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Structural and Energetic Characteristics of Silicas Modified by Organosilicon Compounds

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Abstract. Structural and adsorptive characteristics of unmodified and modified silica gels Davisil 633 and 643, and fumed silica Cab—O—Sil HS-5, were analyzed on the basis of nitrogen adsorption isotherms. The properties of aqueous suspensions of the initial and modified fumed silicas were also studied. Deviation of the pore shape from simple models, cylindrical pores for silica gels and gaps between spherical particles for fumed silica, increases for modified silicas.

Keywords: silica, modification, adsorption, pore shape, aqueous suspension

1. Introduction

The chemical modification of solid surfaces by organosilicon compounds (OSC) is commonly employed for a wide variety of applications. Performing these reactions is a well established method to alter many surface characteristics such as surface free energy, topography, pore size distribution (PSD), and specific surface area (Leyden and Collins, 1989; Blitz and Little, 1999). The structural and adsorptive characteristics of modified silicas are of importance for application of these materials. However, the use of certain pore models may lead to poorly controlled errors in the evaluation of important characteristics because of deviation of the pore shape from the model (Gun'ko and Mikhalovsky, 2004). Therefore estimation of this deviation is useful to better understand and predict various structural and adsorptive characteristics. Additionally, changes in the surface properties of modified silicas in liquid media are of interest from both theoretical and practical points of view. The aim of this work was to study the structural and adsorptive characteristics of modified silicas in different media taking into account the role of different surface functionalities.

2. Materials and Methods

Silica gels Davisil 633 and 643, and fumed silica Cab-O-Sil HS-5 with grafted 3-aminopropyl dimethylsilyl (APDMS), butyl dimethylsilyl (BDMS), octadecyl dimethylsilyl (ODDMS), and trimethylsilyl (TMS)

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Table 1. Structural parameters of initial and modified silicas.

Sample	S_{BET} (m^2/g)	V_p (cm^3/g)	S_{mic} (m^2/g)	S_{mes} (m^2/g)	V_{mic} (cm^3/g)	V_{mes} (cm^3/g)	Δw	C_{OSC} (mmol/g)
Davisil 633	451	0.892	177	274	0.044	0.844	−0.101	
D633/APDMS	320	0.634	28	292	0.005	0.629	0.468	1.1
D633/BDMS	356	0.630	18	338	0.002	0.628	0.656	1.2
D633/ODDMS	244	0.524	36	208	0.008	0.517	0.244	0.52
D633/TMS	399	0.810	150	294	0.041	0.761	−0.090	0.32
Davisil 643	344	1.144	125	217	0.042	1.041	−0.088	
D643/APDMS	259	0.919	22	237	0.004	0.908	0.456	0.84
D643/BDMS	277	0.897	34	243	0.006	0.891	0.402	0.80
D643/ODDMS	192	0.646	7	185	0.001	0.650	0.481	0.60
D643/TMS	279	0.993	96	183	0.026	0.954	−0.058	0.39
Cab-O-Sil HS-5	326	1.310	178	102	0.035	0.467	0.533	
Cab/APDMS	191	0.995	38	108	0.005	0.464	1.284	0.82
Cab/BDMS	232	1.050	61	153	0.010	0.832	0.787	0.73
Cab/ODDMS	151	1.524	17	22	0.002	0.124	1.794	0.44
Cab/TMS	251	1.758	129	35	0.019	0.070	0.877	0.55

S_{BET} is the specific surface area, V_p is the pore volume; V_{mic} and V_{mes} are the pore volumes of micro- (radius $R < 1$ nm) and mesopores (1 $< R < 25$ nm), respectively, calculated from the pore size distribution functions f_V(R); $\Delta w = S_{BET}/S_{sum} - 1$ is the deviation in the pore (gap) shape from that of cylindrical pores for silica gels and a dense cubic lattice with spherical particles ($w \approx 1.36$) for initial and modified Cab—O—Sil HS-5; $S_{sum} = \int_{R_{min}}^{R_{max}} f_S(R)\,\mathrm{dR} = \int_{R_{min}}^{R_{max}} \frac{w}{R}(f_V(R) - \frac{V_p}{R} dR$. Contribution of macropores at $R > 25$ nm is not shown because it is very low.

groups of concentrations shown in Table 1 were studied using the nitrogen adsorption method. Initial and modified Cab-O-Sil HS-5 was also studied by means of photon correlation spectroscopy, electrophoresis, and potentiometric titration methods. Sample preparation and other characteristics were described previously (Gun’ko et al., 2002).

