COLLOIDAL SILICA: SURFACE MODIFICATION AND CATALYSIS

By

RICKEY DON BADLEY

Bachelor of Science

Southwestern Oklahoma State University

Weatherford, Oklahoma

1984

Submitted to the Faculty of the
Graduate College of the
Oklahoma State University
in partial fulfillment of
the requirements for
the degree of
DOCTOR OF PHILOSOPHY
May, 1989

COLLOIDAL SILICA: SURFACE
MODIFICATION AND
CATALYSIS

Thesis Approved:

Warren T Ford
Thesis Adviser

Horacio A Mottola

Richard A. Bunce

H. Olin Spivey

Norman N. Durham
Dean of the Graduate College

ACKNOWLEDGMENTS

I wish to express my sincere gratitude to the individuals who assisted me in this project and during my coursework at Oklahoma State University. In particular, I wish to thank Dr. Warren T. Ford for his advice and guidance. I am also grateful to Dr. Horacio Mottola, Dr. Richard Bunce, and Dr. Olin Spivey for serving on my graduate committee.

Many thanks also go to Dr. Frank McEnroe at Conoco, Inc. and Dr. Roger Assink at Sandia National Laboratories for their assistance in obtaining and interpreting NMR spectra, to Gena Martin, who worked with me during the summer of 1988, and to all members of our research group for their help and friendship. I thank the Oklahoma State University Center for Water Research for their financial support provided through a fellowship.

Special thanks go to my wife, Susan, for her love, support, and encouragement, and to my son, Nathan, whose cheerful face is always there to greet me after a long day. They have made the difficult times much easier.

TABLE OF CONTENTS

Chapter Page

LIST OF TABLES

Chapter I

Chapter II

Chapter III

LIST OF FIGURES

Chapter I

Chapter II

Figure Page

Chapter III

Figure Page

LIST OF SCHEMES

Chapter I

Chapter II

Chapter III

CHAPTER I

INTRODUCTION

In recent years, much attention has been given to the attachment of soluble catalysts to a solid support in order to form heterogeneous catalysts. By using these immobilized catalysts in solution, one may achieve some of the advantages of both homogeneous and heterogeneous catalysts, including higher selectivity, easier reaction workup, catalyst reusability, safer reagents, and increased activity. In most cases, the catalyst can be removed from a reaction mixture by filtration. This makes the workup of a reaction much simpler. Also, if the catalyst can be removed by filtration, it may be reusable or adaptable to continuous flow processes. This is an important factor since most supported catalysts are more expensive than the soluble analog. Many catalysts become safer to use when immobilized since the immobilized species has no vapor pressure. In some cases, increased catalytic activity has been observed with supported catalysts. This is due to adsorption of the substrate to the surface, giving a high local concentration of the substrate near the active sites. But while increased activity may be seen in a few cases, as a general rule, heterogeneous catalysts give lower activity due to the reaction rate being limited by the rate of substrate diffusion through a swollen gel or through pores to the catalytic sites. It is hoped that compensation for this loss in activity will come from the other advantages of a heterogeneous catalyst making the use of supported reagents beneficial.

SURFACE MODIFICATION OF SILICA GEL

One common support used in heterogeneous catalysis is silica gel. It provides a stable, rigid support which is unaffected by solvents.[1] Some of the most common methods for immobilizing functional groups on the surface of silica are shown in Figure 1.[2] By reacting silica with $SiCl_4$, silyl chlorides can be formed on the surface which will then react with lithium or Grignard reagents (Method 1). Due to the acidity of the surface silanols, they can be esterified with alcohols or serve as ligands for adsorption of metal ions (Methods 2 and 3). If a trialkoxyalkylsilane is hydrolyzed along with a tetraalkoxysilane, a silica can be formed containing surface functional groups (Method 4).

Perhaps the most useful method for surface modification is reaction of silica with alkoxysilanes or chlorosilanes (Method 5). Chlorosilanes react faster than alkoxysilanes, but HCl is produced in the reaction. Therefore, alkoxysilanes have seen more use since the by-product of the reaction is an alcohol.[3] The alkoxysilane usually has a general formula of $(RO)(CH_3)_2SiR'$, $(RO)_2(CH_3)SiR'$, or $(RO)_3SiR'$, where R is generally methyl or ethyl. The reactivity decreases as the size of the alkoxy group increases. The monoalkoxysilane has advantages of providing a monolayer of surface coverage, giving reproducible results, and a well-defined surface.[4] However, it leaves residual surface silanols because of steric factors due to the methyl groups, and the surface-bound silanes can be hydrolyzed. The di- or trialkoxysilanes react more completely with surface silanols and give more stable binding since they are bonded to the surface through two or three bonds. They give polymeric silanes on the surface, which gives higher surface coverage, but also presents problems in defining the surface and getting reproducible results in the surface coverage reaction.[4] The choice of silane depends upon the application.

Many different functional groups can be attached directly by using chloro- or alkoxysilanes.[5] If direct attachment cannot be done, the use of silane coupling agents such as aminopropyltrimethoxysilane make it possible to attach nearly any functional group by methods similar to that shown in Scheme 1.[6,7]

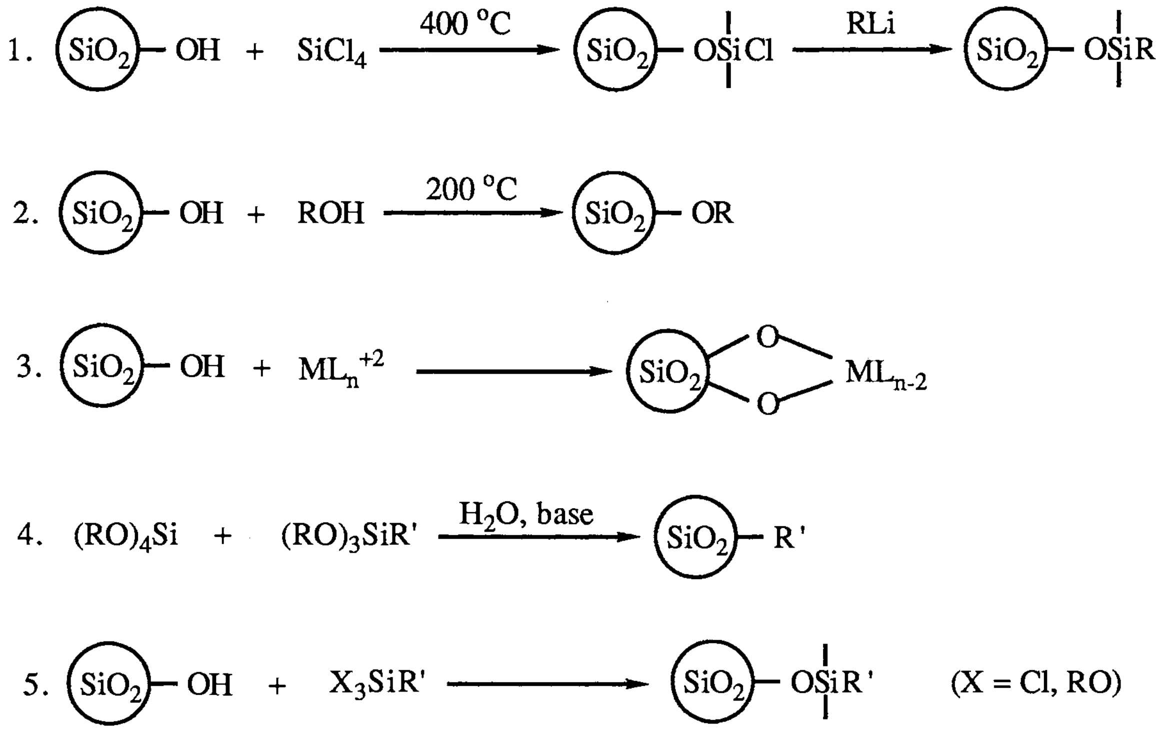
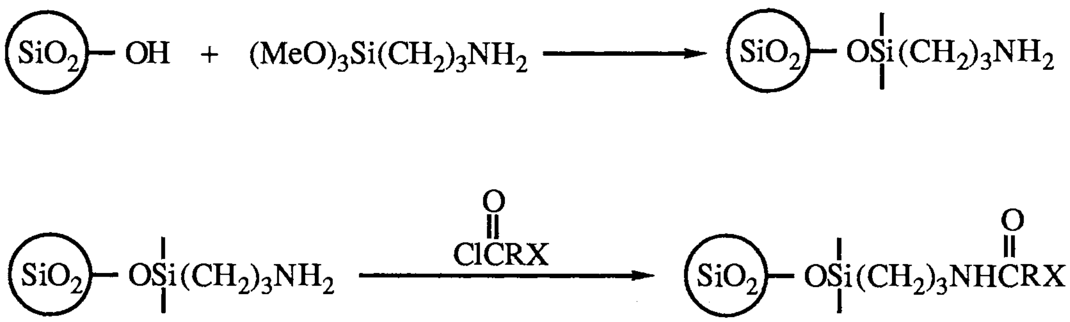


Figure 1. Methods for surface modification of silica.

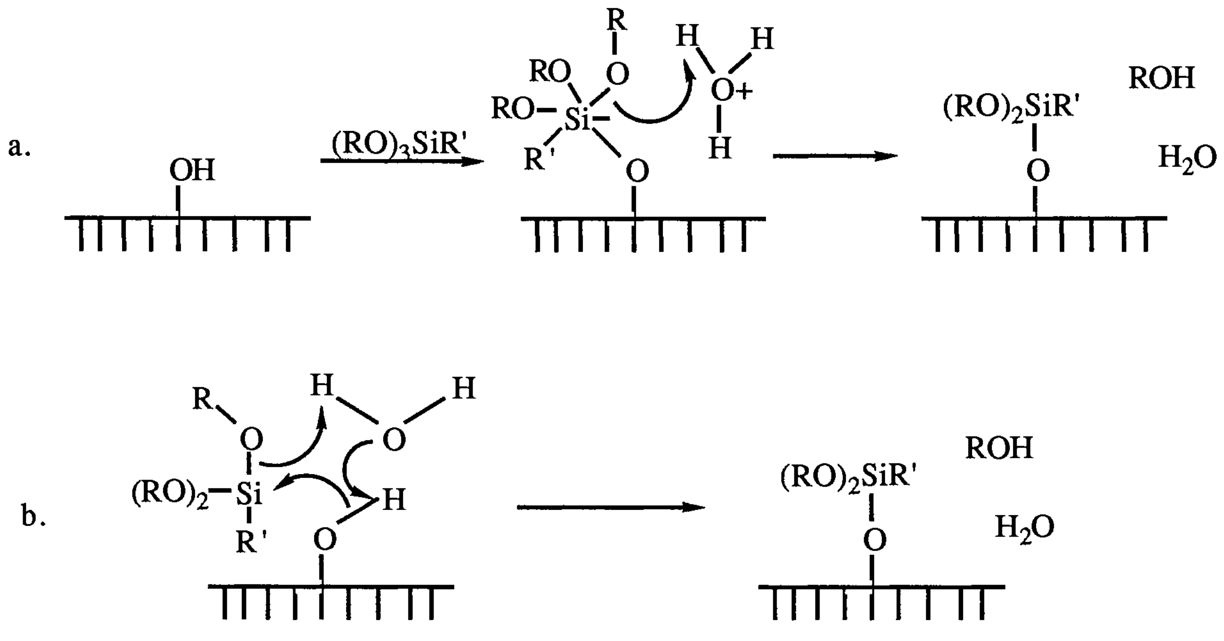
Scheme 1. Attachment of Functional Group to Silica by Use of

Silane Coupling Agent.



An alkoxysilane can react with silica gel in two ways. It can either react directly with the silica surface or it can hydrolyze to form reactive silanol groups, which then react with the surface. Blitz, Murthy, and Leyden have proposed two different mechanisms by which the silane can react directly with the surface (Scheme 2).[8] In the first mechanism, the silanol oxygen bearing a partial negative charge will attack the silane to give a pentacoordinate intermediate which then decomposes to give ethanol, water, and the surface bound silane. The second mechanism goes by a concerted process, involving a cyclic 6-centered transition state, and it gives the same products.

Scheme 2. Mechanisms for Direct Reaction of Trimethoxysilanes with Silica.



Silica usually contains some surface adsorbed water. Unless special precautions are taken to dry the silica thoroughly, the mechanism shown in Scheme 3 is probably the prevalent mode of reaction.[9] By this mechanism, the trialkoxysilane is first hydrolyzed to form a silicic acid. It may then form oligomers in solution which will eventually come into contact with the silica surface and react by condensation. As will be seen later, this is a very simplified mechanism. Complete hydrolysis of the ethoxy groups does not occur unless carried out in aqueous solution.[10] The silanes can also be bound to the surface by one, two, or three bonds and it is possible to have oligomeric siloxanes extending into solution near the surface.[11]

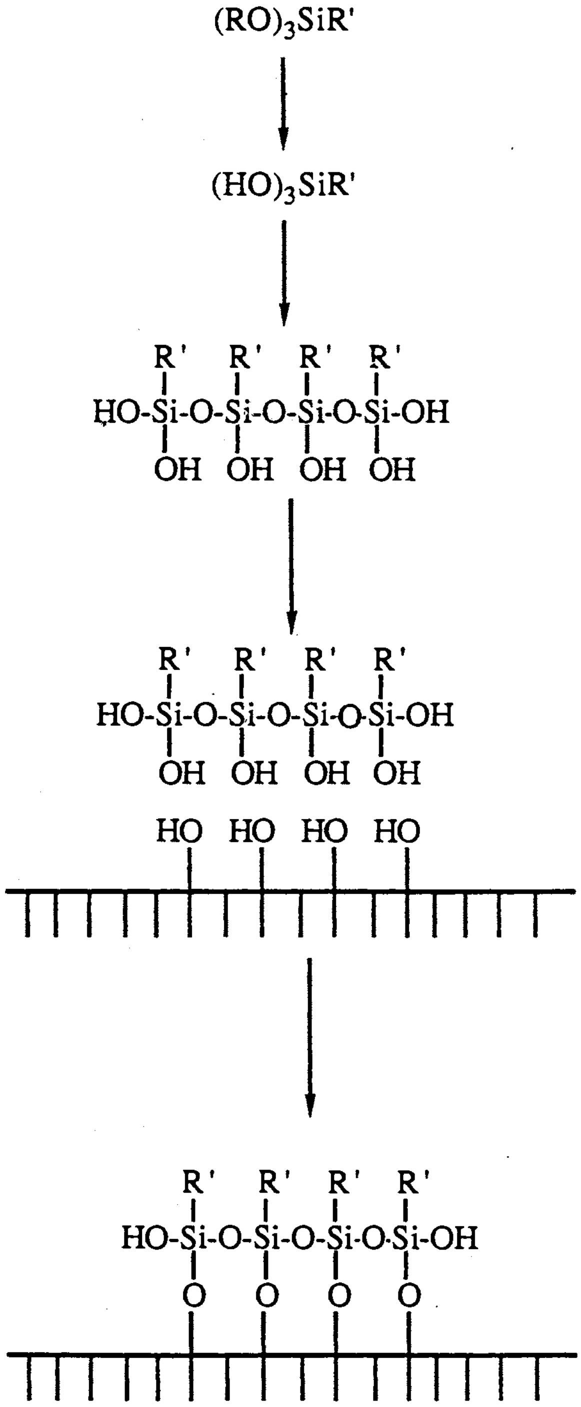
A variety of techniques is available for analysis of these surface modified silicas. One of the most useful methods is cross-polarization magic-angle-spinning nuclear magnetic resonance (CP/MAS NMR) spectroscopy. ^{29}Si NMR gives information on the bonding in the silica core[12] as well as the surface bonds to the organofunctional group.[13] ^{13}C NMR determines the organic surface coverage.[14] NMR spin-lattice relaxation techniques have also been useful in studying the mobility[15] and hydrogen bonding[16] of surface-bound groups.

Diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy provides quantitative analysis of the surface-bound groups by comparing the intensities of the Si-O-Si combination band at 1860 cm^{-1} and surface group absorptions.[8] It has also found use in quantitative analysis of surface silanols.[17]

Other useful methods for determining surface coverage are X-ray photoelectron spectroscopy (XPS),[18] which has been used to give relative concentrations of surface groups, and elemental analysis.[19] Floyd, Sagliano, and Hartwick used gas chromotography to analyze fluorinated alkylsilane derivatives generated by hydrofluoric acid digestion of the modified silica.[20]

The thermal stability of surface-bound groups and weights of physically adsorbed compounds are determined by thermogravimetric analysis (TGA).[19] Surface areas and

Scheme 3. Reaction of Trimethoxysilanes with Silica in the Presence of Water.

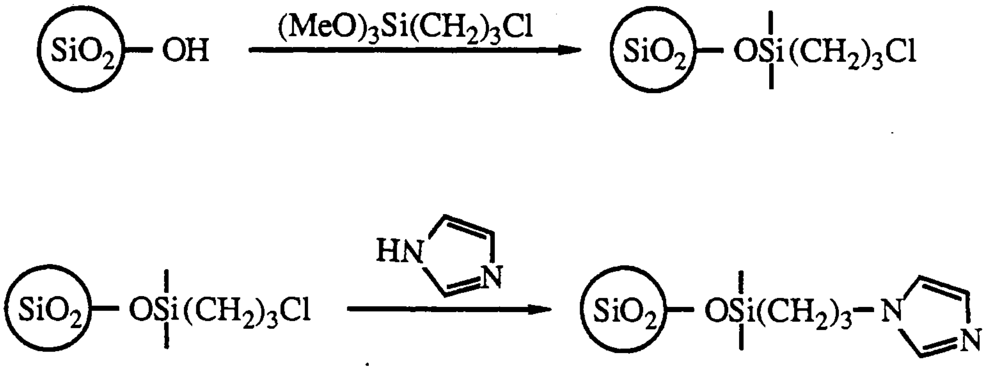


pore size distributions of unmodified or modified silica are normally obtained by Brunauer-Emmett-Teller (BET) analysis in which the amount of nitrogen adsorbed or desorbed by the sample is measured as a function of the nitrogen pressure at -196 °C.[21]

SILICA GEL AS A CATALYST SUPPORT

The reaction of silica with trialkoxyalkylsilanes has been used to immobilize a great number of catalytic species. One of the earliest examples was the binding of imidazole by first attaching a chloropropyl group and displacing the chloride with imidazole (Scheme 4).[22] The bound imidazole was then used as a catalyst for the hydrolysis of p-nitrophenyl acetate. The homogeneous and bound imidazole gave initial rate constants of 11.4 and 8.9 L mole^{-1} min^{-1}, respectively. While the heterogeneous catalyst was less active than the homogeneous catalyst, it was found that it behaved similarly to soluble imidazole, giving the same kinetics. This led to the conclusion that the imidazole groups attached to silica react with p-nitrophenylacetate and water in much the same fashion as in homogeneous solution. This conclusion encourages binding to silica other catalysts designed for use in solution.

Scheme 4. Synthesis of Silica-Bound Imidazole.



