Available online at www.sciencedirect.com

SCIENCE DIRECT®

Microporous and Mesoporous Materials 88 (2006) 63–71

MICROPOROUS AND MESOPOROUS MATERIALS

www.elsevier.com/locate/micromeso

Increasing the hydrothermal stability of mesoporous SiO_2 with methylchlorosilanes—a 'structural' study

Hessel L. Castricum [a,b,*], Marjo C. Mittelmeijer-Hazeleger [a],
Ashima Sah [b], Johan E. ten Elshof [b]

[a] *Van 't Hoff Institute for Molecular Sciences, Faculty of Science, Universiteit van Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands*
[b] *Inorganic Materials Science Group, Department of Science and Technology, MESA+ Institute for Nanotechnology, Universiteit Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands*

Received 28 February 2005; received in revised form 14 July 2005; accepted 19 August 2005
Available online 18 October 2005

Abstract

Mesoporous silica gels with various pore sizes are hydrophobised by liquid-phase silylation with mono- and difunctional methylchlorosilanes. Changes in the pore structure as a result of the silylation reactions are monitored in order to assess the distribution of the hydrophobic groups. Extensive polymerisation of dimethyldichlorosilane (DMDCS) causes blocking of the micropore fraction. For silica with pore sizes in the supermicroporous range (2 nm pore diameter), this leads to hydrophobisation of almost exclusively the outer surface. While for trimethylchlorosilane (TMCS) a smaller number of molecules react with the surface, modification is more homogeneous and an open structure is optimally preserved. Both silanes lead to lower surface polarity and increased hydrothermal stability, i.e., preservation of the porous structure during exposure to water. As DMDCS reacts more extensively, this agent would be recommended for ceramics with pore diameters larger than about 6 nm. TMCS is the most suitable agent for pore diameters smaller than 4 nm and in case preservation of micropores is required.

Keywords: Mesoporous SiO_2 gel; Silylation; Hydrophilic/hydrophobic modification; Hydrothermal stability; Dimethyldichlorosilane; Trimethylchlorosilane

1. Introduction

Many applications in which adsorption processes are involved strongly rely on the use of porous silica. Typical fields include chromatography, heterogeneous catalysis and membrane technology. Characteristics that contribute to the applicability of silica include chemical inertness and high mechanical and thermal stability. As the surface is typically occupied by a large number of hydroxyl groups, enabling strong H-bonding with water, these materials are hydrophilic by nature [1,2]. Application of microporous and mesoporous materials in wet atmospheres will thus lead to rapid filling of the pores, which impairs the applicability in moist gas mixtures. Under severe conditions, water may even cause dissociation of Si–O–Si bonds, which will eventually give rise to another physical structure. In the case of membranes and chromatography, this leads to destruction of the functionality of the separation properties and limits the operating conditions under which they can be applied.

The number of hydroxyl groups can effectively be decreased by calcination at high temperature, but this process is reversible upon exposure to water. Replacement of hydroxyl groups by hydrolytically stable groups with a

---

[*] Corresponding author. Address: Van 't Hoff Institute for Molecular Sciences, Faculty of Science, Universiteit van Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands. Tel.: +31 20 5256493; fax: +31 20 5255604.
E-mail address: castric@science.uva.nl (H.L. Castricum).

1387-1811/$ - see front matter © 2005 Elsevier Inc. All rights reserved.
doi:10.1016/j.micromeso.2005.08.033

hydrophobic character such as CH_3 groups can inhibit the adsorption of water more effectively. One approach is to build in this organic functionality by in situ hydrolysis and condensation of alkoxide precursors with hydrophobic side groups, such as organoalkoxysilanes or bridged silsesquioxanes [3–5]. However, reproduction of such sol–gel derived materials involves full control over all preparation parameters and is consequently generally difficult to achieve. In addition, precursors are usually expensive and preparation is very time-consuming. Although this approach is most suitable for the synthesis of non-porous and ultramicroporous materials, for the above-mentioned reasons it is solely used in small quantities for advanced applications, such as thin layers and coatings.