Approximately 0.3 g of sample was outgassed at 110°C for 4 h prior to N_2 adsorption analysis. Nitrogen adsorption-desorption isotherms were recorded at 77.35 K using a Micromeritics ASAP 2010 adsorption analyzer at $p/p_0 > 10^{-6}$–10^{-5}, where p and p_0 denote the equilibrium pressure and the saturation pressure of nitrogen at 77.35 K, respectively. The specific surface area (S_{BET}) was calculated using the standard BET method. The pore volume (V_p) was estimated from the nitrogen adsorption at $p/p_0 \approx 0.98$–0.99. A description of calculations of the pore size distributions using two types of pore shapes; as cylindrical pores for silica gels and as gaps between spherical particles in their aggregates for fumed silicas, and calculations of the distribution functions of the nitrogen adsorption energy using the Fowler-Guggenheim (FG) equation has been previously described (Gun’ko and Mikhalovsky, 2004; Gun’ko et al., 2002).

Electrophoretic data and particle size distributions were obtained by means of photon correlation spectroscopy (PCS), using a Zetasizer 3000 (Malvern Instruments). Deionized distilled water (pH = 6.22) and 1.0 g of initial or modified oxide per liter of water (oxide concentration $C_{ox} = 0.1$ wt.%) was utilized to prepare the suspensions, which were then treated in an ultrasonic bath for 10 min. The pH values measured by a precision digital pH-meter were adjusted by addition of 0.1 M HCl or NaOH solutions. The salinity was held constant at 10^{-3} M NaCl. The estimated effective diameter (D_{ef}) of the particle size distributions corresponds to the average hydrodynamic diameter.

To evaluate the surface charge density, potentiometric titrations were performed using a teflon thermostated vessel in nitrogen atmosphere free from CO_2 at 25°C. The solution pH was measured using a PHM240 Research pH-meter (G202C and K401 electrodes) coupled with an REC-61 recorder. The surface charge density was calculated using the potentiometric titration data for a blank electrolyte solution and fumed silica suspensions (0.1 wt.%), at a constant salinity of 10^{-3} M NaCl, from the difference of acid or base volume utilized to obtain the same pH value as

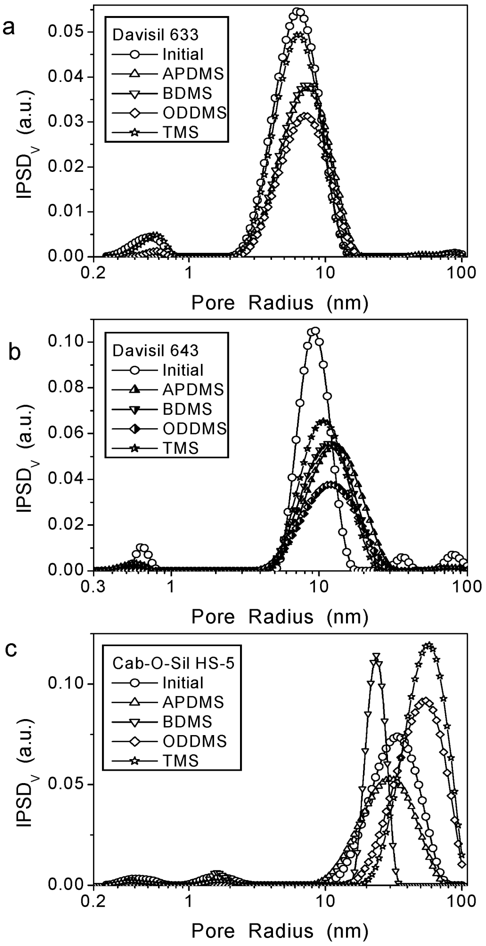

Figure 1. Incremental pore size distributions (calculated using a model of cylindrical pores) with respect to the pore volume for unmodified and modified (a) Davisil 633, (b) Davisil 643, and (c) Cab-O-Sil HS-5.

that for the background electrolyte of the same ionic strength.