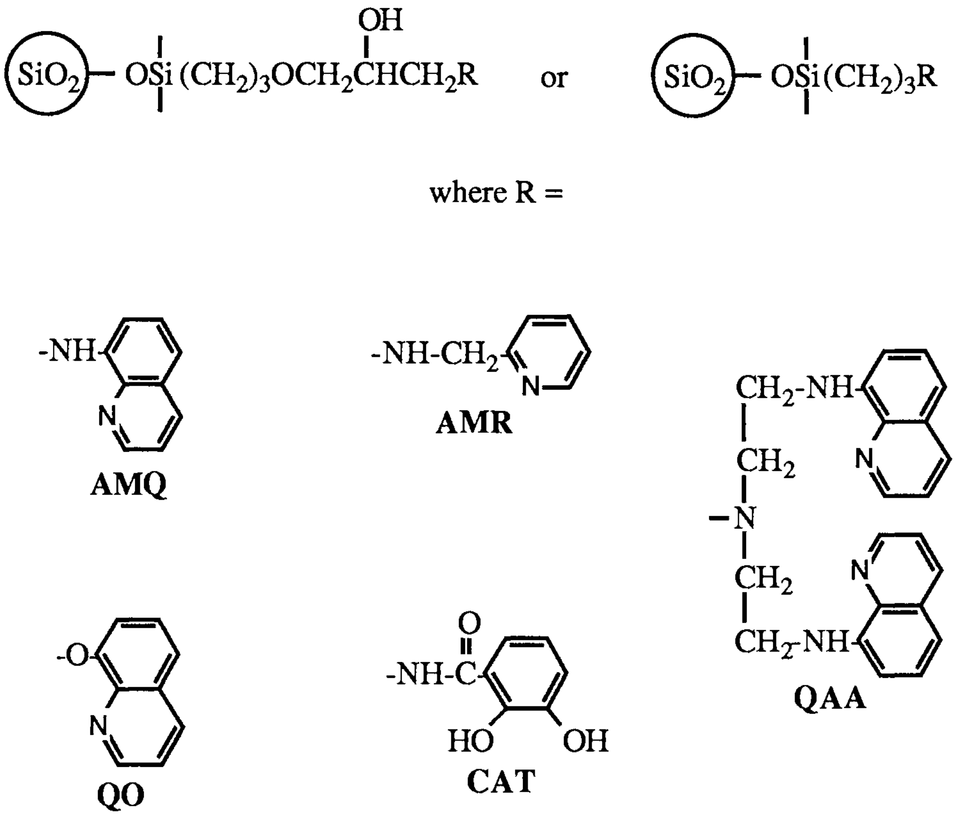
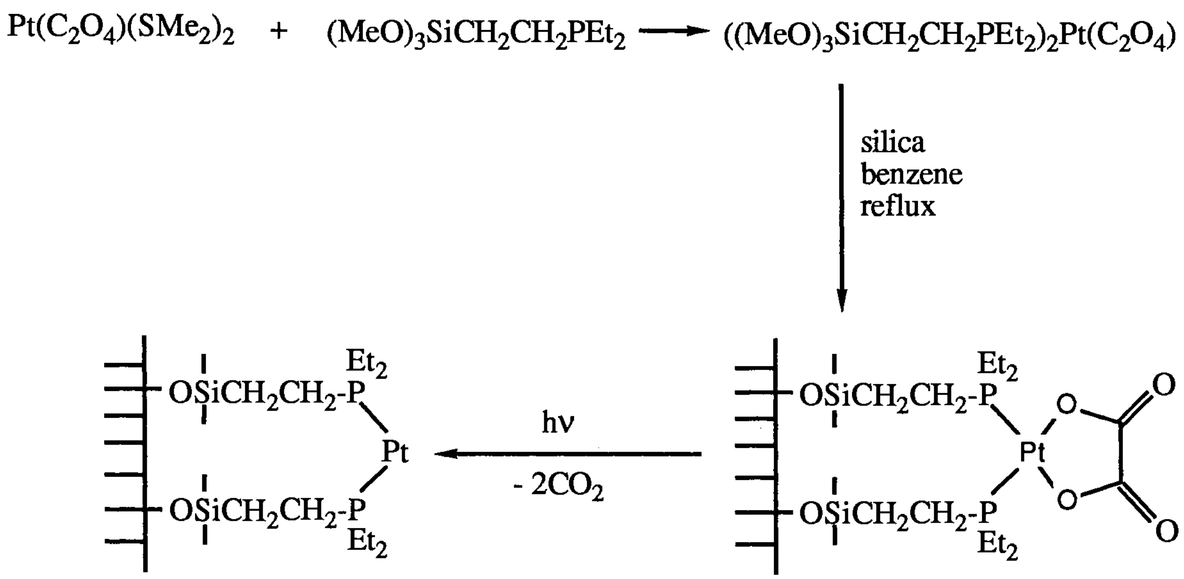


Figure 2. Ligands used for binding of Rh(I), Pd(II), and Pt(II).

One of the most common uses of silica supports is the binding of metal ions for catalysis. Figure 2 shows a number of different ligands which have been immobilized on silica and used for binding of Rh(I), Pd(II), and Pt(II). These have been used as catalysts for hydrogenation of alkenes and alkynes.[7] It was found that **AMQ** was most reactive and is actually more reactive than the soluble analog. **AMR** and **QAA** are slightly less active. When a nitrogen is replaced with oxygen in the ligand as in **QO** and **CAT**, the catalyst becomes much less active. Hennig, Seshadri, and Haupt also found that the length of the spacer chain employed between the silica and the ligand had no effect on the activity.

Scheme 5. Synthesis of Platinum Hydrosilation Catalyst.



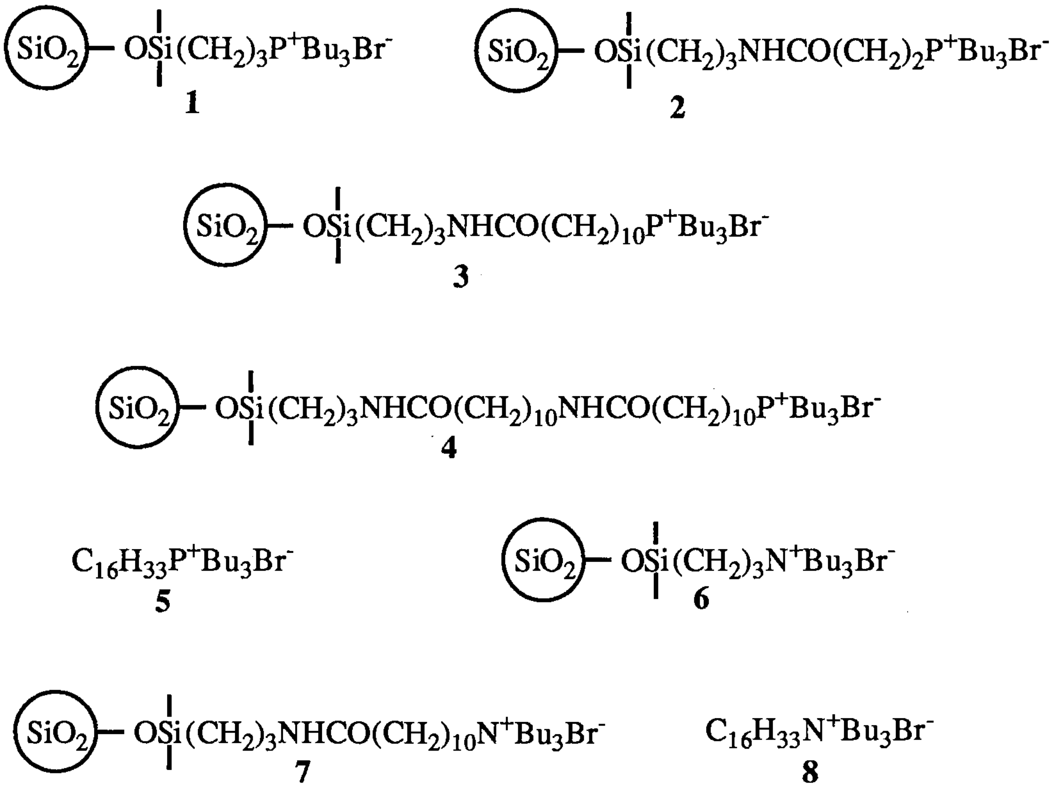
Prignano and Trogler[1] have used a different immobilized ligand, triethylphosphine, to bind Pt(II) for use in hydrosilation reactions. The catalyst is immobilized as shown in Scheme 5. The Pt(II) is first bound to $(CH_3O)_3SiCH_2CH_2P(CH_2CH_3)_2$, which is then reacted with the silica. When this group is irradiated, the oxalate dissociates and is lost as CO_2, giving a coordinatively unsaturated platinum/phosphine complex which is active as a hydrosilation catalyst. When this unsaturated complex is formed in solution, it tends to rearrange to catalytically inactive PtL_3, PtL_4, and Pt metal by bimolecular pathways. However, when the catalyst is attached to a rigid support such as silica, the active sites can be isolated on the surface, preventing the rearrangement to inactive species. Prignano and

Table I. Hydrosilation of $MeCl_2SiH$ to Olefins with Various Catalysts.

catalyst	olefin	olefin/catal. ratio	time(h)	temp (^oC)	Yield(%)
$[SiO_2]L_2Pt(C_2O_4)$	1-pentene	1850	24	30	>90
H_2PtCl_6	1-pentene	10^6	0.5	200	93
$[SiO_2]L_2Pt(C_2O_4)$	1-heptene	4200	5	30	95
$Pt(C_2O_4)(PEt_2)$	1-heptene	84	24	30	93

Trogler found that if the irradiation is carried out for 45 minutes or less using a 200 W Hg-Xe lamp, all formed active sites are isolated and rearrangement does not occur. As shown in Table I, the supported catalyst is now much more active than the soluble analog because the catalyst remains in the most active form. This allows a higher olefin to catalyst ratio and shorter reaction time to be used in the reaction. The supported catalyst requires more catalyst and longer reaction time than chloroplatinic acid, which is the most commonly used hydrosilation catalyst, but it allows the reaction to be run under much milder room temperature conditions. This is one example of how attachment of a catalyst to a rigid support can be very beneficial.

Another type of immobilized catalyst which has been used often is phase transfer catalysts. Tundo, Venturello, and Angeletti[23-24] have prepared a number of different phase transfer catalysts shown in Figure 3. When these catalysts were used in the reaction of butyl bromide with iodide or cyanide (Table II), the immobilized catalysts gave lower



$SiO_2-OSi(CH_2)_3P^+Bu_3Br^-$ **1**

$SiO_2-OSi(CH_2)_3NHCO(CH_2)_2P^+Bu_3Br^-$ **2**

$SiO_2-OSi(CH_2)_3NHCO(CH_2)_{10}P^+Bu_3Br^-$ **3**

$SiO_2-OSi(CH_2)_3NHCO(CH_2)_{10}NHCO(CH_2)_{10}P^+Bu_3Br^-$ **4**

$C_{16}H_{33}P^+Bu_3Br^-$ **5**

$SiO_2-OSi(CH_2)_3N^+Bu_3Br^-$ **6**

$SiO_2-OSi(CH_2)_3NHCO(CH_2)_{10}N^+Bu_3Br^-$ **7**

$C_{16}H_{33}N^+Bu_3Br^-$ **8**

Figure 3. Phase transfer catalysts.

activity than the soluble catalyst in all cases.[23] However, when the same catalysts were used for the reduction of 2-octanone with $NaBH_4$ under phase transfer conditions, all of the heterogeneous catalysts were as active or more active than the homogeneous catalyst.[24] Table III shows the relationship between the adsorption equilibrium constant (K_{ads}) in mmol/g for adsorption of 2-octanone from cyclohexane onto the catalyst surface and the pseudo-first-order rate constant (k_{obsd}) for aqueous borohydride reduction of 2-octanone in cyclohexane. As K_{ads} increases for a catalyst, k_{obsd} also increases. This increase in activity is due to a high local concentration of 2-octanone around the catalytic sites. The enhanced adsorption of **1** with respect to **2-4** must be attributed to the presence of a polar group, the onium salt, with a short alkyl chain that does not have a drastic effect on either

Table II. Observed Pseudo-First-Order Rate Constants for Conversion of Butyl Bromide to Butyl Iodide or Butyl Cyanide by Reaction with KI or KCN under Phase Transfer Conditions Using the Catalysts from Figure 3.

Catalyst	KI	KCN
1	1.88	0.22
3	1.74	0.26
5	7.14	1.14
6	1.18	0.19
7	1.36	0.21
8	9.21	1.52

Table III. Relationship Between Adsorption Constant of 2-Octanone and the Pseudo-First-Order Rate Constant for Aqueous Borohydride Reduction of 2-Octanone in Cyclohexane.

catalyst	$K_{ads} \times 10^2$ (mmol/g)	$k_{obsd} \times 10^4$ (s^{-1})
1	7.4	7.67
2	2.0	3.50
3	0.8	2.17
4	2.0	3.33
5	--	2.17

the polarity of the support or its availability to the substrate. In catalysts **2** and **3**, a hydrophobic chain surrounding the matrix decreases its polarity and hence its adsorption capability. With catalyst **4**, the adsorption and activity once again increase. Apparently, the long alkyl chain begins to act as a solvent for the ketone and thus takes part in the adsorption processes as well. It is apparent from this example that adsorption of a substrate can have a drastic effect on the activity of a heterogeneous catalyst since the same catalysts gave lower activity than the soluble analog in the butyl bromide reaction where no adsorption occurred and higher activity when adsorption occurred in the borohydride reaction.

There are many other examples of silica-supported catalysts in the literature which are much too numerous to discuss here.[25] In most examples, the heterogeneous catalyst shows lower activity than the homogeneous analog, unless substrate adsorption, catalyst stabilization, or some other similar factor has an influence on the activity. This lower activity is due to many of the active sites being inside silica pores. Therefore, the substrate must diffuse into the pores before it can react. This mass transfer limitation is a theme which dominates in heterogeneous catalysis.

COLLOIDAL CATALYSTS

One possibility for reducing the mass transfer limitation is to use colloidal sized particles as a support. In a reaction whose rate is limited by the transport of reactant to active sites on the particle surface, the activity of a catalyst is directly proportional to its surface area.[26] Since surface area is inversely proportional to particle size, by decreasing the particle size, the mass transfer limitations can be reduced and the catalyst should become more active.

This effect was demonstrated by Bernard, Ford, and Taylor,[27] who used phosphonium salts bound to polystyrene as phase transfer catalysts. The effect of particle size on the catalyst activity is shown in Table IV. By decreasing the particle size from 10-37 µm to 0.27 µm, the activity was increased by four times. Even the much more rigid 10% crosslinked particles, which should have more mass transfer limitation inside the particle, show higher activity than the large particles because more of the phosphonium groups must be on or near the surface in the colloidal sized particles.

Table IV. Effect of Catalyst Particle Size on Reaction of Benzyl Bromide and Sodium Cyanide.

% crosslinked	catalyst diameter (µm)	$k_{obsd} \times 10^5$ (s^{-1})
2	10-37	510
2	0.5-1.2	510
2	0.27	2200
10	0.116	990

Fitch[28] found similar results when polystyrene latexes containing surface sulfonic acid groups were used as catalysts for inversion of sucrose. The colloidal catalyst gave an activity 1.8 times greater than soluble sulfuric acid due to adsorption of sucrose to the surface. The colloidal particles were also 40-60 times more active than macroscopic ion exchange beads. The ion exchange beads had active sites inside the particles while the colloidal particles had all sulfonic acid groups on the surface. So many of the active sites in the particles must be inaccessible to sucrose and inactive.

Colloidal palladium (33 mg) reduces 20 mmol of acenapthalene in 15 min. The same reaction requires 5 h when macroscopic palladium black is used as the catalyst.[29]

These examples show that the particle size of the support does have a large effect on the mass transfer limitations and the catalyst activity. Other colloidal catalysts have given high activity due to substrate adsorption. Polystyrene latexes with bound cobalt phthalocyaninetetrasulfonate are 10 and 11 times more active than soluble cobalt phthalocyaninetetrasulfonate in the oxidation of 2,6-di-tert-butylphenol[30] and 1-decanethiol,[31] respectively. Cobalt-pyridine complexes bound to copolymers of styrene and acrylic or methacrylic acid are 3.3 times more active than soluble Co(II) and pyridine in the autoxidation of 1,2,3,4-tetrahydronapthalene.[32,33] In each of these cases, a water insoluble compound is oxidized in an aqueous latex dispersion. The substrate is adsorbed into the latex particles which act somewhat like a solvent. This adsorption accounts for the increased activity.

Other examples of colloidal catalysis have used colloids modelled after enzymes. Hopkins and Williams[34] prepared methacrylate latexes with amine groups situated in cavities in the polymer matrix. These "microgels" possess strong binding properties and are much more active than soluble amines. Histamine and L-histidine bound to styrene/acrylic acid latexes have provided slightly more active catalysts than soluble histamine or L-histidine.[35,36]

COLLOIDAL SILICA

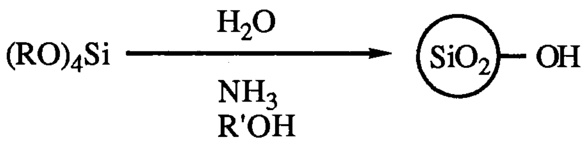
At this time, the field of colloidal catalysis is relatively new and is limited mainly to the use of organic polymer colloids as supports. Even though silica is a widely used support for macroscopic catalysts, and colloidal silica particles can be formed easily, no one has tried using colloidal silica as a catalyst support.

Colloidal silica has been made by many methods. When a dilute solution of sodium silicate is partially neutralized to pH 8-9, a 3% silica dispersion is obtained. Ion exchange is used to remove sodium ions during the process because aggregation occurs if the sodium ion concentration exceeds 0.3 M.[37] An alternative is to pass sodium silicate directly though an ion exchange column, producing a colloidal silica dispersion which can be concentrated to 20% silica by evaporation.[38,39] Electrodialysis has also been used to remove sodium ions, but it did not give stable dispersions.[40]

A 10% silica dispersion is prepared by peptizing silica gel with aqueous ammonia and heating without evaporation of water until colloidal silica is formed.[41] Silicon metal that has been pretreated with hydrofluoric acid to remove the oxide film, reacts rapidly in aqueous ammonia to give 8-35 nm diameter colloidal silica particles.[42]

Pyrogenic silica, made by condensing SiO_2 from the gaseous phase, is the most common type of commercial colloidal silica. Vaporizing silica at 1700 °C in the presence of a reducing agent gives SiO vapor. If the SiO is evaporated into an oxidizing atmosphere, SiO_2 forms and condenses in an extremely divided form giving particles with diameters of 8-28 nm. Ethyl silicate can also be oxidized to give SiO_2 vapor.[43] The most commonly used process is combustion of silicon tetrachloride with hydrogen and oxygen to give SiO_2. Since the gas mixture is homogeneous during combustion, the formation conditions for each particle are the same, resulting in a narrow particle size distribution with diameters of 10-20 nm. After leaving the combustion zone, the silica coagulates to particles with diameters up to 2 μm. These aggregates are difficult to redisperse, but by passing the silica through a homogenizer to break apart the aggregates, colloidal silica is prepared with a specific surface area of 50-400 m^2/g. It can be redispersed in basic solution to give up to 30% by weight silica dispersions. However, the resulting particles are still mainly chain-like aggregates.[43] An alternative procedure is to include a small amount of titanium tetrachloride or aluminum trichloride in the silicon tetrachloride combustion mixture to give a charged silica. Silica particles with diameters of 20-40 nm containing 1.3% aluminum oxide give very stable dispersions containing 40-60% solids.[44] Pyrogenic silica made by these methods usually contains 50-67% fewer surface silanol groups than silica prepared by precipitation methods.

Radczewski and Richter found that spherical colloidal silica particles up to 200 nm in diameter could be prepared by hydrolyzing silicon tetrachloride.[45] Stober, Fink, and Bohn[46] later introduced a convenient method for preparing spherical, monodisperse colloidal silica particles in which the particle size can be controlled. By hydrolyzing tetraalkyl orthosilicates in water, ammonia, and alcohol a very stable dispersion of nearly monodisperse, spherical colloidal silica particles is formed (Equation 1). The particle size, monodispersity, and reaction time depend on the alcohol and tetraalkyl orthosilicate used and on the concentration of water, ammonia, and tetraalkyl orthosilicate.



$$(RO)_4Si \xrightarrow[\substack{NH_3 \\ R'OH}]{H_2O} \boxed{SiO_2}-OH \qquad (1)$$

When the size of the alcohol or the alkyl groups in the tetraalkyl orthosilicate are increased, the particle size and time required for the particles to reach their final size increase. In some cases, the higher alcohols give wider size distributions, and a 1:1 mixture of methanol and butanol is more effective for formation of uniform large particles.

The particle size also strongly depends on the ammonia and water concentrations. Maximum particle sizes were formed using 8 M ammonia and 6 M water. By changing these variables, Stober was able to prepare silica particles ranging from less than 50 nm to 2 µm in diameter.

Bogush, Tracy, and Zukoski[47-49] have studied the tetraethyl orthosilicate/ethanol system more extensively. Equations 2[48] and 3[49] were formulated to relate the final particle diameter (d) in nm to the initial water, ammonia, and tetraethyl orthosilicate (TEOS) concentrations at 25 °C over a range of 0.5-14 M water, 0.5-3 M ammonia, and 0.17-0.5 M TEOS.

$$d = A[H_2O]^2\exp(-B[H_2O]) \qquad (2)$$

where

$$A = [TEOS]^{-1/2}(-1.042 + 40.57[NH_3] - 9.313[NH_3]^2)$$

$$B = 0.3264 - 0.2727[TEOS]$$

$$d = A[H_2O]^2\exp(-B[H_2O]^{1/2}) \qquad (3)$$

where

$$A = [TEOS]^{1/2}(82.06 - 151.3[NH_3] + 1202[NH_3]^2 - 365.8[NH_3]^3)$$

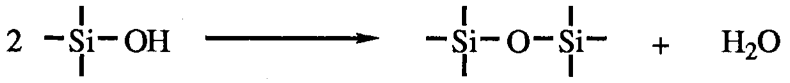
$$B = 1.051 + 0.5230[NH_3] - 0.1283[NH_3]^2$$

These equations can predict the final particle sizes within 20%, with the greatest discrepancies coming with the smaller particles. The tetraethyl orthosilicate/ethanol system can be used to prepare particles 15-700 nm in diameter at 25 °C.[48] As the temperature is increased, the final particle size decreases.[49,50] Occasionally, bimodal distributions are obtained when attempting to prepare particles near the maximum size.

