless. The Pd–resin–silica composites were decanted, rinsed repeatedly with distilled water and dried at 105 °C. Finally, the composites were calcined at 600 °C for 5 h after heating to this temperature at a rate of 1 °C min^{-1} .

Visually the Pd materials obtained after the removal of the ion exchanger consisted of solid and hard brownish spheres. The color intensity was increased with an increase in the palladium solution to composite weight ratio used. A SEM image representative for those spheres is shown in Fig. 1(a). The shape of the particles was identical to the shape of the initial ion

exchange resin beads but the spheres shrunk upon calcination. A similar result was obtained for the silica spheres obtained after calcining the resin–silica composites and correspondingly the shrinkage observed was not related to the insertion of palladium into the composites. The Pd spheres were built up by fine particles with a size of <100 nm which is comparable to the pore size of macroporous resins.⁸ The primary particles of the Pd silica spheres were similar to those of calcined resin–silica composites and no conclusions about the palladium dispersion can be drawn by the SEM investigation.

Pd silica spheres were ground into a powder and X-ray diffraction patterns were recorded in order to identify the form of palladium obtained after the calcination. During the grinding no white material was observed suggesting that the palladium was distributed within the spheres. Fig. 1(b) shows the XRD pattern of the Pd20 sample. Two phases may be seen in this pattern: an amorphous one, emanating from the amorphous silica phase, and a crystalline one, corresponding to the presence of palladium oxide in the spheres.⁹ The XRD patterns of the Pd10 and Pd5 samples were similar to that shown in Fig. 1(b) but with lower peak intensities related to the decreased Pd loading. No additional peaks due to the presence of other

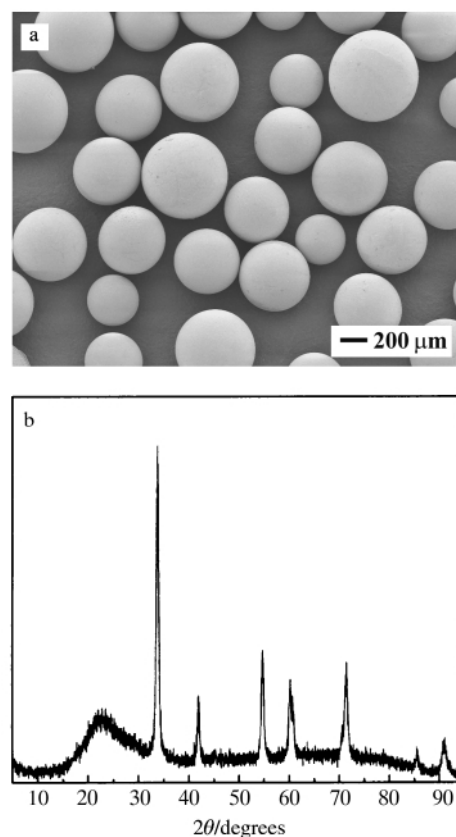


Fig. 1 A representative SEM image of the Pd containing silica spheres (a) and XRD pattern of the Pd20 sample (b). SEM was performed on a Philips XL scanning electron microscope equipped with a LaB_6 emission source. XRD patterns were collected at room temperature with a $\text{Cu-K}\alpha$ X-ray source using a Siemens D5000 instrument.

Table 1 BET surface areas, total pore volumes, yield, Pd loading and Pd uptake for the spheres prepared

Spheres	BET surface/area/m ² g ⁻¹	Total pore volume ^a /cm ³ g ⁻¹	Yield (wt%)	Pd loading/(wt%)	Pd uptake ^b (%)
Silica	93	0.26	38.39	—	—
Pd5	840	0.64	38.84	1.37	99.8
Pd10	1043	0.75	38.05	2.80	99.3
Pd20	1203	0.88	38.08	5.59	97.9

^a Calculated by converting the volume adsorbed at a relative pressure of 0.995 to the volume of the liquid adsorbate. ^b Calculated from the Pd concentration in the initial Pd solution and in the solution after the ion exchange as determined by atomic absorption spectrometry.

