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SYNTHESIS AND CHARACTERIZATION OF SILICA-BOUND PROPANESULFONIC ACID

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Dimethylformamide

Abstract Colloidal silica was prepared by Stöber's method. After the dispersion was transferred to DMF, reaction with mercaptopyltrimethoxysilane gave silica with 0.35 mequiv/g of bound mercaptopropyl groups. The mercaptan was oxidized with *tert*-butylhydroperoxide to give 0.17 mequiv/g of bound sulfonic acid and leave 0.076 mequiv/g of unreacted thiol. The CP/MAS ^{13}C NMR spectrum gives evidence of several partially oxidized intermediates, including a significant amount of disulfide. This is the first example of a functional group transformation on silica in a colloidal state. (10)

INTRODUCTION

Functionalization of silica gel with sulfonic acids is well known in the preparation of ion exchangers. Most silica-bound sulfonic acids are prepared by initially binding an aromatic ring to the silica surface followed by sulfonation of the aromatic ring.^{1,2} While some silica-bound alkane-sulfonic acids have been used as cation exchangers,³ little is known about their catalytic activity.

We set out to prepare silica-bound propanesulfonic acid by a new method in which mercaptopropyltrimethoxysilane is bound to silica and then oxidized to the sulfonic acid. We wish to study the catalytic activity of colloidal silica sulfonic acids in comparison with other well known polymer-bound sulfonic acids. The preparation of colloidal silica sulfonic acid is described here. Catalysis results will be published elsewhere.

Colloidal silica, prepared by the method of Stöber,⁴ was selected as the support instead of commercially available silica gels. Small particles reduce the mass transfer limitations to catalytic activity. Polymers with trialkoxysilane endgroups have been grafted to colloidal silica dispersed in DMF.⁵ However, functionalization of colloidal silica with acid groups has not been reported, and we were interested to see if a stable dispersion could be formed even in the presence of strongly acidic sites.

EXPERIMENTAL

Analytical Methods

CP/MAS ¹³C NMR spectra were obtained by Dr. Frank McEnroe at Conoco, Inc., with an IBM VWP-100 spectrometer at 25 MHz. Transmission electron microscopy was done with a JEOL JSM-35U electron microscope at 25 kV. Formvar and carbon grids were used for samples dispersed in ethanol and DMF (N, N-dimethylformamide) respectively. Diameters of at least 35 particles were measured on a micrograph of each sample. Elemental analyses were done at Galbraith Laboratories.

Materials

3-Mercaptopropyltrimethoxysilane (Petrarch), a 3.0 M solution of *tert*-butylhydroperoxide in toluene (Fluka), 5,5'-dithiobis(2-nitrobenzoic acid) (Aldrich), and ethylenediaminetetraacetic acid (Fisher) were used as received. Tetraethyl orthosilicate (Aldrich) was distilled immediately before use. A 2.5 M solution of ammonia in ethanol was prepared by

passing ammonia gas through a column of NaOH pellets into absolute ethanol at 0 °C for 0.5 h. Ammonia concentration was determined by titration to the methyl red endpoint with 0.9953 M HCl. Water was treated with active carbon, deionized, and distilled in glass. All solvents were reagent grade and used as received.

Colloidal Silica, 1a and 1b

Water (7.2 mL, 400 mmol, 0.999 M), 309 mL of 2.46 M NH₃ in ethanol (760 mmol, 1.90 M ammonia), and 66 mL of absolute ethanol were mixed in a 500 mL Erlenmeyer flask fitted with a teflon stopper. The flask was placed in water in an ultrasonic cleaning bath (Branson model 5200), and 18 mL (80.7 mmol, 0.202 M) of tetraethyl orthosilicate was added during sonication. After 25 min, the reaction mixture began to turn cloudy as silica particles formed. The temperature of the sonicator rose slowly from 20 °C to 45 °C over the first 5-6 h reaction time, and the mixture was sonicated a total of 18 h.