3. Results and Discussion

Investigations of the textural (Table 1 and Fig. 1) and energetic (Fig. 2) characteristics of silica gels and fumed silica show how surface properties depend not only on the morphology of the initial silicas, but also on the characteristics and concentration of grafted modifiers.

Reaction of OSCs reduce the specific surface area of all the silicas, the pore volume and adsorption energy of all the silica gels respond differently.

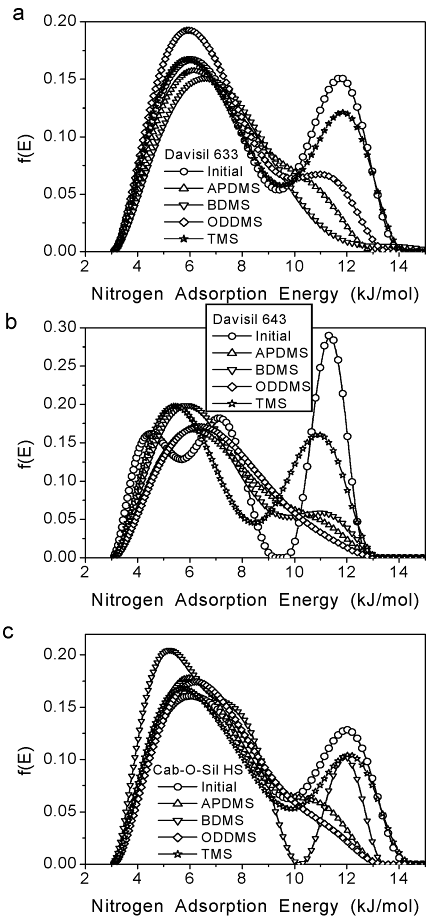

Figure 2. Nitrogen adsorption energy distributions for unmodified and modified silicas (FG method).

The smallest changes are observed for silica/TMS which is the smallest size among the OSCs studied. Since TMS groups do not "lie" on the silica surface, perhaps "windows" in the modifier layer exist making Si—O—Si bonds accessible for adsorption of nitrogen molecules. For other modifiers such windows are practically absent, especially in the case of relatively long octadecyl dimethylsilyl groups, which can "lie" on the surface. This results in a decrease in the high-energy peak of the adsorption energy (Fig. 2) corresponding to direct interaction of nitrogen molecules with the silica surfaces. The mesoporous character of all the studied samples does not change dramatically upon surface modification. The low contribution of micropores for the pristine silicas becomes smaller for modified samples due to blocking by long OSC groups, but not short TMS groups (Table 1). It should be noted that the application of models of ideal cylindrical pores (for silica gels) or gaps between spherical particles (for fumed silica) gives larger errors (Table 1, Δw) for modified silicas. This result shows the complexity of the pore shape of modified silicas. The availability of large pores in the initial Davisil 643 at a pore radius $R > 30$ nm (Fig. 1) causes the appearance of pores at $R > 15$ nm in the modified samples (pores with such sizes are absent in the initial silica). A similar effect is not observed for Davisil 633 possessing a more uniform PSD.

Calculations of electrophoretic mobility and ζ potential were performed taking into consideration the topological structure of "porous" aggregates of primary particles of fumed silica using two different approaches. Changes in surface charge density, the textural, aggregative, and electrophoretic characteristics of modified silicas depend on the type of grafted OSC, its chain length, polarity, and surface concentration. Particle swarms of initial and modified silicas in aqueous suspension are typically characterized by bimodal size distributions between 20–300 nm (aggregates) and 1–3 μm (agglomerates of aggregates). Surface functionalities (APDMS (A), BDMS (B), ODDMS (O), and TMS (T) groups) at different concentrations on Cab—O—Sil HS-5 cause significant changes in such characteristics of aqueous suspensions of modified silicas as the particle swarm size (Fig. 3), surface charge density (Fig. 4), electrokinetic mobility, and ζ potential (Fig. 5). The application of theories taking into consideration the porosity of aggregates of primary particles of unmodified and modified fumed silicas, gives relative diminution of the modulus of the ζ potential and mobility dependence on pH. The difference between parameter values computed according to the Smoluchowski theory and improved approaches increases with increasing pH and is concordant for mobility and ζ potential. Results obtained are in agreement with the tendency that changes in the surface charge density decreases due to surface modification by both hydrophobic and amino groups.