The hydrolysis of tetraethyl orthosilicate to form silica involves two general reactions. They are hydrolysis of ethoxy groups,

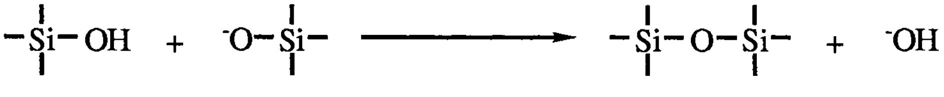
$$-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{OEt} + \mathrm{H_2O} \longrightarrow -\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{OH} + \mathrm{EtOH} \qquad (4)$$

and condensation to form siloxane linkages.[51-53]



$$2\ -\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{OH} \longrightarrow -\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O}-\overset{|}{\underset{|}{\mathrm{Si}}}- + \mathrm{H_2O} \qquad (5)$$

The reaction can be catalyzed by either acid or base. However, only base results in colloidal particles. This is due to a vast difference in the kinetics of the process using acid or base. In base, hydrolysis is the rate limiting step.[51,53] This causes the base catalyzed hydrolysis products to contain a significant number of ethoxy groups even after the condensation reaction is complete. In acid, condensation is the rate limiting step. Thus all ethoxy groups are hydrolyzed early in the reaction. The acid catalyzed reaction also results in linear polymers which form silica gel upon dehydration. The base catalyzed reaction gives discrete silica particles made up of highly crosslinked networks.[54,55] This branching in the presence of base could be due to a number of reasons. In the presence of $\mathrm{OH^-}$, if linear polymers are initially formed, they can depolymerize and rearrange to a more highly condensed form.[55,56] In acid, the polymerization is irreversible. Another reason to expect branched chains in the base catalyzed system is that the condensation probably occurs between protonated and deprotonated silanols, i.e.,



$$-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{OH} + {}^{-}\mathrm{O}-\overset{|}{\underset{|}{\mathrm{Si}}}- \longrightarrow -\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O}-\overset{|}{\underset{|}{\mathrm{Si}}}- + {}^{-}\mathrm{OH} \qquad (6)$$

The middle groups on chains are more acidic than the endgroups, so in base the condensation reaction is more likely to occur between ends and middles of chains giving the highly branched structure.[55]

This branching of chains eventually leads to particle growth which may occur by two different methods. In the first proposed mechanism, a short period of nucleation occurs early in the reaction, followed by growth via molecular addition. The second mechanism proposes that nucleation occurs for almost the entire reaction period with the particles growing primarily by aggregation of large particles with freshly formed nuclei.

The first model, proposed by LaMer and Dinegar[57] and supported by Tan, Bowen, and Epstein,[50] hypothesizes that there is a critical silicic acid concentration, C_{sat}^*, above which nucleation proceeds. C_{sat}^* is significantly higher than the saturation concentration, C_{sat}, above which spontaneous particle growth occurs provided that nuclei are available. Thus, early in the reaction as hydrolysis of tetraethyl orthosilicate occurs, the silicic acid concentration exceeds C_{sat}^* and nucleation occurs. After a sufficient number of nuclei are formed, particle growth permanently reduces the silicic acid concentration below C_{sat}^*. Therefore, nucleation ceases and only particle growth occurs after that point. If all nucleation occurs in a very short time and all particles grow at the same rate, this would lead to monodisperse particles. Tan, Bowen, and Epstein[50] state that this mechanism explains why the particle size is inversely dependent on the reaction temperature. As the temperature is decreased, the rate limiting hydrolysis reaction becomes slower. It then takes a smaller number of nuclei to relieve the high supersaturation of silicic acid. Since fewer particles are nucleated, the final particle size must be larger, assuming that all tetraethyl orthosilicate reacts. The same line of reasoning can be used to explain Stober's observation that as higher alcohols or alkyl silicates are used in the hydrolysis reaction, the rate of reaction becomes slower and the particle size increases.

The second proposed mechanism for particle growth appears to have more supporting evidence. In order for colloidal particles to be stable, the repulsive forces due to the surface charge must be larger than the van der Waal's attractive forces. The time period, τ, required to decrease the number of particles in a suspension by 50% through aggregation can be estimated by

$$\tau = 3\mu W/4Nkt \tag{7}$$

where

$$W = \exp(V_{max}/kT).$$

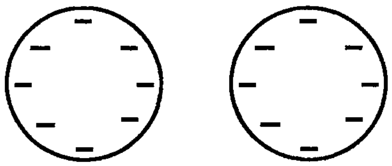
N is the number density of particles and μ is the solvent viscosity.[48] The stability ratio, W, is a measure of the time required for particles to acquire enough thermal energy to surmount the potential energy barrier, V_{max}, which repels the two particles, allowing the particles to collide and aggregate. For surface charged particles, V_{max} increases approximately linearly with particle size and thus, their rate of aggregation decreases exponentially.[58] So as small particles are formed at the beginning of the reaction, they are marginally unstable and will aggregate in order to lower the free energy. As large clusters are formed, they will then sweep through the dispersion picking up freshly formed nuclei and small aggregates until they grow to a colloidally stable size. Since the smaller particles are less stable, they will grow more quickly. The monodisperse particles achieved are thus due to size dependent aggregation rates.[48]

By transmission electron microscopy, Bogush and Zukoski[47] have shown that nucleation occurs for at least the first 30% of the reaction time. For 0.17 M TEOS, 1.3 M ammonia, and 2.0 M water in ethanol, a mixture of large aggregates up to 100 nm in diameter and <10 nm nuclei is observed early in the reaction. As the reaction proceeds, the distribution becomes more narrow until finally monodisperse 200 nm particles are formed.

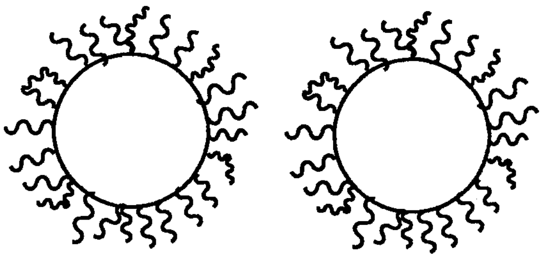
This aggregation mechanism also suggests that the particles may contain pores corresponding to interstices between the packed 10 nm particles. van Helden, Jansen, and Vrij[59] have reported measuring approximately 0.065 mL/g pore volume by the standard de Boer t curve in 21 nm particles due to ultramicropores of less than 1.2 nm. Bogush, Tracy, and Zukoski[49] found the density of particles formed in this process to be 2.04-2.10 g/mL by helium pycnometry. When the pores were then filled by covering the surface with octadecyl groups, a bulk unesterified density of 1.78-1.86 g/mL was calculated. This difference suggests a particle porosity of 11-15%.

Up to this point, the colloidal silica which has been discussed is a charge stabilized material (Figure 4a).[60] The silica is formed in a basic solution containing ammonia, which deprotonates some of the surface silanols giving the silica a negative surface charge. This surface charge gives a repulsive force between two silica particles and prevents coagulation. Charge stabilization gives stable dispersions in a few solvents, i.e., ethanol/ammonia,[46] high pH aqueous solutions,[61] and dimethylformamide.[62] However, to achieve stable dispersions in nonpolar solvents or neutral aqueous solutions, another method of stabilization is needed. The most commonly used method is steric stabilization (Figure 4b).

If polymer chains are attached to the surface, and the silica is dispersed into a good solvent for that polymer, the polymer chains will extend into the solvent around the particle, forming a protective layer. Now when two particles approach, the polymer chains must either interpenetrate or indent, increasing the polymer segment density in the zone between the particles. This changes the local osmotic pressure, causing an increase in the free energy. Therefore, polymer interpenetration results in a repulsive force. Interpenetration of polymer chains also causes a loss in the configurational freedom of the anchored polymer chains. This entropic effect is always repulsive. If the repulsive forces due to resistance of the polymer chains to interpenetration are greater than the van der Waal's attractive forces, the polymer chains can prevent coagulation of the particles.[60]



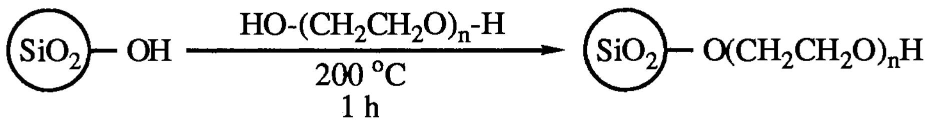
a. charge stabilized



b. sterically stabilized

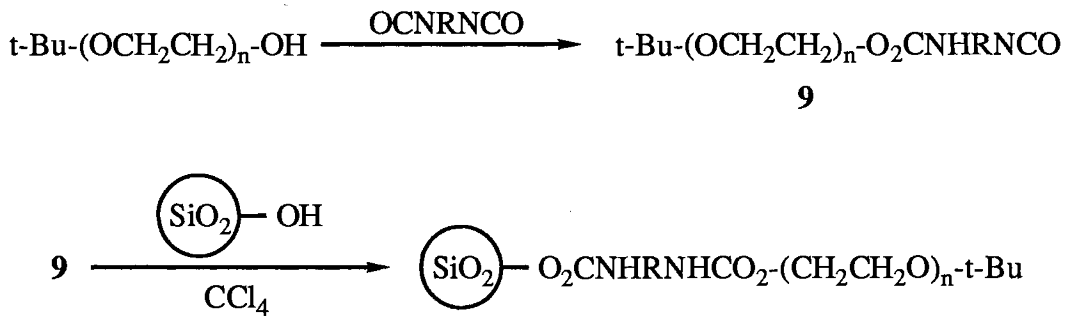
Figure 4. Charge and sterically stabilized colloidal silica.

In aqueous dispersions, poly(ethylene oxide) is commonly used as a steric stabilizer. Two methods of covalently binding poly(ethylene oxide) to the silica surface are shown in Equation 8[63] and Scheme 6.[64] The first method involves a direct surface esterification by heating a mixture of poly(ethylene oxide) and colloidal silica at 200 °C. This is a very easy method of binding poly(ethylene oxide), but the ester linkage is susceptible to hydrolysis. The second method (Scheme 6) gives a more stable urethane linkage although the synthesis is much longer. Ben Ouada, et al.[63] have found that for poly(ethylene oxide) of molecular weight 1880, a critical surface coverage value, σ^*, exists at 0.12 molecules/nm^2. Below this value, the polymer chains have a flat conformation against the surface. Above σ^*, the polymer chains begin to overlap and extend into solution to give steric stabilization.



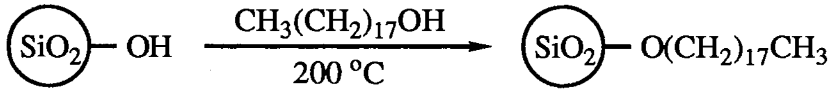
(8)

Scheme 6. Attachment of Poly(ethylene oxide) to Colloidal Silica Through a Urethane Linkage.



When colloidal silica is dispersed into nonpolar solvents such as chloroform and cyclohexane, clear dispersions are obtained because the refractive indexes of amorphous silica and the solvent are similar. This makes these dispersions ideal for light scattering and spectroscopic studies since multiple scattering is minimized during light scattering measurements and more light is transmitted for spectroscopy.[59]

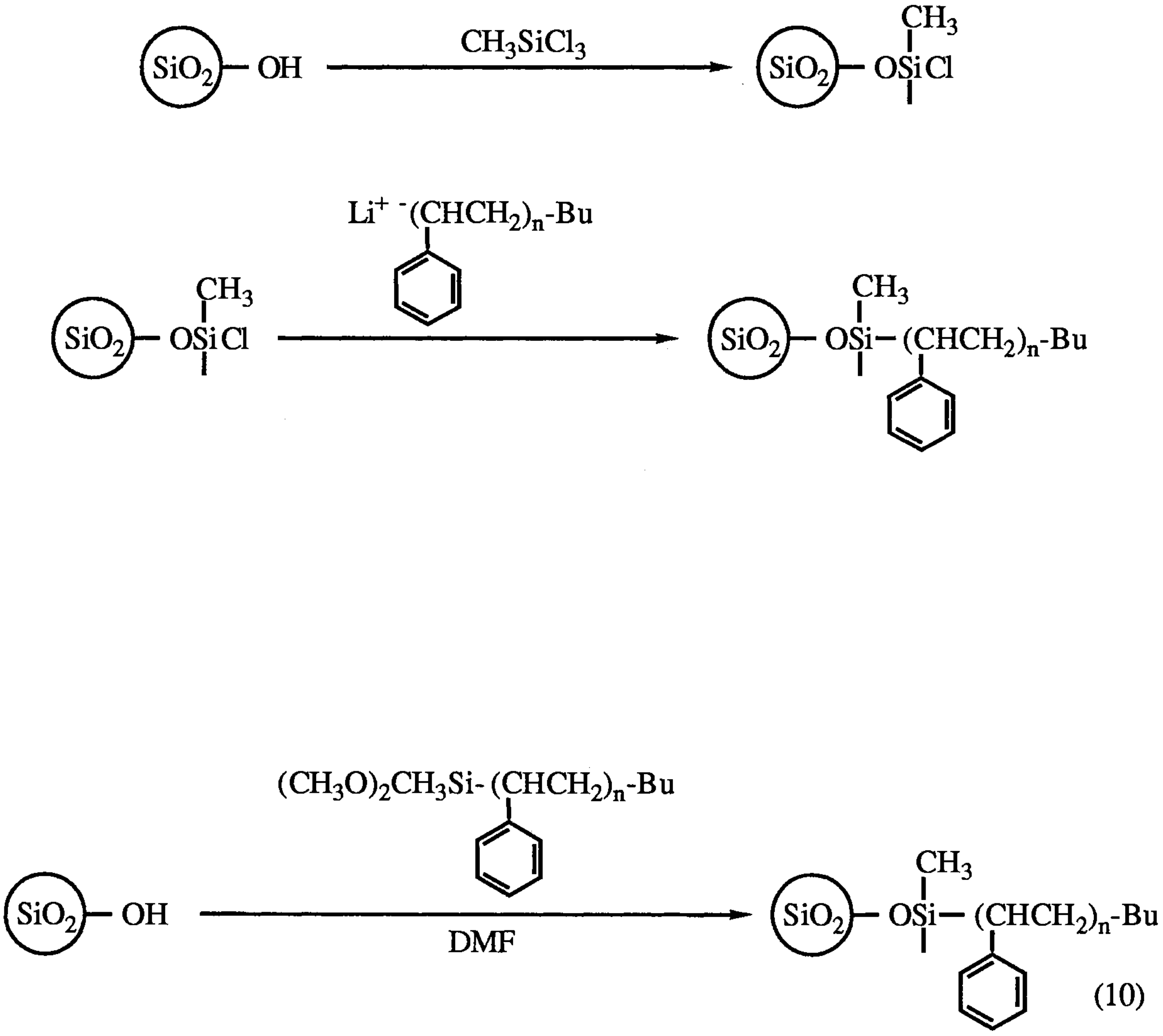
A number of different methods have been used to sterically stabilize colloidal silica in nonpolar solvents. One of the easiest methods is shown in Equation 9, in which the colloidal silica surface is esterified with octadecanol.[59] This gives a dispersion which is readily dispersable in cyclohexane, *n*-alkanes, chloroform, and toluene. However, the ester linkages are hydrolyzable and a thick coverage of C_{18} groups is required for stabilization.



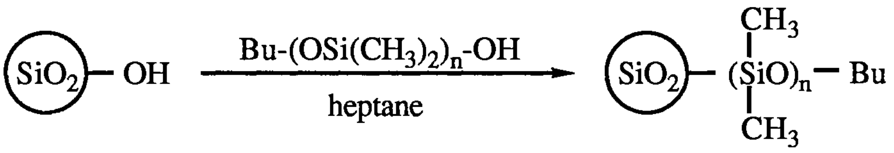
$$\text{SiO}_2\text{—OH} \xrightarrow[200\ ^\circ\text{C}]{CH_3(CH_2)_{17}OH} \text{SiO}_2\text{—O}(CH_2)_{17}CH_3 \qquad (9)$$

Likewise, polystyrene can give stability in a wide range of organic solvents. Two different methods have been used to anchor polystyrene to the surface. By reacting methyltrichlorosilane with the silica surface, chlorosilanes are formed on the surface which can then react with polystyrene living anions (Scheme 7).[65] Also, an alkoxysilane terminated polystyrene can be formed which reacts directly with the surface (Equation 10).[62]

Scheme 7. Attachment of Polystyrene Through Living Anion.

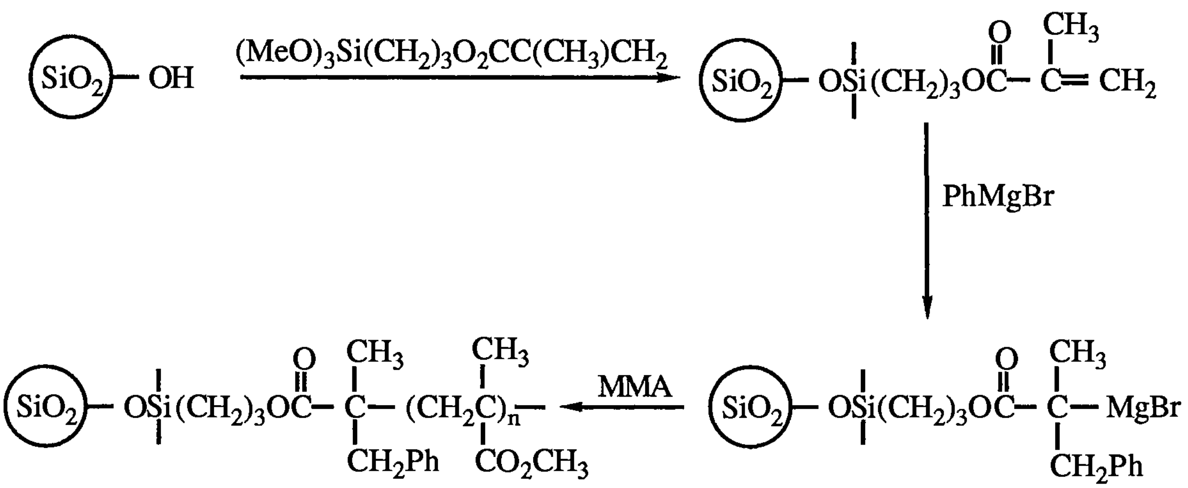


(10)



$$\text{SiO}_2-OH \xrightarrow[\text{heptane}]{Bu\text{-}(OSi(CH_3)_2)_n\text{-}OH} \text{SiO}_2-(\overset{CH_3}{\underset{CH_3}{Si}}O)_n-Bu \qquad (11)$$

Scheme 8. Growth of Poly(methyl methacrylate) on Colloidal Silica.



By reacting a monohydroxy terminated poly(dimethyl siloxane) with the silica surface (Equation 11), dispersions stable in methyl ethyl ketone and bromocyclohexane are formed.[62]

A very different method of attaching polymers to the surface was employed by Challa, et al. (Scheme 8).[66] A methacrylate group is first bound to the surface using 3-(methacryloxy)propyltrimethoxysilane. When this is reacted with phenylmagnesium bromide, an anionic initiating group is formed on the surface which can then be used to grow poly(methyl methacrylate) chains. This results in 85% isotactic poly(methyl methacrylate) with M_n of 5,500-14,000 and $M_w/M_n = 24$.

By using nonionic surfactants such as nonylphenyl terminated poly(ethylene oxide) or block copolymers of poly(ethylene oxide) and poly(propylene oxide), steric stabilization can be achieved without going through long covalent binding procedures.[67] When colloidal silica is dispersed into water containing one of these nonionic surfactants, the nonpolar end is insoluble and lies down on the silica surface while the polar end extends into solution around the particle giving the desired steric stabilization (Figure 5).

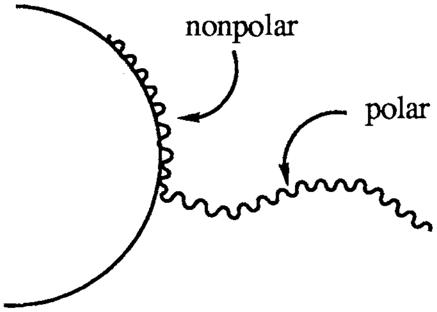


Figure 5. Adsorption of nonionic surfactant onto colloidal silica in water.

RESEARCH OBJECTIVES

It is apparent from the literature that silica gel is a useful support for heterogeneous catalysts, whose major drawback is a reaction rate which is limited by diffusion of the substrate to the catalytic sites. Colloidal supports are known to reduce these mass transfer limitations by giving high surface area. Colloidal silica can be prepared in spherical, monodisperse form and it can be surface modified and stabilized in a wide range of different sol-vents. However, with all of these facts, no one has ever tried using colloidal silica as a catalyst support.

Our goal in this research was to study the use of colloidal silica as a catalyst support. Initially, a sulfonic acid was bound to colloidal silica and compared as a catalyst to silica gel bound sulfonic acids as well as other well known sulfonic acids. These results will be discussed in Chapter II. It was readily apparent from this initial work that more needed to be known about how to work with colloidal silica and how to carry out the surface modifications more easily while at the same time forming more stable dispersions. Chapter III will deal with these factors.