DMF Dispersion of Colloidal Silica, 2

The ethanol and water were slowly distilled from 400 mL of 1b while about 500 mL of DMF was added dropwise from an addition funnel in order to keep a constant volume of dispersion. The distillation was continued until 10-15 mL of distillate was collected at a constant bp of 152 °C.

Mercaptopropyl Functionalized Silica, 3

Mercaptopropyltrimethoxysilane (5.0 mL, 26.5 mmol) was added to 400 mL of 2 (containing 4.9 g silica as SiO₂) and heated to 100 °C for 24 h under nitrogen to give 3. Anal. Found: C, 5.34% (4.45 mg-atom/g); S, 1.11% (0.35 mg-atom/g); H, 2.19% (21.7 mg-atom/g).

Silica-bound Propanesulfonic acid, 4

To 300 mL of 3 was added 88 mL of 3.0 M *tert*-butylhydroperoxide (264 mmol) in toluene under nitrogen. The mixture was stirred at 25 °C for 24

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h and at 60 °C for 24 h to give a pale yellow dispersion of **4** that contained 0.022 g solid/mL. Anal. Found: C, 14.12% (11.8 mg-atom/g); S, 8.32% (2.59 mg-atom/g); H, 3.60% (35.6 mg-atom/g). Ion exchange capacity = 3.82×10^{-3} mequiv/mL = 0.17 mequiv/g.

Ion Exchange Capacity

The colloidal dispersion (20 mL) was added to 75 mL of 2.0 M NaCl. The precipitated silica was removed by gravity filtration and washed with 75 mL of 2.0 M NaCl. The combined filtrate was titrated to the phenolphthalein endpoint with 0.0164 M NaOH.

Preparation of Colloidal Samples for Elemental and NMR Analyses

Silica **3** or **4** was precipitated by adding the dispersion to water and acidifying to pH 2 with 1.0 M HCl. The precipitated particles were removed by vacuum filtration, washed thoroughly with water, acetone, and ethyl ether, and dried at 60 °C under vacuum for 15 h.

Preparation of Ia for BET Analysis

The ethanolic dispersion (20 mL) was placed in a petri dish, evaporated in air, and dried at 165 °C for 24 h.

Determination of Thiol Content with Ellman's Reagent^{6,7}

Standard solutions, 10.0 mL each, were prepared containing 1.0×10^{-5} to 5.3×10^{-5} M mercaptopropyltrimethoxysilane, 1.5×10^{-4} M Ellman's reagent [5,5'-dithiobis(2-nitrobenzoic acid)], and 0.01 M KH_2PO_4 in a pH 8.0 phosphate buffer, 10^{-2} M KH_2PO_4 . After 30 min, the absorbance of each solution was measured using a Spectronic 21 spectrophotometer at 412 nm ($\epsilon = 11,400 \text{ M}^{-1} \text{ cm}^{-1}$). Using samples prepared by the same method as those for elemental and NMR analyses, thiol contents of **3** and **4** were determined by preparing 100 mL solutions containing 0.014 g substrate, 1.5×10^{-4} M Ellman's reagent, and 0.01 M EDTA at pH 8.0.

These solutions were allowed to react at room temperature for 16 h before the absorbance was measured.