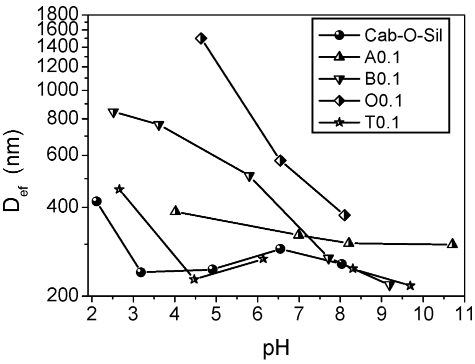

Figure 3. Effective diameter as a function of pH for unmodified and modified Cab-O-Sil at a minimal loading of OSC, $C_{ox} = 0.1$ wt.% and salinity of 0.001 M NaCl.

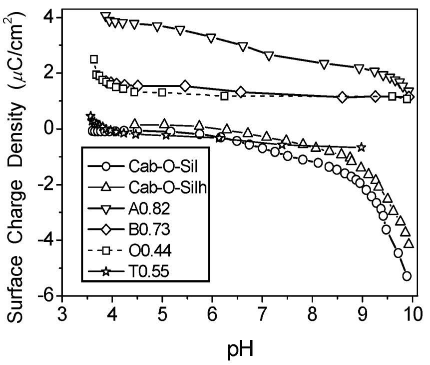

Figure 4. Surface charge density as a function of pH for initial Cab-O-Sil and treated in hexane (Cab-O-Silh), and modified samples (at maximal OSC loading shown in the legends) in the aqueous suspensions at $C_{ox} = 0.1$ wt.% and 0.001 M NaCl.

According to the Smoluchowski theory (Hunter, 1981), there is a linear relationship between the particle mobility U_e and its ζ potential $U_e = A\zeta$, where A is a constant for a thin electrical double layer (EDL) at $\kappa a \gg 1$, where a is the particle radius. For a thick EDL ($\kappa a < 1$), e.g., at pH close to the isoelectric point (IEP), the equation with the Henry correction factor is appropriate

$$U_e = 2\varepsilon\zeta/3\eta, \tag{1}$$

where ε is the dielectric permittivity; and η is the viscosity. However, the relationship between the ζ potential and the mobility for aggregates of primary particles should be corrected taking into consideration the particle volume fraction (ϕ) and the shear-plane potential (Ψ_a) at the particle-fluid interfaces within the porous aggregate which arise from gaps or channels between adjacent primary particles in aggregates (Miller and Berg, 1993). Ohshima proposed a more accurate equation (Ohshima, 1997) which we used to show the dependence of the electrophoretic properties of the dispersion of fumed silica on the structure of secondary particles (Fig. 5). The difference between the obtained results increases far from the isoelectric point of silicas.