REFERENCES

1. Prignano, A. L.; Trogler, W. C. *J. Am. Chem. Soc.* **1987**, *109*, 3586-3595.
2. Iler, R. K. *The Chemistry of Silica*; New York: Wiley, 1979, p. 677.
3. Iler, R. K. *The Chemistry of Silica*; Wiley: New York, 1979, p. 697.
4. Kirkland, J. J.; Glajch, J. L.; Farlee, R. D. *Anal. Chem.* **1989**, *61*, 2-11.
5. Plueddemann, E. P. In: *Silanes, Surfaces, and Interfaces*; Ed: Leyden, D. E.; Gordon and Breach: New York, 1986, pp. 1-24.
6. Gubitz, G. In: *Silanes, Surfaces, and Interfaces*; Ed: Leyden, D. E.; Gordon and Breach: New York, 1986, pp. 391-402.
7. Hennig, T.; Seshadri, T.; Haupt, H.-J. In: *Silanes, Surfaces, and Interfaces*; Ed: Leyden, D. E.; Gordon and Breach: New York, 1986, pp. 569-581.
8. Blitz, J. P.; Shreedhara Murthy, R. S.; Leyden, D. E. *J. Coll. Interface Sci.* **1988**, *126*, 387-392.
9. Arkles, B. *Chemtech* **1977**, *7*, 766-778.
10. de Haan, J. W.; van den Bogaert, H. M.; Ponjee, J. J.; van de Ven, L. J. M. *J. Coll. Interface Sci.* **1986**, *110*, 591-600.

11. Bayer, E.; Albert, K.; Reiners, J.; Nieder, M. *J. Chromatog.* **1983,** *264,* 197-213.

12. Irwin, A. D.; Holmgren, J. S.; Jonas, J. *Materials Letters* **1987,** *6*, 25-30.

13. Sindorf, D. W.; Maciel, G. E. *J. Phys. Chem.* **1982,** *86*, 5208-5219.

14. Caravajal, G. S.; Leyden, D. E.; Quinting, G. R.; Maciel, G. E. *Anal. Chem.* **1988,** *60*, 1776-1786.

15. Albert, K.; Evers, B.; Bayer, E. *J. Magn. Reson.* **1985,** *62*, 3979-3988.

16. Shinoda, S.; Saito, Y. *J. Coll. Interface Sci.* **1982,** *89*, 293-295.

17. Gorski, D.; Klemm, E.; Fink, P.; Horhold, H.-H. *J. Coll. Interface Sci.* **1988,** *126*, 445-449.

18. Kallury, K. M. R.; Krull, U. J.; Thompson, M. *Anal. Chem.* **1988,** *60*, 169-172.

19. Kohler, J.; Chase, D. B.; Farlee, R. D.; Vega, A. J.; Kirkland, J. J. *J. Chromatog.* **1986,** *352*, 275-305.

20. Floyd, T. R.; Sagliano, N.; Hartwick, R. A. *J. Chromatog.* **1988,** *452*, 43-50.

21. Iler, R. K. *The Chemistry of Silica*; Wiley: New York: 1979, p. 467.

22. Burwell, R. L. *Chemtech* **1974,** *4*, 370-377.

23. Tundo, P.; Venturello, P.; Angeletti, E. *J. Am. Chem. Soc.* **1982,** *104*, 6551-6555.

24. Tundo, P.; Venturello, P. *J. Am. Chem. Soc.* **1979,** *101*, 6606-6613.

25. (a) Leyden, D.; Collins, W. *Symposium on Silylated Surfaces*; Gordon and Breach: New York, 1980. (b) Leyden, D. E. *Silanes, Surfaces, and Interfaces*; Gordon and Breach: New York, 1986.

26. Satterfield, C. N. *Mass Transfer in Heterogeneous Catalysis*; MIT Press: Cambridge, MA, 1970.

27. Bernard, M. Ford, W. T.; Taylor, T. W. *Macromolecules* **1984,** *17*, 1812-1814.

28. Fitch, R. M. In: *Macromolecules*; Eds: Benoit, H.; Rempp, P.; Pergamon Press: Oxford, 1982, pp. 39-63.

29. Bradley, J. S.; Hill, E.; Leonowicz, M. E.; Witzke, H. *J. Mol. Catal.* **1987,** *41*, 59-74.

30. Turk, H.; Ford, W. T. *J. Org. Chem.* **1988**, *53*, 460-462.

31. Hassenein, M.; Ford, W. T. *Macromolecules* **1988**, *21*, 525-526.

32. Chandran, R. S.; Ford, W. T. *J. Chem. Soc., Chem. Commun.* **1988**, 104-105.

33. Chandran, R. S.; Srinivasan, S.; Ford, W. T. *Langmuir*, submitted.

34. Hopkins, A.; Williams, A. *J. Chem. Soc., Perkin Trans. II* **1983**, 891-896.

35. Sun, Z.; Yan, C.; Kitano, H. *Macromolecules* **1986**, *19*, 984-987.

36. Kitano, H.; Sun, Z.; Ise, N. *Macromolecules* **1983**, *16*, 1306-1310.

37. Alexander, G. B.; Iler, R. K.; Wolter, F. J. U. S. Patent 2,601,235 (Du Pont), 1952.

38. Bird, P. G.; U. S. Patent 2,224,325, 1941.

39. Bechtold, M. F.; Snyder, O. E. U. S. Patent 2,574, 902 (Du Pont), 1951.

40. Iler, R. K. *Colloid Chemistry of Silica and Silicates*; Cornell University Press: Ithaca, NY, 1955, pp. 36-42, 87-95.

41. Trail, H. S. U. S. Patent 2,572, 578 (Monsanto), 1951.

42. Balthis, J. H. U. S. Patents 2,614,994 and 2,614,995 (Monsanto), 1952.

43. Iler, R. K. *The Chemistry of Silica*; Wiley: New York, 1979, p. 336.

44. Wagner, E. U. S. Patent 2,951,044, 1960.

45. Radczewski, O. E.; Richter, H. *Kolloid-Z.* **1941**, *96*, 1-7.

46. Stober, W; Fink, A.; Bohn, E. *J. Coll. Interface Sci.* **1968**, *26*, 62-69.

47. Bogush, G. H.; Zukoski, C. F. In: *Proceedings of the 44th Annual Meeting of the Electron Microscopy Society of America*; Ed: Bailey, G. W.; San Francisco Press: San Francisco, 1986, pp. 846-847.

48. Bogush, G. H.; Zukoski, C. F. In: *Proceedings of the Third International Conference on Ultrastructure Processing of Ceramics, Glasses, and Composites*; in press.

49. Bogush, G. H.; Tracy, M. A.; Zukoski, C. F. *J. Non-Cryst. Solids*, **1988**, *104*, 95-106.

50. Tan, C. G.; Bowen, B. D.; Epstein, N. *J. Coll. Interface Sci* .**1987**, *118*, 290-293.

51. Assink, R. A.; Kay, B. D. *Mat. Res. Soc. Symp. Proc.* **1984**, *32*, 301-306.

52. Assink, R. A.; Kay, B. D. *J. Non.-Cryst. Solids* **1988**, *99*, 359-370.

53. Kay, B. D.; Assink, R. A. *Mat. Res. Soc. Symp. Proc.* **1986**, *73*, 157-164.

54. Klemperer, W. G.; Ramamurthi, S. D. In: *Better Ceramics Through Chemistry III*; Eds: Brinker, C. J.; Clark, D. E.; Ulrich, D. R.; Materials Research Society: Pittsburgh, 1988, pp. 1-13.

55. Brinker, C. J.; Keefer, K. D.; Schaefer, D. W.; Assink, R. A.; Kay, B. D.; Ashley, C. S. *J. Non.-Cryst. Solids* **1984**, *63*, 45-59.

56. Brinker, C. J.; Scherer, G. W. *J. Non.-Cryst. Solids* **1985**, *70*, 301-322.

57. LaMer, V. K.; Dinegar, R. *J. Am. Chem. Soc.* **1950**, *72*, 4847-4854.

58. Verwey, E. J. W.; Overbeek, J. T. G. *Theory of the Stability of Lyophobic Colloids*; Elsevier: New York, 1948.

59. van Helden, A. K.; Jansen, J. W.; Vrij, A. *J. Coll. Interface Sci.* **1981**, *81*, 354-368.

60. Buscall, R.; Ottewill, R. H. In: *Polymer Colloids*; Eds: Buscall, R.; Corner, T.; Stageman, J. F.; Elsevier: New York, 1985, pp. 141-217.

61. Iler, R. K. *The Chemistry of Silica*; Wiley: New York, 1979, p. 324

62. Edwards, J.; Lenon, S.; Toussaint, A. F.; Vincent, B. *ACS Symp. Ser.* **1984**, *240*, 281-295.

63. Ben Ouada, H.; Hommel, H.; Legrand, A. P.; Balard, H.; Papirer, E. *J. Coll. Interface Sci.* **1988**, *122*, 441-449.

64. Bridger, K.; Vincent, B. *Europ. Polym. J.* **1980**, *16*, 1017-1021.

65. Bridger, K.; Fairhurst, D.; Vincent, B. *J. Coll. Interface Sci.* **1979**, *68*, 190-195.

66. Schomaker, E.; Zwarteveen, A.-J.; Challa, G.; Capka, M. *Polym. Commun.* **1988**, *29*, 158-160.

67. van den Boomgaard, T.; Tadros, T. F.; Lyklema, J. *J. Coll. Interface Sci.* **1987**, *116*, 8-16.

CHAPTER II

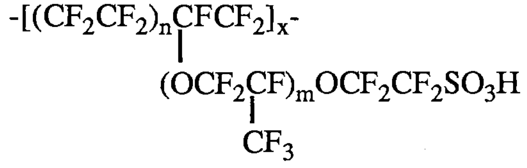
SILICA-BOUND SULFONIC ACID CATALYSTS

INTRODUCTION

Because bound sulfonic acids are readily available as ion exchange resins, there is also a large amount of information available on their use as catalysts. As with most supported reagents, they can be easily removed from reaction mixtures and they are often observed to give purer products and fewer side reactions than homogeneous acids. Another tremendous advantage of sulfonic acid resins over their homogeneous analogs is that the acid sites are effectively encapsulated. This minimizes the contact of the acid with the surface of the containing vessel, causing the corrosion problems to be minimal. Highly crosslinked resins are also useful under flow conditions.[1]

The ion exchange resins most commonly used as acid catalysts are 2-10% crosslinked sulfonated polystyrene beads or similarly modified species based on macroporous resins.[1] Many organic reactions which are acid catalyzed have been carried out using these ion exchange resins.[1-3]

Another widely used sulfonic acid which functions similarly is Nafion, a perfluorinated polymer with the general structure shown below.[4,5]



$$\begin{array}{l}-[(CF_2CF_2)_n\,CFCF_2]_x-\\ \qquad\qquad\qquad\;|\\ \qquad\qquad\quad (OCF_2CF)_mOCF_2CF_2SO_3H\\ \qquad\qquad\qquad\quad\;|\\ \qquad\qquad\qquad\; CF_3\end{array}$$

Nafion

Although Nafion is not crosslinked as polystyrene resins are, it possesses a highly ordered structure. Since it contains both hydrophilic sulfonate groups and a hydrophobic fluorocarbon backbone, the sulfonate groups tend to form clusters, causing the production of water-containing pockets in a hydrophobic matrix. In this manner, Nafion can be swollen by most solvents even though it is insoluble in them.[6]

Nafion is a much stronger acid than sulfonated polystyrenes due to the perfluorinated polymer backbone. It is also highly resistant to strong bases and oxidizing and reducing agents. This makes it convenient to use in a large number of reactions.[6,7] The major disadvantage to the use of Nafion is its price. If reactivity or selectivity are only marginally better than less expensive catalysts, the incentive to use Nafion is lost.[6]

Aliphatic[8] and aromatic[9-12] sulfonic acids bound to silica gel are another type of material which has been used as ion exchangers. Similar to macroporous polystyrene ion exchange beads, silica gel gives a rigid structure with most of the acid sites contained inside pores. But while these materials are well known as ion exchangers, their use as acid catalysts has not been previously reported. This chapter will report methods for binding both aliphatic and aromatic sulfonic acids to silica gel and their use as acid catalysts.

Many heterogeneous catalysts such as the ion exchange resins described above are known to exhibit lower activity than the corresponding homogeneous catalyst because of mass transfer limitations. One possible way of reducing the mass transfer limitations is to use colloidal silica as the support rather than commercial silica gels.[13] By using colloidal silica, most of the active sites will be on the outside of the particles rather than in pores, and the catalyst particles will be suspended in the reaction mixture. This will reduce the mass transfer limitations, since the substrate needs only to diffuse from the bulk liquid to the particle surface.

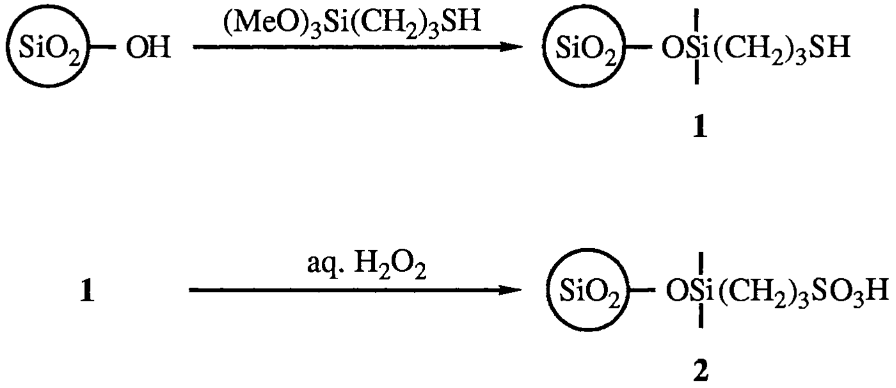
In order to test the above theory, we have prepared colloidal silica by the method of Stober[14] and have bound propanesulfonic acid to the surface. This material was tested as a catalyst in the hydrolysis of triphenylmethyl fluoride and diazinon [(diethyl(2-isopropyl-6-methyl-4-pyrimidinyl)phosphorothioate)]. Its catalytic activity in these reactions was compared with the silica gel-bound sulfonic acids, Amberlyst 15 and Dowex 50W-X4 (sulfonated polystyrenes), Nafion, and soluble acid catalysts.

RESULTS

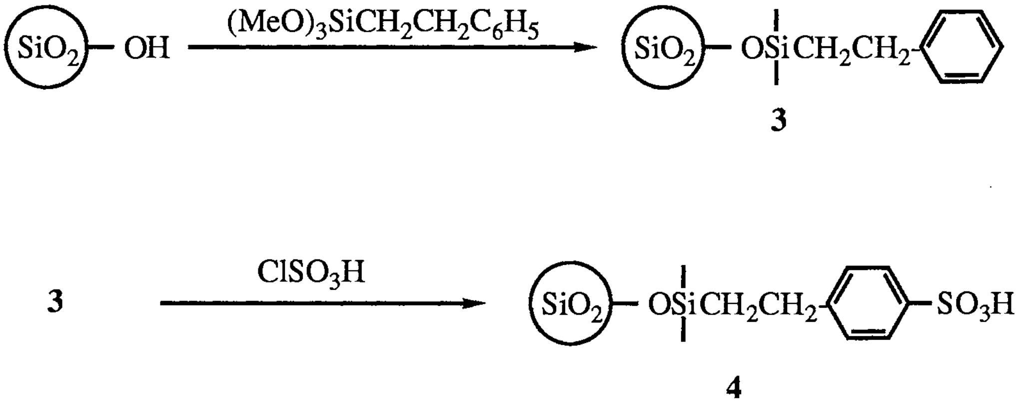
Silica Sulfonic Acids. Silica-bound propanesulfonic acid has been reported previously by Panster, Grethe, and Kleinschmit,[8] who bound bis[3-(trimethoxysilyl)propyl]-disulfide to the surface of silica gel and oxidized the disulfide to a sulfonic acid with aqueous H_2O_2. Prior to disclosure of their results, we used the method shown in Scheme 1. Silica gel (Davisil, surface area = 480 m^2/g, ave. pore diameter = 6 nm) was treated with 3-mercaptopropyltrimethoxysilane, and the mercaptan was oxidized to the sulfonic acid using aqueous H_2O_2. This method gave 0.34 mequiv/g of bound sulfonic acid (25% of total sulfur atoms). Oxidation with dimethylsulfoxide, HBr, and water by the method of Lowe[15] was also attempted and resulted in an ion exchange capacity of only 0.084 mequiv/g.

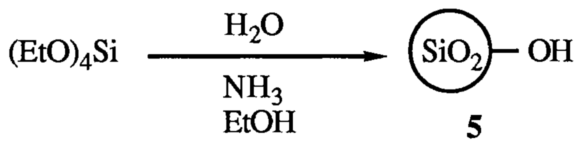
An aromatic sulfonic acid was bound to silica gel according to the method of Cox and coworkers (Scheme 2).[9] 2-Phenylethyltrimethoxysilane was bound to silica gel and then sulfonated with chlorosulfonic acid to give the para sulfonic acid.[16] This resulted in an ion exchange capacity of 0.56 mequiv/g. When the same synthesis was attempted with phenyltrimethoxysilane, an ion exchange capacity of only 0.04 mequiv/g was achieved. Frechet[17] has shown that aromatic silanes can be cleaved by acid, and it is likely that this occurred during the reaction with chlorosulfonic acid. This makes the ethylene spacer of **3** very important in this synthesis. The sulfonation reaction was also attempted with a 1:1 mixture of acetic acid and concentrated sulfuric acid according to Asmus, Low, and Novotny,[10] but this resulted in an ion exchange capacity of only 0.094 mequiv/g.

Scheme 1. Binding of Propanesulfonic Acid to Silica Gel.



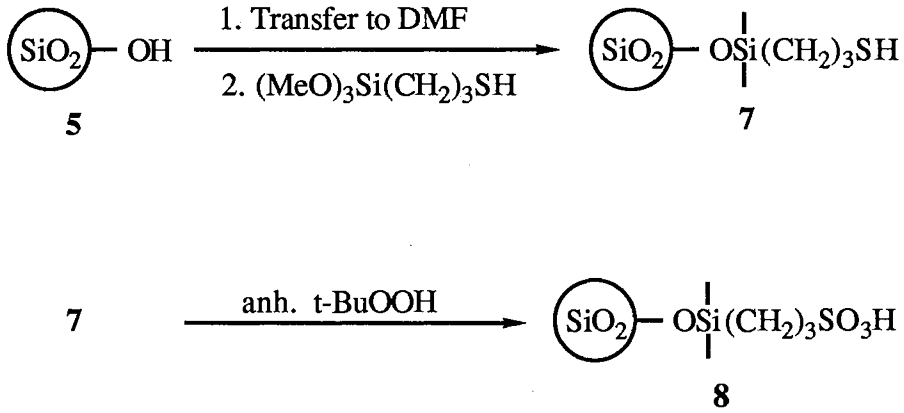
Scheme 2. Synthesis of 2-(4-Hydrogensulfonatophenyl)ethylsilica.





(1)

Scheme 3. Binding of Propanesulfonic Acid to Colloidal Silica.



The synthesis of colloidal silica-bound propanesulfonic acid is shown in Equation 1 and Scheme 3. An ethanolic dispersion of colloidal silica was prepared by hydrolyzing tetraethyl orthosilicate in water, ammonia, and ethanol. The sizes of silica particles formed in this reaction were measured on transmission electron micrographs (TEM). 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 samples were dried on the TEM grid, only single

Table I. Particle Diameters Determined by TEM.

Sample	d_n, nm	d_w, nm	d_w/d_n
5	51.8	53.9	1.04
6	50.2	52.7	1.05
7	52.7	55.4	1.05
8	53.1	55.0	1.04

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 (Table I):

$$d_n = \Sigma n_i d_i / \Sigma n_i \tag{2}$$

$$d_w = [\Sigma n_i d_i^6 / \Sigma n_i d_i^3]^{1/3} \tag{3}$$

Chapter III will give more details on the structure and properties of colloidal silica formed in this process.

When the colloidal silica was functionalized with mercaptopropyltrimethoxysilane in the original ethanol, water, and ammonia mixture, a gel was obtained which could not be redispersed. Therefore, the colloidal silica was transferred to DMF before functionalization.[18] 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 **6** show no signs of precipitation for 6 months, after which some precipitation begins to occur.

After the silica is transferred to DMF, mercaptopropyl groups can be attached by reaction with mercaptopropyltrimethoxysilane. The CP/MAS ^{13}C NMR spectrum of **7** in Figure 1 shows that the sample still contains ethoxy groups (61.1 and 17.7 ppm) from incomplete hydrolysis of tetraethyl 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*-butyl hydroperoxide in toluene gave dispersion **8** with 2.59 mg-atom S/g and an ion exchange capacity of 0.17 mequiv/g. Reaction with Ellman's reagent showed 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 **8** (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 (C(1) bonded to Si), 19 (C(2)), and 53 ppm (C(3))[19] 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 23.0 and 41.9 ppm are attributed to C(2) and C(3) of disulfide. Other peaks at 30.3 and 39.2 ppm are due to $(CH_2)_3S$ groups with sulfur in intermediate oxidation states[19,20] and have not been assigned.