RESULTS AND DISCUSSION

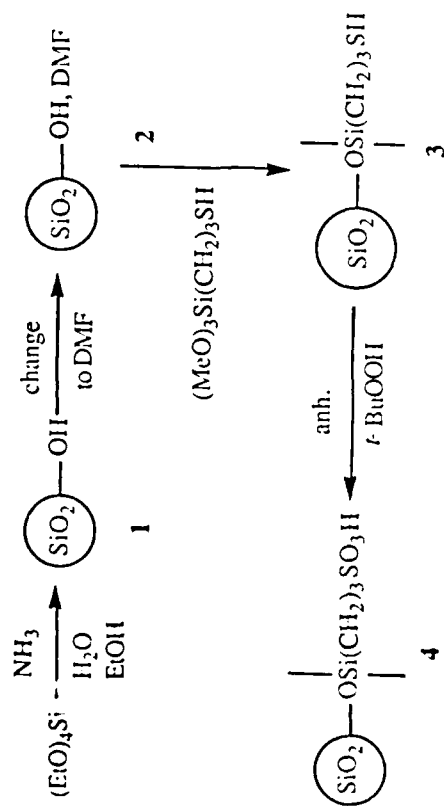
Scheme 1 shows the synthesis of silica-bound propanesulfonic acid. The synthesis begins with hydrolysis of tetraethyl orthosilicate to give an ethanolic dispersion of colloidal silica. The sizes of particles formed were measured on transmission electron micrographs (TEM). The results are shown in Table I. Some particle clusters appeared in the micrographs, but since it is not known if the clusters were formed in the original dispersion or as the sample was dried on the TEM grid, only single primary particles were measured. The number average and weight average particle diameters (d_n and d_w) and uniformity ratio (d_w/d_n) were determined according to the following equations:

$$d_n = \frac{\sum n_i d_i}{\sum n_i}$$

$$d_w = \left[\frac{\sum n_i d_i^3}{\sum n_i d_i} \right]^{1/3}$$

TABLE I. Particle diameters determined by TEM.

Sample	d_n , nm	d_w , nm	d_w/d_n
Ia	53.2	55.0	1.04
Ib	51.8	53.9	1.04
2	50.2	52.7	1.05
3	52.7	55.4	1.05
4	53.1	55.0	1.04



Scheme 1. Synthesis of Silica-Bound Propanesulfonic Acid

The surface area of **1a** was determined to be 67.4 m²/g by the BET nitrogen adsorption isotherm method. Smooth spheres with a uniform diameter of 55.0 nm (from Table I) and that surface area would have a density of 1.62 g/mL, compared with 2.20 g/mL for amorphous SiO₂.⁸ The pore size distribution determined from a BET nitrogen desorption isotherm is shown in Table II. The pores of >60 nm diameter are due to spaces between loosely packed particles. The major fraction of the pore volume in the 10 - 30 nm diameter range is due to interstices between spherical particles that we assume have amorphous packing. There is almost no significant porosity in the 2 - 10 nm range. A density of 1.87 g/mL determined by centrifugation was reported by van Helden, Jansen, and Vrij⁹ for a sample prepared by the same method and with particle diameter ca. 40 nm. Their low density was rationalized on the basis of <1.2 nm ultramicropores. Our anomalously low density could be due to

TABLE II. Pore Size Distribution of Silica **1a**.

pore diameter, nm	pore volume, mL/g
> 60	0.098
60-40	0.004
40-30	6.006
30-20	0.075
20-15	0.141
15-10	0.039
10-8	0.0015
8-2	0.000

Pore volume above 2.0 nm = 0.365 mL/g.

Average pore diameter = 20.0 nm.

errors in the surface area and the particle size and to residual ethoxy groups and water in the sample.

The colloidal silica was transferred to DMF before functionalization.⁵ Stable dispersions were obtained only when the total volume was kept constant throughout the process and the water was completely removed. Otherwise, the silica precipitated after one to two weeks. Our most stable dispersions of **2** have shown no signs of precipitation after standing for four months.

After the silica is transferred to DMF, mercaptopropyl groups can be attached by reaction with mercaptopropyltrimethoxysilane. The CP/MAS ¹³C NMR spectrum of **3** in Figure 1 shows that the sample still contains ethoxy groups (61.1 and 17.7 ppm) from incomplete hydrolysis of tetrachethyl orthosilicate and methoxy groups (50.7 ppm) from attachment of the trimethoxysilane. The C(1) signal of the propyl group (bound to silicon) appears at 10.9 ppm, and the C(2) and C(3) signals are

unresolved at 27.5 ppm. Surface coverage was determined by sulfur analysis to be 0.35 mg-atom/g, but only 0.22 mequiv/g of thiol in the precipitated sample reacted with Ellman's reagent.