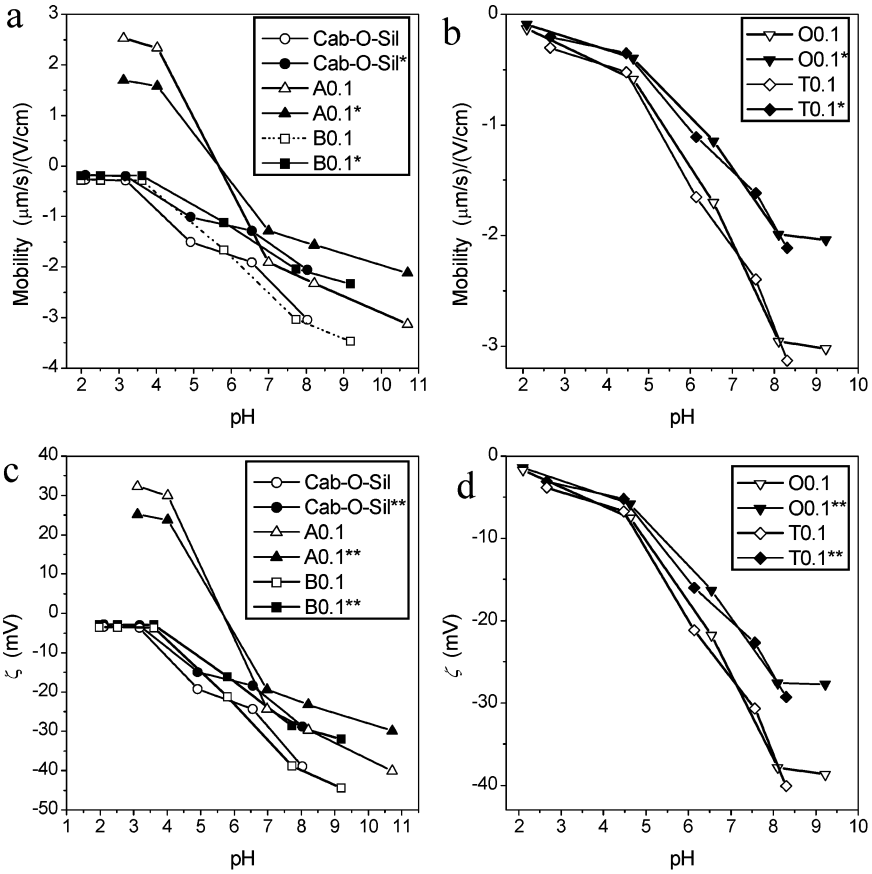

Figure 5. Electrokinetic mobility (a, b) and ζ potential (c, d) of initial and modified samples (at minimal OSC loading 0.1 mmol/g) in aqueous suspensions at $C_{\mathrm{ox}} = 0.1$ wt.% and salinity of 0.001 M NaCl. One asterisk shows the mobility computed according to Ohshima and two asterisks label the ζ potential computed with Miller and Berg equation; and unlabeled curves correspond to data handled with Smoluchowski's theory.

4. Conclusion

Investigations of the textural and energetic characteristics of silica gels and fumed silica, modified to different extents by different OSC with groups of various length and distinct chemical structure, show their marked dependence on both the morphology of the initial silicas and on the characteristics and concentration of grafted modifiers. All the OSC reactions reduce the specific surface area of all the silicas, the pore volume, adsorption potential, and the adsorption energy of the silica gels are affected differently. Minimal changes are observed for silica/TMS possessing the smallest size among the OSCs studied. This may be due to the existence of remaining free "windows" in the modifier layer making Si—O—Si bonds accessible for nitrogen molecule adsorption. For other modifiers, such windows are practically absent. This results in a decrease in the high-energy peak of the adsorption energy, and diminution of the adsorption potential, corresponding to direct interaction of nitrogen molecules with the adsorbent surfaces. The pore type of all the studied samples does not change dramatically upon surface modification. The low contribution of micropores for the pristine silicas becomes smaller for modified samples.

Surface functionalities on Cab-O-Sil HS-5 cause significant changes in such characteristics of aqueous suspensions of modified silicas as particle swarm size, surface charge density, electrokinetic mobility, and ζ potential. Secondary particles of unmodified and modified silicas in aqueous suspension are typically characterized by bimodal size distributions between 20–300 nm (aggregates) and 1–3 μm (agglomerates of aggregates). The application of theories taking into consideration the porosity of aggregates of primary particles of unmodified and modified fumed silicas, gives relative diminution of the modulus of the ζ potential and pH dependence on mobility. The difference between parameter values computed according to the Smoluchowski theory and improved approaches increases with increasing pH and is concordant for mobility and ζ potential. Results obtained are in agreement with the tendency that changes in the surface charge density decreases due to surface modification by both hydrophobic and amino groups.

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