The elemental analysis of **8** shows a much higher sulfur content than that of its precursor, **7**. Apparently, precipitation of the samples for elemental analysis by washing with water, acetone, and ether removes unbound silanes from **7**. However, after the mercaptans are partially oxidized to sulfonic acid **8**, the previously unbound silanes are either more tightly adsorbed or covalently bound to the silica and cannot be removed by washing. This

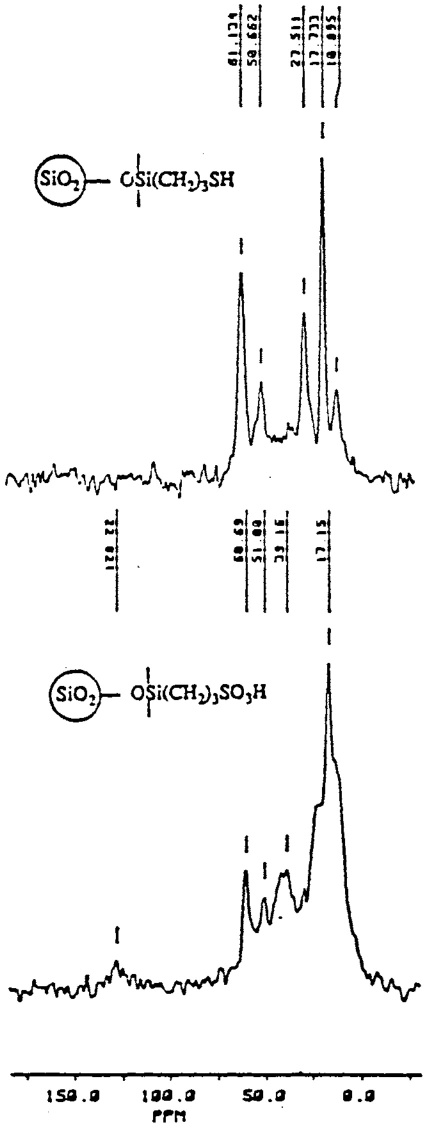


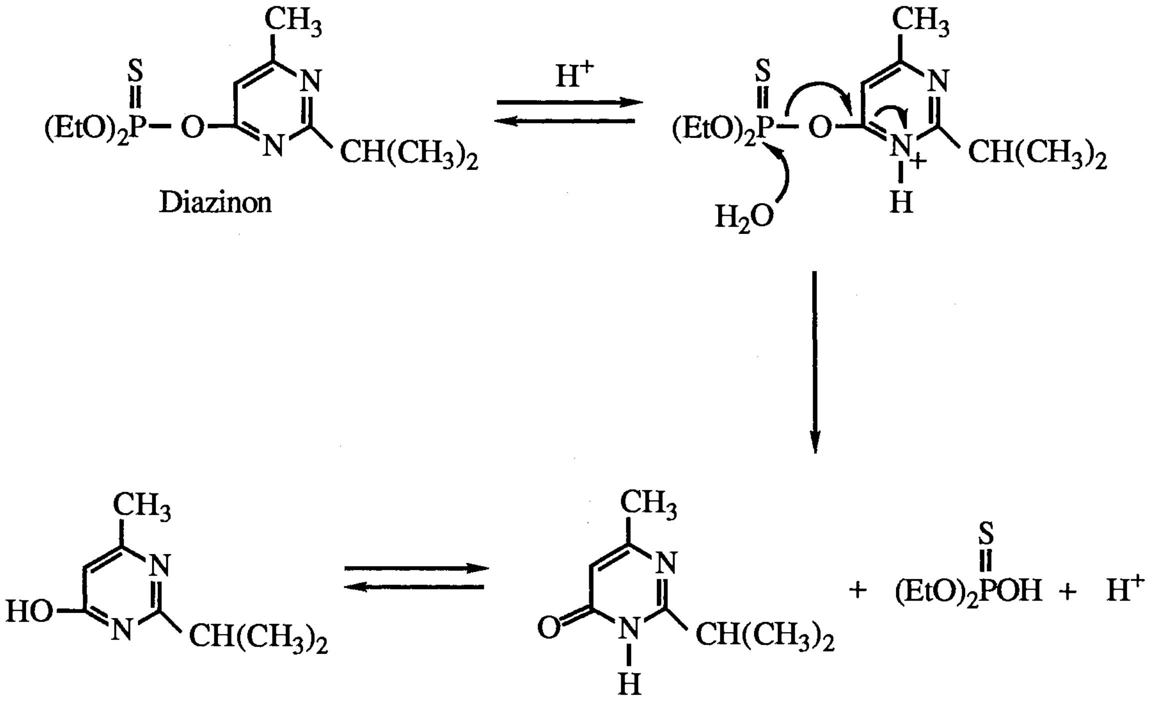
Figure 1. CP/MAS ^{13}C NMR Spectra of **7** and **8**.

hypothesis was confirmed by isolating the non-volatile residues from the filtrates of **7** and **8** after the washing procedure. The filtrates and wash solutions from 20 mL each of **7** and **8** contained 234 mg and 36 mg of residue, respectively. In a separate control experiment, reaction of monomeric mercaptopropyltrimethoxysilane with *tert*-butyl hydroperoxide under the same conditions used to oxidize the mercaptopropylsilica to sulfonic acid gave a siloxane polymer. Thus polymerization of silanes adsorbed to **7** during the oxidation procedure could give non-extractable polymer adsorbed to **8**. However, in this control reaction, acid produced during the reaction may catalyze the polymerization. With mercaptopropylsilica present, the basic silica surface could neutralize the acid and prevent it from acting as a catalyst.

Diazinon Hydrolysis. In order to test the catalytic activity of these silica-bound sulfonic acids, the hydrolysis reactions of diazinon and triphenylmethyl fluoride were chosen to serve as simulants for hydrolysis of the highly toxic phosphonyl fluoride nerve agents. Both give reaction rates which are easy to follow. The hydrolysis of triphenylmethyl fluoride is not strongly catalyzed by acid, but we were interested to see if HF produced during the reaction would react with the silica support, thereby, giving a catalyst which could both carry out the hydrolysis and at the same time remove the HF from the solution.

The hydrolysis of diazinon is strongly acid catalyzed[21] because the pyrimidine nitrogen can be protonated, allowing hydrolysis to occur by the mechanism in Scheme 4. The pK_a of 4-hydroxy-2,6-dimethylpyrimidine is 3.06.[22] Therefore, at initial pH 3, as our reactions were carried out, a substantial fraction of the diazinon was protonated, allowing the reaction to proceed by this mechanism.

Scheme 4. Mechanism for Acid Catalyzed Hydrolysis of Diazinon.



Gomaa, Suffet, and Faust[21] reported that the acid-catalyzed hydrolysis of diazinon follows second-order kinetics:

$$-d[\text{diazinon}]/dt = k[\text{diazinon}][\text{catal}] \tag{4}$$

where [diazinon] and [catal] are the concentrations of diazinon and acid catalyst in moles/L at time t. As shown in Scheme 4, diethylphosphorothioic acid ($pK_a = 1.83$)[23] is produced in this reaction, causing [catal] to increase as the reaction proceeds. This autocatalytic effect is shown in Figure 2. When the uncatalyzed reaction is buffered at pH 7, the reaction

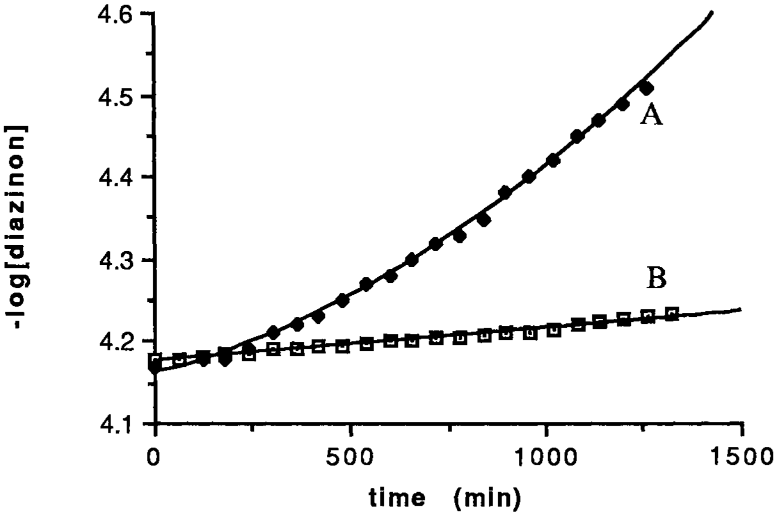


Figure 2. First order plot for disappearance of diazinon from 6.688 x 10^{-5} M unbuffered (A) and pH 7 buffered (B) aqueous solutions at 62.0 ± 0.2 °C.

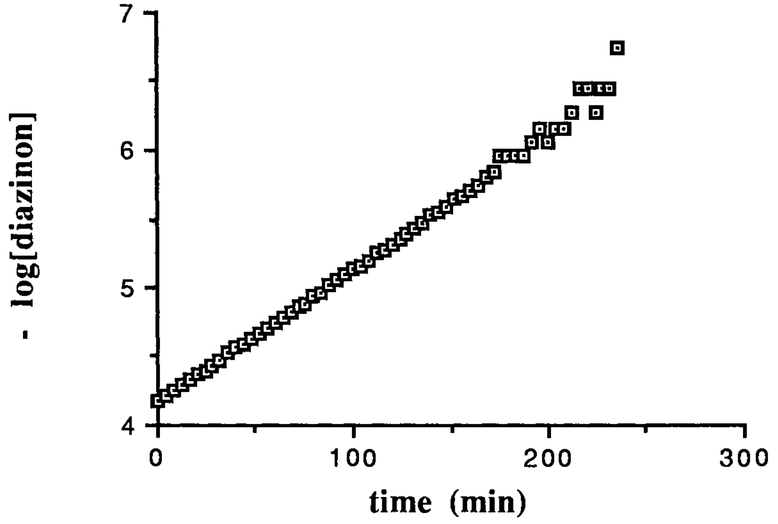


Figure 3. First-order plot for disappearance of diazinon from 6.688 x 10^{-5} M diazinon and 10^{-3} M HCl at 62.0 ± 0.2 °C.

gives a linear first-order plot. But when the reaction is unbuffered, the reaction rate increases with time.

If [catal] >> [diazinon], the rate equation becomes pseudo-first-order,

$$-d[\text{diazinon}]/dt = k_{obsd}[\text{diazinon}] \qquad (5)$$

and $k_{obsd} = k[\text{catal}]$. The reaction now follows first-order kinetics as shown in Figure 3 for 10^{-3} M HCl and 6.688 x 10^{-5} M diazinon.

The first-order rate constants, k_{obsd}, for diazinon hydrolysis are shown in Table II for a variety of acid catalysts. The colloidal silica-bound catalyst, **9**, appears to be quite effective in this reaction, giving a rate constant equal to that with HCl, and it is 2.8 times more active than soluble Nafion. It is also at least 2.8 times more active than the other heterogeneous catalysts with Dowex 50W-X4, a sulfonated polystyrene gel, being the next most active heterogeneous catalyst. Colloidal silica catalyst **9** is 21.5 and 7.5 times more active than silica gel catalysts **2** and **4**, respectively, when these silica gel based catalysts are added as a dry powder. But there is apparently a problem with wetting the surfaces of **2** and **4** with water. When the catalysts were first wetted with 0.1 mL of ethanol for 15 min, they were only 3.4 and 5.3 times less active than the colloidal catalyst **9**. Prewetting the surface makes a drastic difference in the activity of **2**. This could be due to the surface of **2** being hydrophobic since only 34% of the mercaptopropyl groups were oxidized to the sulfonic acid. In **4**, 63% of the aromatic rings are sulfonated which should make the surface more hydrophilic, and prewetting the surface does not have as large an effect.

When mercaptopropylsilica, **7**, was added to the reaction mixture, a first-order plot with two different slopes was found (Figure 4). Over the first 7 h reaction time,

Table II. Hydrolysis of 6.688 x10^{-5} M Diazinon Catalyzed by 10^{-3} M Acid at 62.0 ± 0.2 °C.

catalyst	mg catalyst[a]	k_{obsd}(x10^4)[b], s^{-1}	% Conversion Observed[c]
HCl	--	230	99
9	7.4	209	99
Dowex 50W-X4[d]	1.5	76.3[e]	94
Nafion solution	3.3	75.5	99
4	5.3	28.0	55
		39.4[f]	75
Amberlyst 15[g]	0.64	27.8[e]	85
Nafion powder	3.3	12.3	55
		13.3[e,f]	55
2	11.4	9.72	51
		61.9[f]	80
uncatalyzed[h]	--	0.937	15

[a] Amount of catalyst in 3.0 mL reaction volume. [b] All measured rate constants except for Amberlyst 15 are averages from two runs which differed by ≤6%. [c] % conversion of diazinon on which the calculation of k_{obsd} is based. [d] Sulfonated polystyrene gel. [e] Adsorption of diazinon and reaction products occurred. k_{obsd} was determined from

Table II (Continued)

concentrations remaining in solution after adsorption was complete. [f]Catalyst was placed in UV cell and wetted with 0.1 mL of ethanol for 15 min before adding the remaining 2.9 mL of the reaction mixture. [g]Macroporous sulfonated polystyrene. [h]Buffered at pH 7 with 0.01 M phosphate buffer.

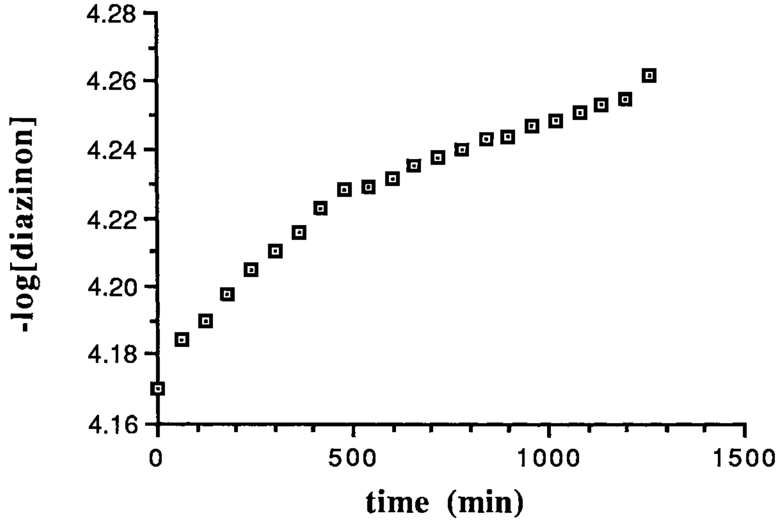


Figure 4. First-order plot for diazinon hydrolysis in the presence of mercaptopropylsilica (7).

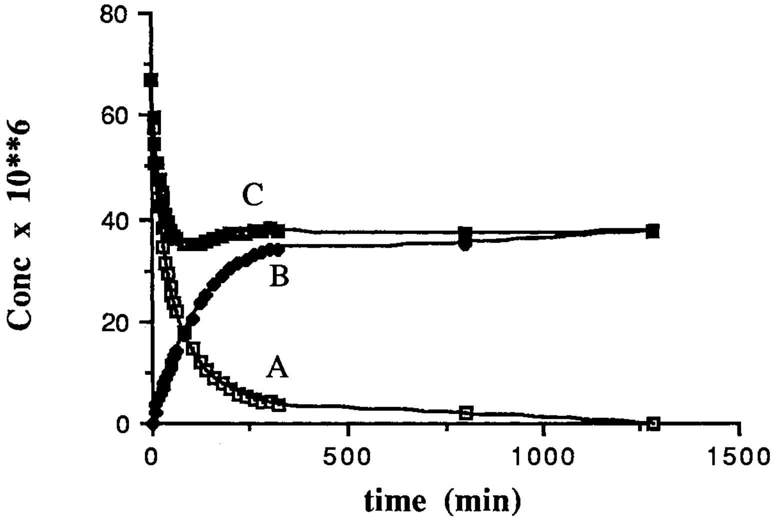


Figure 5. Concentrations of diazinon (A), product (B), and diazinon + product (C) in solution during Dowex 50W-X4 catalyzed hydrolysis.

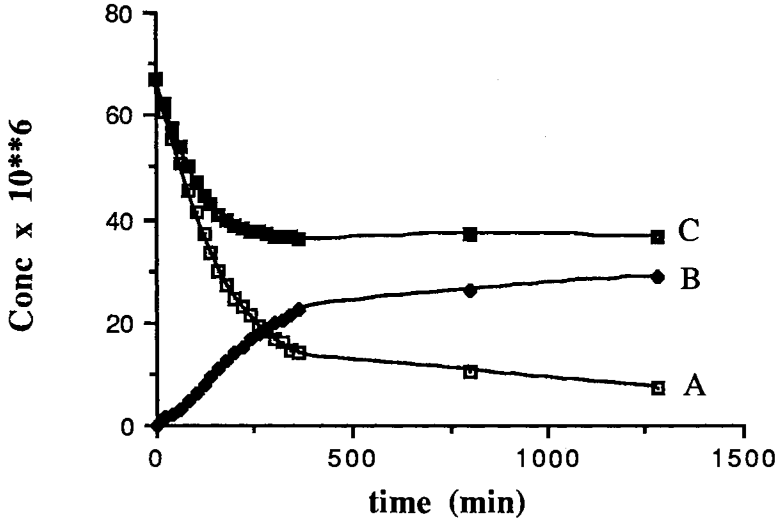


Figure 6. Concentrations of diazinon (A), product (B), and diazinon + product (C) in solution during Amberlyst 15 catalyzed hydrolysis.

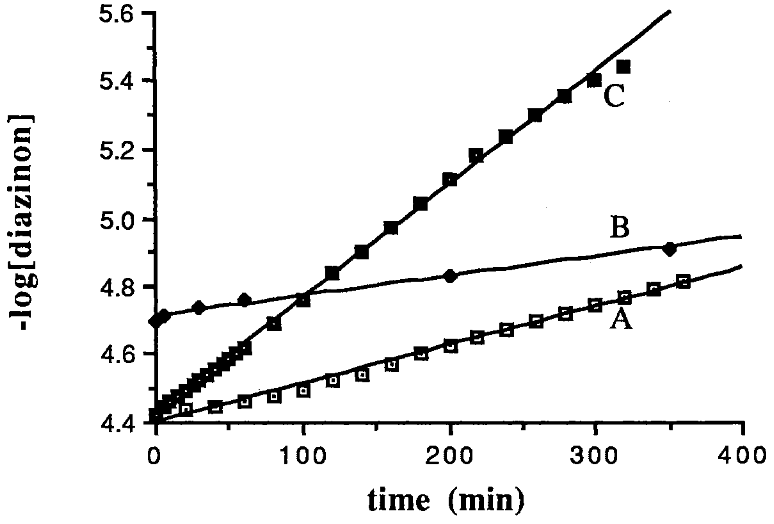


Figure 7. First-order plots for hydrolysis of diazinon remaining in solution after adsorption by Amberlyst 15 (A), Nafion powder (B) and Dowex 50W-X4 (C) is complete. time = 0 in this plot corresponds to 1.0 h actual reaction time, at which time adsorption reached equilibrium.

k_{obsd} is 2.73 x 10^{-4} s^{-1}. However, after 7.3% of the diazinon has reacted, k_{obsd} becomes 0.94 x 10^{-4} s^{-1} which is very close to that of the uncatalyzed reaction. Apparently, there is a small amount of impurity, possibly ammonia from the colloidal silica synthesis, which speeds up hydrolysis of diazinon. After this impurity is used up, the mercaptopropylsilica has no effect on the rate.

Unfunctionalized silica, **5**, can catalyze the hydrolysis of diazinon when buffered at pH 7. With 3.00 mL of 6.688 x 10^{-5} M diazinon and 7.4 mg of **5**, k_{obsd} was 5.35 x 10^{-4}

s^{-1}. This is most likely due to surface silanols being deprotonated and acting as a nucleophilic catalyst. At pH 7, silica gel contains approximately 0.41 SiO^-/nm^2,[24] which would give 1.1×10^{-4} M SiO^- in the reaction mixture.

Most of these reactions showed simple pseudo-first-order kinetics when the acid catalyst concentration was 1500 times the diazinon concentration. Exceptions were the sulfonated polystyrenes and Nafion powder when it was prewetted with ethanol. Using 1.5 mg Dowex 50W-X4, 0.64 mg Amberlyst 15, and 3.3 mg Nafion powder, these catalysts adsorbed 8.76×10^{-8} moles (44%), 9.06×10^{-8} moles (45%), and 1.42×10^{-7} moles (71%) of diazinon and reaction products during the first 1.0 h reaction time from 3.0 mL of a solution initially containing 6.688×10^{-5} M diazinon. The concentrations of diazinon, product, and (diazinon + product) are shown in Figures 5 and 6 for Dowex 50W-X4 and Amberlyst 15, respectively. If a first-order plot is made for the disappearance of diazinon remaining in solution after adsorption has reached equilibrium and the concentration of (diazinon + product) becomes constant, a linear plot is found (Figure 7). Since in any practical use, the amount of catalyst will be much less than the amount of substrate, the catalyst will become saturated, and the hydrolysis rate of diazinon remaining in solution under adsorption equilibrium conditions will be the important factor. Therefore, this is the value reported in Table II for Dowex 50W-X4, Amberlyst 15, and prewetted Nafion powder.