In case bulk quantities are required of hydrophobised ceramics with larger pores, i.e. meso- and macropores, the most obvious approach is post-modification by grafting the internal pore surface with hydrophobic groups. One of the possible hydrophobisation methods is a chemical reaction between chloride groups of an organochlorosilane with the surface hydroxyl groups. A thermally stable chemically bound layer is thus formed, which imparts the desired hydrophobicity. Successful modification has been carried out of unsupported materials for chromatography [6–9] and of composite materials such as membranes, e.g. by fluorinated silanes [10,11], chloro- and organoalkoxysilanes [12,13]. Except for hydrophobisation, a large number of post-modification procedures with various functional groups have been studied for catalyst preparation with silica as the active phase carrier, e.g. [14]. Preservation of the structure [15,16] can however also be an important additional requirement for separation applications.

High hydrophobicity can be achieved by using agents with long organic tails, as only one bond with the solid material is needed for the creation of a large hydrophobic surface. However, constraints in the application of such agents are set by the pore size of the materials due to steric hindrance. Another method that can give rise to effective surface hydrophobisation is the use of organosilanes with two or more reactive groups. As these agents may couple with two adjacent OH groups, they may more effectively reduce the number of vicinal OH groups that are responsible for the strongest hydrophilic interaction [1,2,17]. However, the functional groups may also react with each other, thereby forming a polymeric layer that has limited covalent attachment but can still be very effective in surface hydrophobisation [18,19]. A high extent of modification of γ-Al_2O_3 membranes was thus found for multifunctional methylalkoxysilanes, and included the inner surface of pores with a diameter of 5 nm [20]. The pore volume was however strongly reduced, which was explained by polymerisation reactions. Modification of mesoporous γ-Al_2O_3/TiO_2 multilayer membranes with difunctional C1 and C8 organochlorosilanes showed the highest hydrophobicity for C8 silanes [21], which supports the view that silanes with long organic tails are advantageous. For microporous membranes, it was shown that silane coupling reactions took place in pores situated at the outer membrane surface, while reactions at the internal surface were sterically hindered for both C1 and C8 silanes.

In earlier work on γ-Al_2O_3 powders [22] we demonstrated that both monofunctional ($(CH_3)_3SiCl$) and a difunctional ($(CH_3)_2SiCl_2$) methylchlorosilanes can be effective for bulk modification of mesoporous materials with pore sizes around 4–5 nm. Steric hindrance limits the use of silanes with long organic tails to materials with much larger pore sizes. Similarly, (trifunctional) methyltrichlorosilane led to extensive modification of mostly the outer surface due to polymerisation reactions and is thus also unsuitable for bulk modification of materials with small mesopores. In the present paper, we study hydrophobisation of silica gel with DMDCS (dimethyldichlorosilane) and TMCS (trimethylchlorosilane). Silica materials are studied with various pore sizes in order to assess the limits of application of these two agents for hydrophobisation. To this end, the extent of grafting and the resulting hydrothermal stability are studied with respect to changes in the pore structure. Simply applicable liquid-phase silylation with the addition of a nucleophile (water) was chosen for its high reaction rate at low temperatures [15]. Surface and pore modification were studied by N_2 and CO_2 physisorption, TPO-MS, and SEM.

2. Experimental

2.1. Materials preparation

Silica gel powders (35–70 μm, >99% SiO_2) were obtained from Grace Davison. Analytical data as provided by the supplier are given in Table 1. In order to remove any adsorbed species and to obtain similar degrees of hydroxylation, all materials were first heated in air at 773 K for 5 h. Hydrophobisation was carried out by dropwise addition of silanes to 8.67 g of material in a mixture of 50 ml water and 21.6 ml of isopropanol (Aldrich, 99.9% pure), and subsequent refluxing for 30 min during continuous stirring. Prior to addition of the silane, the material was left in the liquid mixture for 5 min. This procedure was expected to give rise to homogeneous hydrophobisation. As the OH group is smaller than the Cl group, the large amount of water ensures sufficient hydrolysis of the silanes and thus minimum steric hindrance upon the reaction with the surface OH groups. Trimethylchlorosilane ($(CH_3)_3SiCl$, TMCS, 99% purity) and dimethyldichlorosilane ($(CH_3)_2SiCl_2$, DMDCS, 99% purity) were obtained from Aldrich.

Table 1
Physical characteristics of silica materials as provided by the supplier

Sample	Material	Pore volume (ml/g)	Surface area (m^2/g)	Pore diameter (nm)
S1	SI 1401	0.4	750	2
S2	SI 1404	0.9	540	6
S3	SI 1301	1.15	320	14.5