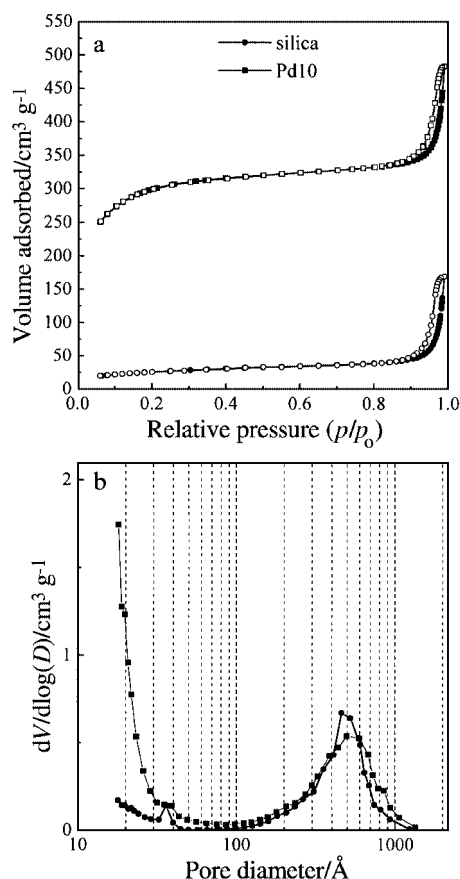


Fig. 2. Nitrogen adsorption isotherms at 77 K for calcined silica and Pd10 spheres; solid symbols, adsorption; open symbols, desorption (a) and the corresponding pore size distributions (b). The pore size distributions were calculated from the desorption branch of the nitrogen isotherm by the BJH method. The data was collected with a Micromeritics 2010 Gas Adsorption Analyser after the materials were degassed at 300 °C for 12 h.

palladium phases were detected in the XRD patterns of the Pd containing spheres prepared.

Fig. 2(a) shows nitrogen adsorption isotherms for calcined silica and Pd10 spheres. The isotherm for the calcined silica spheres was of type IV which is typical for mesoporous materials.¹⁰ Langmuir type isotherms typical of microporous materials, with identical, nearly horizontal, adsorption and desorption branches, were obtained for the Pd containing spheres. Some mesopores were also present in these spheres as seen from the distinct hysteresis loop at high relative pressures. From the pore-size distributions presented in Fig. 2(b) is seen that the amount of mesopores (imposed by the removal of the ion exchange resin) is approximately the same for the two samples, whereas the amount of micropores is increased for the

Pd containing spheres. The surface area values, calculated with the BET equation as well as the total pore volumes are listed in Table 1. Judging from these values and the pore-size distributions one can conclude that: (i) the insertion of palladium into the resin-silica composites leads to substantially larger BET surface areas of the calcined samples; (ii) the increase in the surface area is related to the amount of palladium present within the spheres; and (iii) the increase in the surface areas may be related to an increase in the micropore volume of the calcined materials. These results are surprising and further investigations are needed in order to explain the rather dramatic changes observed.

Finally, the yield, the amount of solid material obtained per gram of composite, was determined from the weight difference between dried composites at 150 °C and calcined spheres (Table 1). From the yield and from the similar hardness of the silica and the Pd silica spheres one may conclude that there was no substantial silica leakage from the resin-silica composites during the Pd ion exchange. Based on the yields, the Pd loading was calculated and listed in Table 1. Considering the Pd uptake data (also included in Table 1) one may conclude that the ion exchange of Pd into the resin-silica composites was almost complete.

The results presented show that hard and solid silica spheres containing a controllable amount of palladium can be prepared using macroporous ion exchange resins as templates. Owing to the high surface areas and large pore volumes, these materials are interesting for catalytic applications. Currently our efforts are directed to further characterise the palladium in the silica spheres and results will be presented in a subsequent publication. The procedure may also be used for the preparation of silica spheres containing other active catalytic phases.

We thank the Swedish Research Council for Engineering Sciences (TFR) for partial financial support of this work.

Notes and references

- 1 N. K. Raman, M. T. Anderson and C. J. Brinker, *Chem. Mater.*, 1996, **8**, 1682.
- 2 T. J. Barton, L. M. Bull, W. G. Klemperer, D. A. Loy, B. McEnaney, M. Misono, P. A. Monson, G. Pez, G. W. Scherer, J. C. Vartuli and O. M. Yaghi, *Chem. Mater.*, 1999, **11**, 2633.
- 3 O. D. Velev, P. M. Tessier, A. M. Lenhoff and E. W. Kaler, *Nature*, 1999, **401**, 548.
- 4 P. Jiang, J. Cizeron, J. F. Bertone and V. L. Colvin, *J. Am. Chem. Soc.*, 1999, **121**, 7957.
- 5 C. A. Morris, M. L. Anderson, R. M. Stround, C. I. Merzbacher and D. R. Rolison, *Science*, 1999, **284**, 622.
- 6 L. Tosheva, V. Valtchev and J. Sterte, *Microporous Mesoporous Mater.*, 2000, **35-36**, 621.
- 7 L. Tosheva, V. Valtchev and J. Sterte, *J. Mater. Chem.*, 2000, **10**, 2330.
- 8 C. E. Harland, in *Ion Exchange: Theory and Practice*, The Royal Society of Chemistry, Cambridge, 1994, p. 46.
- 9 PDF file 6-515, PDF-2 Database Sets 1-45, ICDD, 1995.
- 10 S. J. Gregg and K. S. W. Sing, in *Adsorption, Surface Area and Porosity*, Academic Press, New York, 1982.