Nafion powder is surprisingly much less active than the other heterogeneous catalysts in diazinon hydrolysis. It was felt that the fluorocarbon network might not be wetted well when added to water as a dry powder. However, when the surface was prewetted with ethanol, the rate constant changed very little even though a large amount of adsorption occurred as described above.

Triphenylmethyl Fluoride Hydrolysis. According to Coverdale and Kohnstam,[25] the rate equation for hydrolysis of triphenylmethyl fluoride is given by:

$$-d[Ph_3CF]/dt = [Ph_3CF](k_o + k_{HF}[HF] + k_{H^+}[H^+]) \qquad (6)$$

where k_o is the uncatalyzed rate constant, $[H^+]$ is the concentration of added catalyst and k_{H^+} is the rate constant due to added catalyst. $k_{HF}[HF]$ is an autocatalytic term due to HF produced during the hydrolysis (Equation 8). In order to simplify the calculations, we chose to determine the initial rate constant, k_{obsd}, from the first 20% of the reaction where $k_{HF}[HF]$ is negligible and the reaction is pseudo-first-order:

$$-d[Ph_3CF]/dt = [Ph_3CF]k_{obsd} \qquad (7)$$

where $k_{obsd} = k_o + k_{H^+}[H^+]$.

$$(C_6H_5)_3CF \; + \; H_2O \xrightarrow{H^+} (C_6H_5)_3COH \; + \; HF \qquad (8)$$

Rates of trityl fluoride hydrolysis were followed by the increase in fluoride ion concentration measured with an ion selective electrode. The results are given in Table III. The reaction is not strongly acid catalyzed, and only slight increases in rate are observed during the reaction. Only 10 mole% *p*-toluenesulfonic acid increased the observed rate constant by a factor of more than 1.4. The relative activities of the catalysts contrast in several ways with the results observed during diazinon hydrolysis. The colloidal catalyst **9**, is less active than soluble Nafion and slightly less active than *p*-toluenesulfonic acid, whereas in diazinon hydrolysis, **9** was as active or more active than the homogeneous catalysts and much more active than any other heterogeneous catalyst. In triphenylmethyl fluoride

Table III. Initial Rate Constants, k_{obsd}, for Hydrolysis of Triphenylmethyl Fluoride with Various Catalysts at 45.0 ± 0.5 °C.[a]

Catalyst	mg catalyst[b]	mole%	$k_{obsd} \times 10^{-2}$, h^{-1}
Nafion solution	220.0	2.0	12.1
$CH_3C_6H_4SO_3H$	38.0[c]	2.0	10.5
9	1,176	2.0	10.2
Nafion powder	220.0	2.0	10.1
$CH_3C_6H_4SO_3H$	190.2[c]	10.0	16.2
Amberlyst 15	212.8	10.0	9.6
4	178.6	10.0	8.9
2	294.1	10.0	8.9
5	284.6	--	8.6
uncatalyzed	--	--	8.6

[a] Reactions were run with 0.1 M triphenylmethyl fluoride, 0.01 M or 0.002 M acid catalyst in 70:30 (v/v) tetrahydrofuran/water. [b] In 100 mL of reaction mixture. [c] Added as p-toluenesulfonic acid monohydrate.

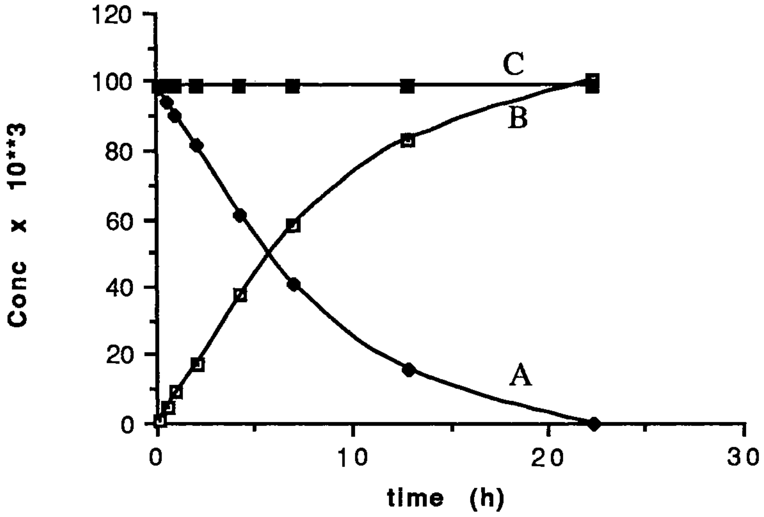


Figure 8. Concentrations of A: triphenylmethyl fluoride, B: HF, and C: triphenylmethyl fluoride + HF during hydrolysis in the presence of **5**.

hydrolysis, Nafion powder gives about the same activity as **9**. Even 10 mole% of the silica gel catalysts, **2** and **4**, show almost no catalysis. Amberlyst 15 is only slightly more active than **2** or **4**.

HF produced in the reaction did not react with the silica supports in any of the catalysts reported here. Even with unmodified colloidal silica, [HF] at the end of the reaction is equal to the initial triphenylmethyl fluoride concentration (Figure 8).

DISCUSSION

The syntheses of **2** and **4** are two good methods of binding sulfonic acids to silica gel. The major drawback to silica-bound propanesulfonic acid **2** is that only 34% of the sulfur is in the sulfonic acid form. The sulfur present in other oxidation states could become a problem in some applications. Silica-bound aromatic sulfonic acids such as **4** require an alkyl spacer chain between the aromatic ring and silane to avoid acid catalyzed aromatic desilanation.[17]

The colloidal catalyst **9**, has a high ion exchange capacity per surface area when compared with **2** and **4**. However, the synthesis of **9** is difficult because it is carried out on a colloidal dispersion. Care must be taken not to add salts or solvents which can precipitate the silica, because often when the silica precipitates during a reaction it cannot be redispersed. This causes the synthesis to be longer than desired since two solvent changes must be made without ever drying out the silica. This stability factor also necessitates the use of anhydrous *tert*-butyl hydroperoxide, which gives a lower conversion of mercaptan to sulfonic acid than the aqueous H_2O_2 used with silica gel. Dispersions of **9** in water precipitate after 1-2 weeks. This presents a problem in storing the catalyst for long periods of time before use. The problems listed above are all related to the stability of the dispersion and can be corrected by using other stabilization methods. This will be addressed in Chapter III.

The data in Table II show that colloidal silica-bound catalysts are capable of giving activity as high as that of HCl, and higher than that of other well known heterogeneous catalysts. Apparently, diffusion of diazinon to the surface of dispersed colloidal silica does not limit the reaction rate. But with macroscopic silica gel, most of the active sites are inside pores, and mass transfer limitations cause lower rates of reaction. This effect has been observed previously by Fitch, who found that polystyrene latexes containing only surface sulfonic acid groups were 40-60 times more active than macroscopic ion exchange beads in the inversion of sucrose.[26] For sulfonic acid resins, the pK_a is <1.[27] So all of the catalysts in Table II are completely dissociated under the conditions used and the acid strength should not be a factor in the activity differences. The rate differences are mostly due to the rate of substrate diffusion into the resins where the protons are located.

The difference in activity of the catalysts between diazinon hydrolysis and triphenylmethyl fluoride hydrolysis reflects minor environmental effects on intrinsic reactivity.

Colloidal silica appears to be a good candidate for a catalyst support. It gives activity similar to soluble catalysts and should still provide some of the benefits of other heterogeneous catalysts such as ease of separation. It can be removed from a reaction mixture by ultrafiltration or by precipitating with a salt or organic solvent and filtering. Another possibility is to use larger 400-500 nm particles which can be centrifuged out of a reaction mixture in a matter of minutes. These results open the door for the use of colloidal silica as a support for a wide range of catalysts.

EXPERIMENTAL SECTION

Materials. Davisil silica gel, grade 634 (100-200 mesh, surface area = 480 m^2/g; pore volume = 0.75 cc/g; ave. pore diameter = 6 nm) was obtained from Aldrich. 2-Phenylethyltrimethoxysilane and 3-mercaptopropyltrimethoxysilane were obtained from Petrarch and used as received.

Solutions of ammonia in ethanol (3-5 M) were prepared by passing ammonia gas through a column of NaOH pellets into absolute ethanol (U. S. Industrial Chemicals Co.) at 0 °C for 20-30 min. 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 (1.0 μmhos). Tetraethyl orthosilicate (Petrarch or Fisher) was distilled immediately before use. When used as solvents for trityl fluoride, acetonitrile and tetrahydrofuran (THF) were dried by refluxing over calcium hydride or sodium metal, respectively, and then distilling. The acetone used as a solvent for diazinon was dried by standing over Drierite (calcium sulfate) for 4 days and distilling. Fluoride standard solutions were prepared by diluting a 1.00 M fluoride solution obtained from Orion.

Chlorosulfonic acid (Aldrich), hydrogen peroxide (Aldrich), anhydrous 3 M *tert*-butyl hydroperoxide in toluene (Fluka), 5,5'-dithiobis(2-nitrobenzoic acid) (Aldrich), anhydrous potassium fluoride (Aldrich), triphenylmethyl chloride (Aldrich), and diazinon (Crescent Chemical Co., purity = 98%) were used as received.

Nafion (1100 equivalent weight) was obtained as a powder (passes through 100 mesh sieve) or as a 5% solution in a mixture of water and lower alcohols from C. G. Processing, Inc. (Box 133, Rockland, DE 19732). Dowex 50W-X4 was obtained as wet beads (50-100 mesh) from Baker. Ion exchange capacities of commercial resins were determined by washing the resin with 0.1 M HCl, and with water until the washings were neutral, suspending the beads in 2.0 M NaCl for 30 min, filtering, and titrating the filtrate to the phenolphthalein endpoint with 0.02 M NaOH. Ion exchange capacities of 1.99 and 4.70 mequiv/g were found for wet Dowex 50W-X4 and dry Amberlyst 15 (Aldrich, 20-50 mesh), respectively.

All other solvents were reagent grade and were used as received.

Analytical Methods. CP/MAS ^{13}C NMR spectra were obtained by Dr. Frank McEnroe at Conoco, Inc., with an IBM WP-100 spectrometer at 25 MHz. The conditions used are given in Chapter III. Fluoride ion determinations were done on an Altex Zeromatic IV pH meter using an Orion combination fluoride electrode, model no. 960900. UV spectrophotometry was done on a Varian DMS-200 UV/vis spectrophotometer fitted with a magnetic stirrer and thermostatted sample cell holders. A Hewlett-Packard 5840A gas chromatograph with thermoconductivity detectors was used. Elemental analyses were done at Galbraith Laboratories (Knoxville, TN). Transmission electron microscopy was done on a JEOL JEM-100 CX II microscope at 75 kV. Formvar and carbon grids were used for samples in ethanol and DMF, respectively. Particle sizes were determined by measurement of at least 35 particles on photographic negatives.

Colloidal samples were prepared for analysis by adding the dispersion to water and acidifying to pH 2 with 1.0 M HCl to precipitate the colloids. The precipitated particles were recovered by vacuum filtration, washed thoroughly with water, acetone, and ethyl ether, and dried at 60 °C under vacuum for 15 h.

Ion exchange capacities of the silica-bound sulfonic acids were determined by adding 0.5 g of the silica gel sulfonic acid or 20 mL of the dispersion of colloidal silica-bound sulfonic acid to 75 mL of 2.0 M NaCl (this caused the colloidal samples to precipitate). This suspension was titrated potentiometrically with 0.0185 M NaOH, or the silica was removed by gravity filtration, washed with 75 mL of 2.0 M NaCl, and the combined filtrate was titrated to the phenolphthalein endpoint with 0.0185 M NaOH. Both methods gave the same ion exchange capacity.

Thiol contents were determined by reaction with Ellman's reagent.[28,29] Standard solutions, 100 mL each, were prepared containing 1.0×10^{-4} M Ellman's reagent [5,5'-dithiobis(2-nitrobenzoic acid)], 1.5×10^{-5} M to 5.3×10^{-5} M mercaptopropyltrimethoxysilane, and 0.01 M EDTA 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 ($\varepsilon = 11{,}400\ M^{-1}\ cm^{-1}$). Using precipitated samples prepared for analysis as described above, thiol contents 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. The absorbance of these solutions was measured after 16 h, when the absorbance at 412 nm became constant.

Silica Gel Pretreatment. Silica gel (45.00 g) was suspended in 150 mL of 2 M HCl and refluxed for 4 h. The silica gel was removed by vacuum filtration and washed repeatedly with water and acetone until the filtrate contained no acid. It was allowed to air dry before further use.

Mercaptopropylsilica Gel (1). Pretreated silica gel (26.25 g) and 150 mL of toluene were mixed in a 250 mL flask fitted with a Dean-Stark trap. Upon refluxing for 5 h under nitrogen, 10.0 mL of water was collected, leaving 16.25 g of dry silica gel. The Dean-Stark trap was then removed and 16.3 g (83.04 mmol) of 3-mercaptopropyltrimethoxysilane was added and the mixture was refluxed for 26 h. The functionalized silica was separated by vacuum filtration and washed repeatedly with toluene and acetone. It was then dried under vacuum at 60 °C for 15 h to give 20.0 g of mercaptopropylsilica, **1**.

Anal Found: C, 7.39% (6.15 mg-atom/g); S, 4.72% (1.47 mg-atom/g); H, 1.71% (16.93 mg-atom/g) Calculating from the carbon and sulfur analyses, the hydrogen is due to mercaptopropyl (10.29 mg-atom H/g), ethoxy and methoxy (4.35 mg-atom H/g), and surface OH (2.29 mg-atom H/g).

Silica Gel-Bound Propanesulfonic Acid (2). Mercaptopropylsilica gel, **1** (7.91 g), was stirred under nitrogen in 40 mL of water and 96 mL of 30% hydrogen peroxide (959 mmol, 6.95 M) for 7 h at room temp. The modified silica was removed by vacuum filtration, washed once with dilute hydrochloric acid, and washed repeatedly with water, acetone, and toluene with acetone as the final washing solvent. It was dried under vacuum for 16 h at 60 °C to give 5.83 g of **2**.

Anal. Found: C, 4.99% (4.15 mg-atom/g); S, 3.25% (1.01 mg-atom/g); H, 1.36% (13.47 mg-atom/g) due to $(CH_2)_3S$ (7.07 mg-atom H/g), ethoxy and methoxy (2.80 mg-atom H/g), and surface OH (3.60 mg-atom H/g). Ion exchange capacity = 0.34 mequiv/g.

2-Phenylethylsilica Gel (3). Pretreated silica gel (26.0 g) and 150 mL of toluene were mixed in a 250 mL flask fitted with a Dean-Stark trap and a condenser. Upon refluxing under nitrogen for 5 h, 10.9 mL of water was collected, leaving 15.1 g of dry silica gel. The Dean-Stark trap was removed, 13.0 g (57.0 mmol) of 2-phenylethyltrimethoxysilane was added, and the mixture was refluxed for 24 h. The functionalized silica gel was separated by vacuum filtration and washed repeatedly with toluene and acetone. It was dried under vacuum for 15 h at 60 °C to give 17.1 g of **3**.

Anal. Found: C, 7.74% (6.44 mg-atom/g); H, 1.02% (10.10 mg-atom/g) due to 2-phenylethyl (7.24 mg-atom H/g) and surface OH (2.86 mg-atom H/g).

2-(4-Hydrogensulfonatophenyl)ethylsilica (4). 2-Phenylethylsilica gel, **3** (16.11 g) was suspended in 112 mL of chloroform under a nitrogen atmosphere. Then 38 mL (557 mmol) of chlorosulfonic acid was added dropwise over a period of 45 min. The mixture was refluxed for 3.5 h giving a dark brown suspension. The modified silica gel was recovered by vacuum filtration and washed repeatedly with chloroform, acetone, and water until the filtrate was colorless. It was dried under vacuum for 16 h at 60 °C to give 15.8 g of light brown **4**.

Anal. Found: C, 6.45% (5.37 mg-atom/g); S, 1.65% (0.52 mg-atom/g); H, 1.06% (10.5 mg-atom/g) due to phenylethyl (2.61 mg-atom H/g), ethylbenzenesulfonic acid (4.68 mg-atom H/g), and surface OH (3.21 mg-atom H/g). Ion exchange capacity = 0.56 mequiv/g.

Colloidal Silica (5). All glassware was cleaned with 2% HF and rinsed with purified water. Water (7.2 mL, 400 mmol, 0.999 M), 309 mL of 2.46 M ammonia 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 rapidly during sonication. After 25 min, the reaction mixture began to turn cloudy as silica particles were 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.

Anal. Found: C, 2.47% (2.06 mg-atom/g); H, 1.49% (14.8 mg-atom/g) due to ethoxy (5.15 mg-atom H/g) and surface OH (9.65 mg-atom H/g).

DMF Dispersion of Colloidal Silica (6). The ethanol and water were slowly distilled from 400 mL of **5** while about 500 mL of dimethylformamide (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 Colloidal Silica (7). Mercaptopropyltrimethoxysilane (5.0 mL, 26.5 mmol) and 400 mL of **6** (containing 4.9 g silica as SiO_2) were heated to 100 °C for 24 h under nitrogen to give **7**.

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) due to mercaptopropyl (2.45 mg-atom H/g), ethoxy and methoxy (8.5 mg-atom H/g), and surface OH (10.8 mg-atom H/g). ^{13}C NMR: 17.7 and 61.1 ppm (ethoxy); 50.7 ppm (methoxy); 10.9 (C(1)) and 27.5 ppm (C(2) and C(3) of mercaptopropyl). Mercaptan content determined by Ellman's reagent = 0.22 mequiv/g.

Colloidal Silica-Bound Propanesulfonic Acid (8). To 300 mL of **7** 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 h and at 60 °C for 24 h to give a pale yellow dispersion of **8** 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) due to $(CH_2)_3S$ (18.1 mg-atom H/g), ethoxy and methoxy (10.1 mg-atom H/g), and surface OH (7.4 mg-atom H/g). ^{13}C NMR: 17.1 and 60.6 ppm (ethoxy); 51.0 ppm (methoxy and C(3) of sulfonic acid); 23.0 (C(2)) and 42.0 ppm (C(3) of disulfide); 32 and 39 ppm (unassigned). Ion exchange capacity = 3.82 x 10^{-3} mequiv/mL = 0.17 mequiv/g. Mercaptan content determined by Ellman's reagent = 0.076 mequiv/g.

Colloidal Silica-Bound Propanesulfonic Acid in Water (9). All but 50 mL of solvent was removed from 200 mL of **8** on a rotary evaporator. Then 50 mL of water was added to precipitate the solids. The functionalized silica was separated by vacuum filtration and washed with 300 mL of 2 M HCl, with water until the filtrate was neutral, and with acetone, ethyl ether, acetone, and water. The silica was redispersed in 75 mL of water by sonicating for 6 h to give **9**.

Ion exchange capacity = 7.63 x 10^{-3} mequiv/mL.

Preparation of Triphenylmethyl Fluoride. Potassium fluoride (24.74 g, 426 mmol) was placed in a flame dried 250 mL three necked flask fitted with a Dean-Stark trap and condenser. Toluene (100 mL) was added and refluxed for 4 h under nitrogen to remove 0.25 mL of water, and 16.36 g (58.7 mmol) triphenylmethyl chloride in 100 mL of dry acetonitrile was added and refluxed. After 5.0 h, the progress of the reaction was checked by GC (20% SE-30; Inj temp: 250 °C; TCD temp: 300 °C; Column temp: 150 °C for 3.0 min, then rising to 250 °C at 25 °C/min). It showed 96.5% triphenylmethyl fluoride (RT = 8.37 min) and 3.5% triphenylcarbinol (RT = 9.42 min). No unreacted triphenylmethyl chloride remained. The triphenylmethyl fluoride was extracted from the acetonitrile with 12 x 75 mL portions of hexane. The hexane was removed under vacuum giving 12.61 g (82%) of a pale yellow solid which was >99% triphenylmethyl fluoride by GC analysis. mp = 103-104.5 °C. IR: 3000, 1450, 1376, 1038, 917, 746 cm^{-1}.

Calc.: C, 86.98%; H, 5.77%; F, 7.24%. Anal. Found: C, 86.77%; H, 5.81%; F 7.11%.

Triphenylmethyl Fluoride Hydrolysis. Hydrolysis reactions were run in a teflon bottle using a wrist-action shaker for mixing. Triphenylmethyl fluoride (2.62 g, 0.01 moles, 0.1 M) and either 1.0 or 0.20 mmol of acid catalyst were placed in enough THF to give 70 mL of solution. This solution was placed in a 45.0 ^{o}C water bath for 30 min and then 30 mL of water (45 ^{o}C) was added to start the reaction. At timed intervals, two 1.00 mL samples were taken and worked up in the following way.

Sample A: The sample (1.00 mL) was added to 20.0 mL of pH 5.0 buffer (0.10 M acetic acid/0.17 M sodium acetate). The fluoride concentration was determined using a fluoride ion selective electrode, from a standard plot of mV vs log[F$^-$]. Sample A gave a measurement of [HF] in the reaction mixture:[HF] = 21[F$^-$]$_{A}$, where [F$^-$]$_A$ = measured [F$^-$] for sample A, and the dilution factor = 21.