Oxidation of the mercaptan with *tert*-butylhydroperoxide in toluene gave dispersion **4** with 2.59 mg-atom S/g and an ion exchange capacity of 0.17 mequiv/g. Reaction with Ellman's reagent showed only 0.076 mequiv/g of unreacted thiol. The remaining sulfur atoms are present in various intermediate oxidation states. The CP/MAS ^{13}C NMR spectrum of **4** (Figure 1) shows the presence of methoxy (51.0 ppm) and ethoxy groups (60.7 and 17.2 ppm). The expected peaks of the propanesulfonic acid around 14, 19, and 53 ppm¹⁰ are hidden by other strong peaks in all of these regions. The concentration of mercaptopropyl groups is low as shown by the absence of the 27.5 ppm peak. Peaks at 41.9 and 23.0 ppm are attributed to disulfide. Other peaks at 30.3 and 39.2 ppm are due to $(\text{CH}_2)_3\text{S}$ groups with sulfur in intermediate oxidation states^{10,11} and have not been assigned.

The elemental analysis of **4** shows a much higher surface coverage than that of its precursor, **3**. Apparently, preparation of the samples for elemental analysis by washing with water, acetone, and ether, removes unbound silanes from **3**. However, after the mercaptans are partially oxidized to the sulfonic acid **4**, the previously unbound silanes are either more tightly adsorbed or covalently bound to the silica and cannot be removed by washing. This hypothesis was confirmed by isolating the non-volatile residue from the filtrates of **3** after the washing procedure. The filtrates and wash solutions from 20 mL each of **3** and **4**, contained 234 mg and 36 mg of residue, respectively. In a separate control experiment, reaction of monomeric mercaptopropyltrimethoxysilane with *tert*-butylhydroperoxide formed a polymer. Thus polymerization of silanes adsorbed to **3** during the oxidation procedure could give non-extractable polymer adsorbed to **4**.

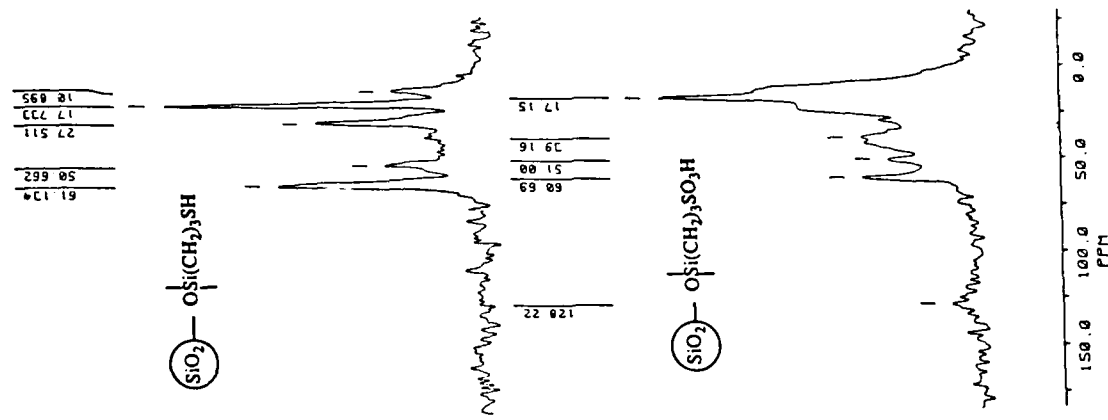


Figure 1. ^{13}C CP/MAS NMR Spectra of Modified Colloidal Silica

CONCLUSIONS

Colloidal silica, prepared by hydrolysis of tetraethyl orthosilicate, can be functionalized in DMF with mercaptopropyltrimethoxysilane to give 0.35 mequiv/g of bound mercaptan. Oxidation with *tert*-butylhydroperoxide gives a functionalized silica containing 0.17 mequiv/g of sulfonic acid as well as other sulfur function groups in intermediate oxidation states. This is the first functional group transformation on silica in a colloidal state. Each of the dispersions has shown no signs of precipitation after standing for four months.

Acknowledgments

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