Sample B: The sample (1.00 mL) was added to 2.00 mL of 2.0 M NaCl. In the case of the colloidal catalyst, this caused precipitation, and the silica was removed by filtration. Then 1.00 mL of 0.05 M NaOH and 60 mL of 70% THF/30% water (v/v) were added, and the mixture was boiled for 2 h in a teflon beaker covered with a watchglass to hydrolyze unreacted triphenylmethyl fluoride. After 2 h, the watchglass was removed and the solvent was distilled off. Then 20.0 mL of pH 5.0 buffer was added, and [F$^-$] was determined by fluoride ion selective electrode. Since all unreacted triphenylmethyl fluoride was hydrolyzed before analysis, sample B gave a measurement of the total fluorine concentration where: $[F]_{total} = 20[F^-]_B = [HF] + [(C_6H_5)_3CF]$. Since [HF] was determined from sample A, $[(C_6H_5)_3CF]$ can be calculated.

The initial rate constant was determined for disappearance of triphenylmethyl fluoride during the first 20% of the reaction where pseudo-first-order kinetics were followed, by plotting $-\log[(C_6H_5)_3CF]$ vs. time, and determining the slope by linear least squares analysis.

Diazinon Hydrolysis. A stock solution of 2.508 x 10^{-2} M diazinon in acetone was prepared. From this stock solution, 1.00 mL was placed in a 250 mL volumetric flask, and the acetone was removed by passing a stream of nitrogen over it. The volumetric flask was filled with water and the diazinon was dissolved by placing it on the wrist-action shaker for 1 h giving a 1.003 x 10^{-4} M solution.

A 1.00 mL portion of this solution was placed in a UV cell, equilibrated to 62.00 ± 0.2 °C, and 1.00 mL of a 62 °C solution of 3.00 x 10^{-3} M acid in water (for the soluble catalyst), or 1.00 mL of water and 3.00 x 10^{-6} equiv of insoluble catalyst were added to start the reaction. This gives 6.69 x 10^{-5} M diazinon and 1.00 x 10^{-3} M acid in the reaction mixture.

The reaction was carried out in a UV spectrophotometer at 62.0 ± 0.2 °C with magnetic stirring. The progress of the reaction was followed by measuring the absorbance every 4 min at 229 and 274 nm where ε is 6,130 and 1,500 for diazinon and 22,000 and 9,400 for the reaction product. The Beer's law plots are shown in Figures 9 and 10 for diazinon and product, respectively.

The concentrations of diazinon and product were calculated by using $A = A_1 + A_2 = \varepsilon_1bc_1 + \varepsilon_2bc_2$ and solving simultaneous equations for the absorbances at 229 and 274 nm. Using at least 25 data points, -log[diazinon] vs. time was plotted, and the slope was determined by linear least squares analysis. In cases where adsorption of diazinon and product occurred, the concentration of diazinon free in solution was determined from [Total] - [Product], where [Total] is the constant total concentration of (diazinon + product) at the end of the reaction, and [Product] is the measured concentration of the product. This excludes the adsorbed compounds from the calculation and gives the rate of hydrolysis of unadsorbed diazinon.

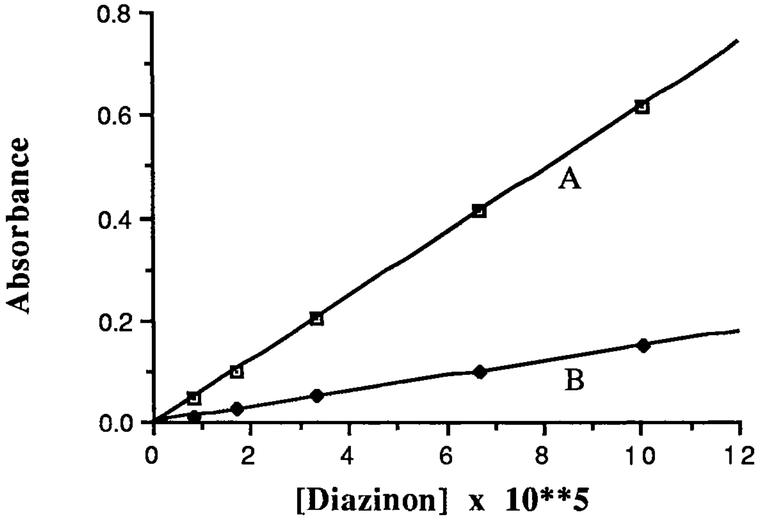


Figure 9. Beer's law plot for diazinon at A: 229 nm and B: 274 nm.

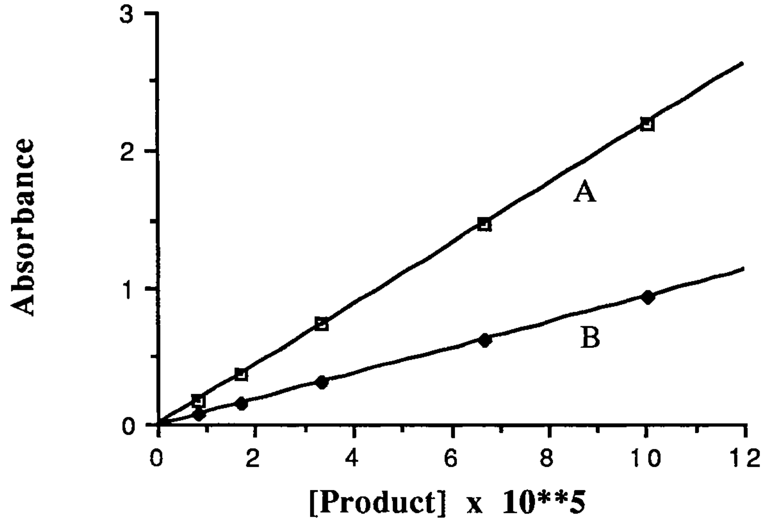


Figure 10. Beer's law plot for diazinon hydrolysis product at A: 229 nm and B: 274 nm.

All reactions followed pseudo-first-order kinetics using this data analysis. Standard deviations within a reaction were <2.5%. Duplicate reactions gave results within 3% of the average value reported in Table II.

REFERENCES

1. Sherrington, D. C. In: *Polymer-Supported Reactions in Organic Synthesis*; Eds: Hodge, P.; Sherrington, D. C.; Wiley: New York, 1980, pp. 157-194.
2. Akelah, A.; Sherrington, D. C. *Chem. Rev.* **1981**, *81*, 557-587.
3. Widdecke, H. In: *Syntheses and Separations Using Functional Polymers*, Eds: Sherrington, D. C.; Hodge, P.; Wiley: New York, 1988, pp. 149-179.
4. Sondheimer, S. J.; Bunce, N. J.; Fyfe, C. A. *J. Macromol. Sci. - Rev.* **1986,** *26*, 353-413.
5. Connolly, D. J.; Gresham, W. F. (to du Pont) U. S. Patent 3,282,875, 1966.
6. Waller, F. J. In: *Polymeric Reagents and Catalysts*; Ed: Ford, W. T.; Am. Chem. Soc.: Washington, 1986, pp. 42-67.
7. Olah, G. A.; Iyer, P. S.; Prakash, G. K. S. *Synthesis*, **1986**, *7*, 513-531.
8. Panster, P.; Grethe, H.; Kleinschmit, P. U. S. Patent 4,552,700 (to DeGussa); *Chem. Abst.* **1989**, *100*, P122170j.
9. Cox, G. B.; Loscombe, C. R.; Slucutt, M. J.; Sugden, K.; Upfield, J. A. *J. Chromatog.* **1976**, *117*, 269-278.
10. Asmus, P. A.; Low, C.-E.; Novotny, M. *J. Chromatog.* **1976**, *123*, 109-118.
11. Unger, K.; Nyamah, D. *Chromatographia* **1974**, *7*, 63-68.
12. Saunders, D. H.; Barford, R. A.; Magidman, P.; Olszewski, L. T.; Rothbart, H. L. *Anal. Chem.* **1974**, *46*, 834-838.
13. Satterfield, C. N. *Mass Transfer in Heterogeneous Catalysis*; MIT Press: Cambridge, MA, 1970.

14. Stober, W.; Fink, A.; Bohn, E. *J. Coll. Interface Sci.* **1968**, *26*, 62-69.

15. Lowe, O. G. *J. Org. Chem.* **1976**, *41*, 2061-2063.

16. Hodson, H. F.; Batchelor, J. F. U. S. Patent 4,103,015, 1978.

17. Frechet, J. M. J. *Pure Appl. Chem.* **1988**, *60*, 353-364.

18. Edwards, J.; Lenon, S.; Toussaint, A. F.; Vincent, B. *Am. Chem. Soc. Symp. Ser.* **1984**, *240*, 281-296.

19. Freeman, F.; Angeletakis, C. N. *Org. Magn. Res.* **1983**, *21*, 86-93.

20. Freeman, F.; Angeletakis, C. N. *J. Org. Chem.* **1982**, *47*, 4194-4200.

21. Gomaa, H. M.; Suffet, I. H.; Faust, S. D. *Residue Rev.* **1969**, *29*, 171-186.

22. Brown, D. J. *The Pyrimidines; Supplement I*; Wiley: New York, 1970, p. 368.

23. Toropova, V. F.; Saikina, M. K.; Aleshov, R. Sh. *Zh. Obshch. Khim.* **1967**, *37*, 725-728; *Chem. Abstr.* **1968**, *67*, 26388r.

24. Iler, R. K. *The Chemistry of Silica*; Wiley: New York, 1979, p. 661.

25. Coverdale, A. K.; Kohnstam, G. *J. Chem. Soc.* **1960**, 3806-3811.

26. Fitch, R. M. In: *Macromolecules*, Eds: Benoit, H.; Rempp, P.; Pergamon Press: Oxford, 1982, pp. 39-63.

27. Helfferich, F. *Ion Exchange*; McGraw Hill: New York, 1962, p. 86.

28. Ellman, G. L. *Arch. Biochem. Biophys.* **1959**, *82*, 70-77.

29. Benedict, R. C.; Stedman, R. L. *Analyst* **1970**, *95*, 296-301.

CHAPTER III

COLLOIDAL SILICA

INTRODUCTION

The preparation and analysis of stable dispersions of colloidal silica and its surface modification are important in ceramics, colloids, and catalysis.

Stober[1] reported a method for preparing colloidal silica by hydrolysis of tetraalkyl orthosilicates. This is also one of the basic reactions used in the preparation of ceramics.[2] Thus, it is important to know as much as possible about the structure and properties of the silica formed in this process in order to alter the properties of ceramic materials by making changes on a molecular level.[3]

Stober's synthesis gives spherical, monodisperse particles of colloidal silica. When the silica is dispersed into organic solvents such as chloroform and cyclohexane, clear dispersions are achieved because the refractive indexes of the silica and solvent are nearly equal. This makes it an ideal candidate for studying the equilibrium and transport properties of concentrated colloidal dispersions by light scattering.[4] Octadecanol,[4] polystyrene,[5-7] and poly(dimethylsiloxane)[7] have been covalently bound to the surface of colloidal silica in order to stabilize it in organic solvents.

Finally, colloidal silica may be useful as a catalyst support. As shown in Chapter II, colloidal silica-bound propanesulfonic acid exhibits a catalytic activity equal to that of soluble catalysts while at the same time giving advantages of a heterogeneous catalyst such as ease of separation from a reaction mixture. The synthesis of the catalyst was long because the silica was first formed in ethanol. Binding of mercaptopropyl groups in ethanol gave an undispersible gel. Therefore, the silica was transferred to DMF before the surface modification. The resulting surface modified silicas had only short-term stability in solvents other than DMF. Methods to stabilize dispersions of surface modified colloidal silica in a wide range of solvents would allow a shorter synthesis since the silica preparation and surface modification could be carried out as a one-pot synthesis. It would also make the catalyst more convenient to use since it could be stored as a dispersion for long periods of time rather than preparing a fresh batch of catalyst for each application.

In this chapter, the synthesis of colloidal silica particles in the range of 50-630 nm in diameter is reported. The structures and properties of these particles have been studied by ^{13}C and ^{29}Si NMR, BET surface analysis, pycnometry, thermogravimetric analysis, mass spectrometry, and elemental analysis.

The surface modification of 50-60 nm colloidal silica particles with aminopropyl, octadecyl, and mercaptopropyl groups has been studied. Aminopropyl groups will allow immobilization of a variety of groups on colloidal silica through the amine functionality. Colloidal silica whose surface has been esterified with octadecanol is one of the most common materials used for light scattering studies.[4] The currently used synthesis is long with a workup involving several ultracentrifugation steps. An easier synthesis of octadecylsilica would be very useful. Mercaptopropylsilica is the precursor to the silica-bound propanesulfonic acid catalyst reported in Chapter II.

It has previously been shown that covalently bound poly(ethylene oxide) stabilizes colloidal silica in aqueous dispersions.[8,9] Several new methods for sterically stabilizing surface modified colloidal silica have been studied. The methods used involve covalent binding of a trimethoxysilyl terminated poly(ethylene glycol), surface esterification with poly(ethylene glycol), and adsorption of a poly(ethylene oxide)/poly(propylene oxide) copolymer. These methods have been studied in the preparation and stabilization of mercaptopropylsilica, but they also are general methods which can be used to bind other functional groups to colloidal silica for use in polar solvents.

EXPERIMENTAL

Materials. Solutions of ammonia in ethanol (3-6 M) were prepared by passing ammonia gas through a column of NaOH pellets into absolute ethanol (U. S. Industrial Chemicals Co.) at 0 °C for 20-30 min. The ammonia concentration was determined by titrating to the methyl red endpoint with 0.9953 M HCl. All reactions using ammonium hydroxide were run within a two week period using the same bottle of ammonium hydroxide (Fisher) which was found to contain 15.14 M ammonia and 35.5 M water by density and titration to the methyl red endpoint.

Water was treated with active carbon, deionized, and distilled in glass. Tetraethyl orthosilicate (Petrarch or Fisher) was distilled immediately before use. Poly(ethylene glycol) (Aldrich) was dried by stirring at 115 °C under vacuum for 15 h. Toluene and diethyl ether were dried by refluxing over CaH_2 and sodium metal, respectively, and distilling.

Octadecyltrimethoxysilane (Petrarch), iodopropyltrimethoxysilane (Petrarch), aminopropyltrimethoxysilane (Aldrich), mercaptopropyltrimethoxysilane (Petrarch or Fluka), and octadecanol (Aldrich) were used as received. Pluronic surfactants were supplied by BASF Corp.

All other solvents were reagent grade and used as received.

All glassware was cleaned with 2% HF and rinsed with deionized water before reactions involving colloidal silica. A Branson model 5200 ultrasonic cleaning bath was used.

Analytical Methods. CP/MAS ^{13}C NMR spectra were obtained by Dr. Frank McEnroe at Conoco, Inc. on an IBM WP-100 spectrometer at 25 MHz. Quantitative ^{13}C NMR spectra were obtained using direct polarization and magic angle spinning with a 15 s delay, 3 ms contact time, and 10,000 scans. Delrin was used as an internal standard. Determination of the peak area by electronic integration or by cutting and weighing the peaks with the baseline drawn to give the least possible area and the most possible area all gave peak areas within 5.5% of the average. Variable contact time experiments showed that the relative areas with a 3 ms contact time were within 2% of relative areas when the contact time was extrapolated to zero. Therefore, no correction factor was used.[10]

Direct polarization ^{29}Si NMR spectra were obtained by Dr. Roger Assink at Sandia National Laboratories using a RIDE pulse sequence[11] at 39.6 MHz. Spin-lattice relaxation times ranged from 30 to 40 s, so a pulse repetition time of 150 s was used. Deconvolution of the spectra with gaussian lineshapes was done by manually adjusting the height, width, and frequency to give the best visual fit.

Solution ^{13}C NMR spectra were obtained at 75 MHz on a Varian XL-300 spectrometer. Typical conditions used 240 acquisitions, a spectral width of 20,000 Hz, and a 3.0 s delay. Solution ^{1}H NMR spectra were obtained at 300 MHz on a Varian XL-300 using 230 acquisitions and a spectral width of 4,000 Hz.

Transmission electron microscopy was done at the OSU Electron Microscopy Laboratory by Denise Rex on a JEOL JEM-100CX II microscope at 75 kV. One drop of the colloidal dispersion was placed on the sample grid, allowed to stand for 30-40 s, and the solvent was wicked away using filter paper. This procedure was repeated with a 3% uranyl acetate solution to stain the sample. Formvar grids were used for samples in water and ethanol. Carbon grids were used for samples in nonpolar solvents. Particle sizes were determined by measuring at least 35 particles on the photographic negative and calculating the number average and weight average diameters by Equations 4 and 5.

Thermogravimetric analysis was done on a Perkin-Elmer TGS-2 with a TADS computer, by heating the sample at 20 ^{o}C/min from 30 to 900 ^{o}C. Mass spectrometry was done on a ZAB-SE by heating the samples at 20 ^{o}C/min and ionizing the vapors by electron impact.

Elemental analyses were done at Galbraith Laboratories. Some elemental analyses were also done at Phillips Petroleum Co. using an analyzer developed by Phillips, in which a vanadium wire was placed in the sample to give more complete combustion at a higher temperature.

Pycnometer calibration was done by weighing the clean, dry pycnometer, filling with solvent at 25.0 °C and reweighing. Reported solvent densities were used to calculate the pycnometer volume. Six different measurements were made using water (d = 0.997 at 25 °C), toluene (d = 0.862 at 25 °C), and acetonitrile (d = 0.777 at 25 °C) as solvents. This gave an average pycnometer volume of 1.041 ± 0.002 mL.

Density measurements were done by weighing the dry pycnometer, adding approximately 200 mg of finely ground sample, and reweighing the pycnometer to give the sample weight. The pycnometer was filled to approximately 75% of full volume with acetonitrile and a slight vacuum was applied to pull all air out of the sample. It was then filled with acetonitrile and placed in a constant temp bath at 25.0 °C. After temp equilibration, the pycnometer was again weighed to give the acetonitrile weight. The volume of acetonitrile was calculated using a density of 0.777 g/mL. The difference in acetonitrile volume and pycnometer volume gave the sample volume, and with the sample weight gave the density. Reported densities are the average of two measurements. Standard deviations were $\leq$2%.

Solids contents were determined by placing 5.0 mL of dispersion in a petri dish, evaporating the solvent by heating at 120 °C for 1.0 h, and weighing the residue.

All samples were prepared for analysis by precipitating the colloids, recovering by vacuum filtration, washing, and drying at 60 °C under vacuum for 16 h. The precipitation methods and washing solvents were as follows:

Unmodified colloidal silicas: The sample was precipitated by acidifying to pH 2 with 1.0 M HCl or by adding 2.0 M NaCl. It was repeatedly washed with water (until the filtrate was neutral), acetone, and diethyl ether.

Sterically stabilized samples: The sample was precipitated by adding it dropwise to diethyl ether (a nonsolvent for poly(ethylene oxide)). It was washed repeatedly with diethyl ether and acetone (a poor solvent for poly(ethylene oxide) at room temperature).

This procedure forces adsorption of polymer which was not adsorbed in the original dispersion. Therefore, the isolated colloids may contain more adsorbed polymer than when dispersed.

Aminopropylsilicas: The sample was precipitated by acidifying to pH 2 with 1.0 M HCl. It was then washed repeatedly with water (until the filtrate was neutral), acetone, and diethyl ether.

Octadecylsilicas: These samples were isolated during the purification procedure and only needed to be dried as described above.

Colloidal Silica (58 nm) (1a). Water (7.2 mL, 400 mmol, 1.00 M), 309 mL of 2.46 M ammonia 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 glass stopper. The flask was placed in water in an ultrasonic cleaning bath, and 18 mL (80.7 mmol, 0.202 M) of tetraethyl orthosilicate was added rapidly during sonication. After 30 min, the reaction mixture began to turn cloudy as silica particles were formed. The temperature of the sonicator rose slowly from 20 ^oC to 45 ^oC over the first 5-6 h reaction time, and the mixture was sonicated a total of 18 h.

Anal. Found: C, 2.47% (2.06 mg-atom/g); H, 1.49% (14.8 mg-atom/g).

Colloidal Silica (>60 nm) (1b-1g). Enough ammonium hydroxide and ethanol were mixed in a stoppered Erlenmeyer flask to give the concentrations shown in Table I. This solution was placed in a water bath at 30.0 ^oC for 30 min. With magnetic stirring, the tetraethyl orthosilicate was added quickly. After 2-30 min, depending on the water and ammonia concentrations used, the reaction mixture began to turn cloudy as silica particles were formed. Stirring was continued for a total of 8 h to give an ethanolic dispersion of colloidal silica.

Seed Growth Technique (2).[12] A seed suspension (200 mL) was prepared as described above for **1b** by hydrolyzing 9 mL (0.202 M, 40.3 mmol) of tetraethyl orthosilicate in an ethanolic solution containing 1.78 M water and 0.76 M ammonia at 30 °C to give 70.7 nm seed particles. After 8 h, 18 mL (80.7 mmol) of tetraethyl orthosilicate and 2.91 mL (161 mmol) of water were added. After an additional 8 h, 18 mL of tetraethyl orthosilicate was again added, and sonicated for 8 h to give **2**.

Mercaptopropylsilica Stabilized by Adsorption of Poly(vinylpyrrolidone). Water (1.8 mL, 100 mmol, 0.999 M), 43.2 mL (190 mmol, 1.90 M ammonia) of 4.40 M ammonia in ethanol, and 50.5 mL of absolute ethanol were mixed in a stoppered Erlenmeyer flask. While this mixture was being sonicated, 4.5 mL (20.2 mmol, 0.202 M) of tetraethyl orthosilicate was added. After 30 min, the reaction mixture began to turn cloudy. After 5.0 h, a solution of poly(vinylpyrrolidone) in ethanol (11.5 g/L) was added dropwise over a period of 45 min, followed by rapid addition of 0.9 mL (4.76 mmol) of mercaptopropyltrimethoxysilane. Sonication was continued for an additional 20 h.

Colloidal Silica Esterified with Poly(ethylene glycol) (3). To 200 mL of **1a** (containing 2.42 g silica as SiO_2), a solution of poly(ethylene glycol) in ethanol (2.56 g/L) was added dropwise to give 0.02-0.10 g polymer/g SiO_2. Approximately 20 mL of solvent was removed by distillation to return the dispersion to its original volume of 200 mL. As the remaining ethanol and water were being distilled off under a nitrogen atmosphere, 550 mL of acetonitrile was added dropwise in order to keep a constant volume of dispersion. The distillation was continued until 50 mL of distillate was collected at a constant bp of 82 °C.

Mercaptopropylsilica Stabilized by PEG Ester (4). To 50 mL of **3** (containing 0.60 g silica as SiO_2), 3-mercaptopropyltrimethoxysilane and water were added in a

1:4.5 ratio to give 0.25-4.05 mmol silane/g SiO_2. In cases where the amount of added silane was very small, the silane was added as an acetonitrile solution. The mixture was refluxed for 24 h to give **4**.

4 (0.25 mmol silane/g SiO_2). Anal. Found: C, 4.16% (3.84 mg-atom/g); H, 1.84% (18.2 mg-atom/g); S, 0.33% (0.10 mg-atom/g).

PEG Monomethyl Monotrimethoxysilylpropyl Ether (5). Dry poly(ethylene glycol monomethyl ether) (PEGME) (15 g, 7.9 mmol, MW = 1,900) in 66 mL of dry toluene was added dropwise under nitrogen to a suspension of 0.40 g (16.2 mmol) of sodium hydride in 60 mL of dry toluene. This suspension was stirred at room temperature for 1.0 h and filtered in a nitrogen atmosphere to remove NaOH and unreacted NaH. This solution was added dropwise to 4.6 g (16 mmol) of iodopropyltrimethoxysilane in 50 mL of toluene and stirred at room temperature under nitrogen for 14 h. The polymer was precipitated by adding to 1300 mL of dry diethyl ether and centrifuging. The solvent was decanted off and the polymer was again dissolved in 150 mL of toluene, reprecipitated, and dried under vacuum at 40 ^oC for 17 h to give 12.6 g of **5**.

^1H NMR ($CDCl_3$): δ 0.8 (1.52 H) and 1.95 (1.49 H) (sharp peaks due to C(1) and C(2) of propylsilanes); δ 3.05 (0.12 H) (unreacted CH_2I); δ 3.38 (3 H) (CH_3O-PEGME); and δ 3.5-3.8 (CH_2CH_2O).

Mercaptopropylsilica Stabilized by Bound 5 (6). A typical synthesis is given below using 0.10 g **5**/g SiO_2. Other syntheses were done with the amount of polymer varying from 0.02-0.10 g/g SiO_2.

Water (7.2 mL, 400 mmol, 1.00 M), 178 mL (760 mmol, 1.90 M) of 4.27 M ammonia in ethanol, and 197 mL of ethanol were mixed in a 500 mL stoppered Erlenmeyer flask and placed in a sonicating bath. During sonication, 18 mL (80.8 mmol, 0.202 M) of tetraethyl orthosilicate was added. After 30 min, the reaction mixture began to turn cloudy.

After 5.0 h, 486 mg (256 µmol, 0.10 g/g SiO_2, 52.7 µmol/g SiO_2) of **5** in 25 mL of ethanol was added dropwise. After 20.0 h, 0.92 mL (4.86 mmol, 1.0 mmol/g SiO_2) of 3-mercaptopropyltrimethoxysilane was added and sonication was continued for an additional 24 h to give a dispersion of **6a**. Precipitation occurred within 10 h leaving a clear solution above. So 200 mL of solvent was decanted off and replaced with water. Sonicating for 3 h then gave a stable dispersion.

6a (0.10 g **5**/g SiO_2) Anal. Found: C, 3.97% (3.31 mg-atom/g); S, 1.97% (0.61 mg-atom/g); H, 1.68% (16.6 mg-atom/g). CP/MAS ^{13}C NMR: 10 and 27 ppm (mercaptopropyl); 17 and 57 ppm (ethoxy); 39 ppm (disulfide). Particle size: D_n = 60.2 nm, D_w = 63.3 nm, D_w/D_n = 1.05.

6b (0.02 g **5**/g SiO_2) Anal. Found: C, 4.46% (3.71 mg-atom/g); S, 1.99% (0.62 mg-atom/g); H, 1.80% (17.8 mg-atom/g). CP/MAS ^{13}C NMR: 10.8 and 27.3 ppm (mercaptopropyl); 16.7 and 59.0 ppm (ethoxy); 46.3 ppm (methoxy); 40.2 ppm (disulfide).

Mercaptopropylsilica Stabilized by Pluronic Surfactants (7-10). Water (3.6 mL, 200 mmol, 1.00 M), 113.5 mL ethanol, and 73.9 mL (380 mmol, 1.90 M ammonia) of 5.14 M ammonia in ethanol were mixed in a 250 mL stoppered Erlenmeyer flask. While this solution was being sonicated, 9 mL (40.4 mmol, 0.202 M) of tetraethyl orthosilicate was added rapidly. After 30 min, the reaction mixture began to turn cloudy. The temperature rose slowly from 20 °C to 45 °C over a period of 5-6 h. After 5 h, a solution of the Pluronic surfactant in 25 mL of ethanol was added dropwise over a period of 10 min, followed by rapid addition of 0.5 mL (2.65 mmol, 1.10 mmol/g SiO_2) of mercaptopropyltrimethoxysilane. Sonication was continued for an additional 18 h to give sterically stabilized mercaptopropylsilica.

DMF Dispersion of Colloidal Silica (11). The ethanol and water were slowly distilled from 400 mL of **1a** while about 500 mL of dimethylformamide (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.

Aminopropylsilica in DMF (12). To 200 mL of **11** (containing 2.56 g silica as SiO_2) was added 1.7 mL (9.74 mmol) of 3-aminopropyltrimethoxysilane. This mixture was stirred at 100 °C under nitrogen for 24 h to give a dispersion of **12** containing 2.23% solids by weight.

Anal. Found: C, 6.11% (5.08 mg-atom/g); H, 2.29% (22.7 mg-atom/g); N, 1.13% (0.81 mg-atom/g).

Aminopropylsilica in Ethanol (13). Water (3.6 mL, 200 mmol, 1.00 M), 80.4 mL (380 mmol, 1.90 M ammonia) of 4.73 M ammonia in ethanol, and 107 mL of absolute ethanol were mixed in a stoppered Erlenmeyer flask and placed in water in an ultrasonic cleaning bath. Upon sonication, 9.0 mL (40.3 mmol, 0.202 M) of tetraethyl orthosilicate was added. After 30 min, the reaction mixture began to turn cloudy as silica particles were formed. After 5.0 h, 1.7 mL (9.74 mmol) of 3-aminopropyltrimethoxysilane was added and sonication was continued for an additional 20 h to give a dispersion of **13** containing 2.16% solids by weight.

Anal. Found: C, 3.79% (3.16 mg-atom/g); H, 2.04% (20.2 mg-atom/g); N, 0.90% (0.64 mg-atom/g).

Octadecylsilica from Octadecanol (14). To 200 mL of **1a**, 12.1 g (44.7 mmol) of 1-octadecanol was added dropwise. The ethanol, water, and ammonia were distilled off under a nitrogen atmosphere giving a suspension of silica in octadecanol which was heated at 190 °C for 3.0 h. Upon cooling, a solid dispersion of octadecylsilica in octadecanol was formed. The dispersion was mixed with 200 mL of 1,4-dioxane and the octadecylsilica was precipitated by centrifuging at 2,000 rpm for 5 min. The silica was filtered and washed repeatedly with dioxane. The filtrate was isolated and the solvent removed by distillation. When no more octadecanol was observed in the filtrate, the octadecylsilica was washed with an additional 4 x 100 mL portions of dioxane to remove the last traces of unbound octadecanol. The octadecylsilica was placed in 200 mL of solvent (toluene, benzene, cyclohexane, or chloroform) and sonicated for 15 min to give a stable dispersion of **14**.

Anal. Found: C, 6.65% (5.54 mg-atom/g); H, 2.26% (22.4 mg-atom/g).

Octadecylsilica from Octadecyltrimethoxysilane (15). Water (3.6 mL, 20 mmol, 1.00 M), 126 mL of ethanol, and 61 mL (380 mmol, 1.90 M ammonia) of 6.25 M ammonia in ethanol were mixed in a 250 mL stoppered Erlenmeyer flask and placed in an ultrasonic cleaning bath. Upon sonication, 9.0 mL (40.4 mmol, 0.202 M) of tetraethyl orthosilicate was added rapidly. The reaction mixture began to turn cloudy after 30 min. After 5 h, octadecyltrimethoxysilane (0.5, 1.0, or 3.0 mmol/g SiO_2 for **15a**, **15b**, and **15c**, respectively) was added and sonication was continued for an additional 20 h. At this time, the octadecylsilica had precipitated. It was removed by vacuum filtration and washed thoroughly with 1,4-dioxane to remove any unbound silanes. The octadecylsilica was placed in 200 mL of benzene and redispersed by sonicating for 15 min.

15a. Anal. Found: C, 10.03% (8.35 mg-atom/g); H, 2.81% (27.8 mg-atom/g).

15b. Anal. Found: C, 16.38% (13.64 mg-atom/g); H, 3.63% (35.9 mg-atom/g).

15c was colloidally unstable and was not analyzed.

Transfer of Colloids to Water. From samples which did not contain Pluronic surfactants (**4**, **6**, **11**, **13**), the ethanol, ammonia and water (or acetonitrile for **4**) were slowly distilled from the dispersion while water 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 100 °C. With samples containing Pluronic surfactants (**7-10**), foaming occurred when the dispersion was boiled. So the ammonia and ethanol were removed by heating the dispersion to just below the bp and passing a stream of nitrogen through the flask. With the samples sterically stabilized by poly(ethylene glycol) or Pluronic surfactants, precipitation of the colloids generally occurred during the distillation. Sonication for 1-24 h was required to redisperse the colloids.

RESULTS

Colloidal Silica. Colloidal silica was prepared according to the method of Stober[1] by hydrolyzing tetraethyl orthosilicate in a mixture of water, ammonia, and ethanol (Equation 1). Concentrations used were 0.202 M tetraethyl orthosilicate, 1.0-7.0 M water, and 0.76-3.0 M ammonia as shown in Table I. The initial reaction mixtures were clear liquids. After 2-30 min, the reaction mixture began to turn cloudy as silica particles were formed, and eventually a light blue to white dispersion was formed. The slowest reaction was with **1a**. As the water and ammonia concentrations were increased, the reaction became faster. Very stable dispersions of **1a** were prepared by using a sonicator for mixing. However, with the larger particles, thermostatting of the reaction mixture and rapid addition of the tetraethyl orthosilicate were required to give stable dispersions.

$$\mathrm{(EtO)_4Si} \xrightarrow{\mathrm{H_2O,\ NH_3,\ EtOH}} \underset{\mathbf{1}}{\textcircled{\mathrm{SiO_2}}\!-\mathrm{OH}} \qquad (1)$$

Table I. Concentrations Used During Colloidal Silica Syntheses.

Sample	$(EtO)_4Si$, M	H_2O, M	NH_3, M
1a	0.202	1.00	1.90
1b	0.202	1.78	0.76
1c	0.202	2.13	0.91
1d	0.202	2.49	1.06
1e	0.202	3.55	1.51
1f	0.202	4.70	2.01
1g	0.202	7.01	3.00

The effect of changing the concentrations in the reaction was studied extensively by Zukoski,[12,13] who used the two following equations to correlate the final particle diameter in nm (d) to the water, ammonia, and tetraethyl orthosilicate (TEOS) concentrations.

$$d = A[H_2O]^2\exp(-B[H_2O]^{1/2}) \qquad (2)$$

where

$$A = [TEOS]^{1/2}(82.06 - 151.3[NH_3] + 1202[NH_3]^2 - 365.8[NH_3]^3)$$

$$B = 1.051 + 0.5230[NH_3] - 0.1283[NH_3]^2$$

$$d = A[H_2O]^2\exp(-B[H_2O]) \qquad (3)$$

where

$$A = [\mathrm{TEOS}]^{-1/2}(-1.042 + 40.57[NH_3] - 9.313[NH_3]^2)$$

$$B = 0.3264 - 0.2727[\mathrm{TEOS}]$$

Table II. Predicted and Measured Colloidal Silica Average Particle Diameters.

	Measured (nm)			Predicted (nm)	
Sample	D_n	D_w	D_w/D_n	eqn. 2	eqn. 3
1a	57.7	59.6	1.03	150	71
1b	70.7	72.9	1.03	114	106
1c	90.1	92.4	1.03	170	160
1d	139.0	142.1	1.02	232	221
1e	337.2	343.3	1.02	409	417
1f	623.0	623.8	1.001	532	589
1g	630.9	631.1	1.0003	260	602

Zukoski states that these equations come within 20% of the actual experimentally measured particle diameters, with the greatest difference coming from the smaller particles.

In Table II, the predicted particle size from Equations 2 and 3 is compared to the number average (d_n) and weight average (d_w) particle diameters measured from electron micrographs and calculated by the following equations:

$$d_n = \Sigma n_i d_i / \Sigma n_i \qquad (4)$$

$$d_w = (\Sigma n_i d_i^6 / \Sigma n_i d_i^3)^{1/3} \qquad (5)$$

Equation 3 gives good agreement with the measured particle sizes, especially with >600 nm diameter particles which are within 5% of the predicted size. Samples **1b**, **1c**, and **1d** deviate from Equation 3 by more than 20%. However, Zukoski formulated these equations for reactions run at 25 °C. Our reactions were thermostatted at 30 °C. An increase in temperature is known to decrease the particle size and could account for this difference. But even at 30 °C, Equation 3 can give a good idea of the particle size range to be expected from a reaction. With Equation 2, the differences between predicted and measured particle sizes is much larger and Equation 2 does not appear very useful.

As shown by D_w/D_n in Table II, the particles become more monodisperse as the particle size increases. In dispersion **1a**, the particles had diameters of 40-70 nm. However, in dispersion **1g**, all particles measured were between 629 nm and 631 nm. There is also a large difference in the appearance of the particles in the TEM as the size is increased (Figure 1). The smaller particles (<100 nm) are distorted spheres with rough surfaces, while the large particles appear to be perfectly monodisperse, smooth spheres.

Particles with diameter <100 nm remain dispersed for approximately one year. As the particle size is increased, precipitation occurs much quicker until with >350 nm

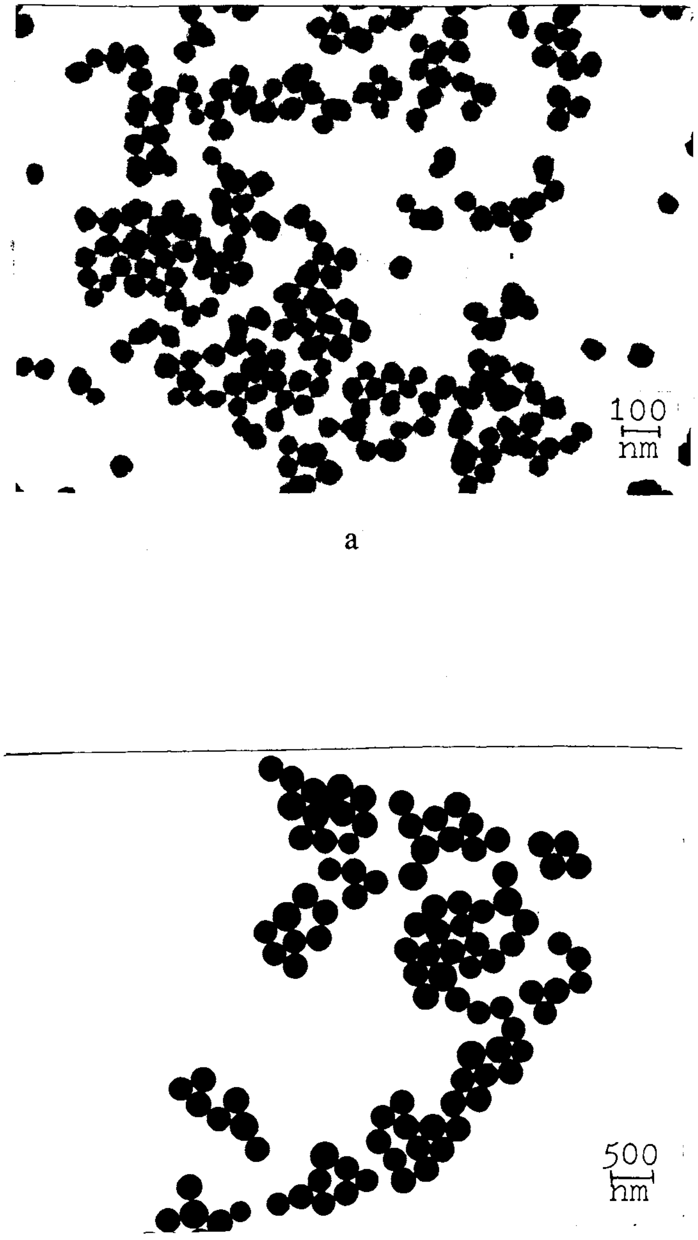
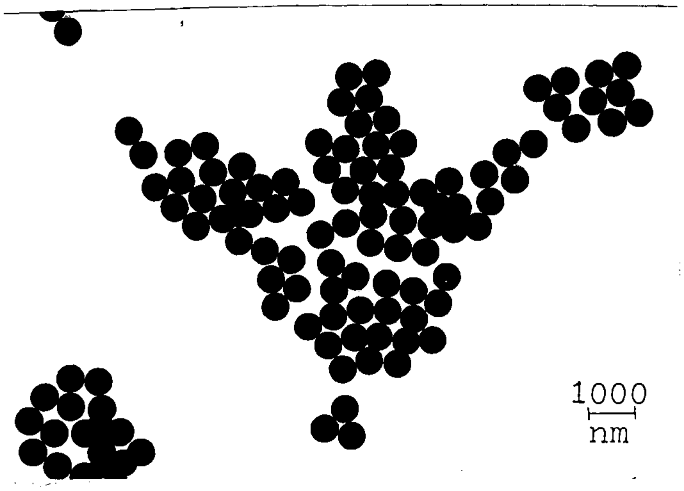


Figure 1. TEM of colloidal silica particles. a: silica **1a**, b: silica **1e**, c: silica **1g**.



c

Figure 1. (Continued)

particles, precipitation begins to occur within 12 h. However, all of these particles are easily redispersed by shaking or sonication.

Another method for preparing larger or more monodisperse particles is a seed growth technique reported by Zukoski.[12] In this procedure, seed particles are prepared as described above. Then at 8 h intervals, TEOS (up to twice the number of moles as in the seed reaction) and water can be added in a 1:2 mole ratio. Assuming no new particles are nucleated during the reaction, the final particle size (d) is predicted by the following equation:

$$d = d_o(V/V_o)^{1/3} \qquad (6)$$

where d_o is the average diameter of the seed particles, V_o is the volume of TEOS used to prepare the seed particles, and V is the total volume of TEOS added to the solution (including V_o). When 70.7 nm seed particles were used for two seed growth cycles, a final particle size of 121 nm was achieved, very close to the expected size of 125 nm. D_w/D_n also dropped from 1.03 to 1.01 and the silica content (as SiO_2) was increased from 1.21% (w/v) to 3.33%. The TEM shows no evidence of nucleation of new, smaller particles during the seed growth reactions.

Assink and Kay[14,15] have reported that silica formed by base catalyzed hydrolysis of tetraethyl orthosilicate contains a significant number of ethoxy groups because hydrolysis is the rate limiting step in the polymerization. As shown in Table III, the colloidal silica samples contain 2.25-2.53% C. The quantitative ^{29}Si NMR spectrum of **1a** is shown in Figure 2. It shows that three different types of silicon atoms are present. They are Q_2, Q_3, and Q_4 (Figure 3) silicon species whose relative abundances are 4.1%, 38.0%, and 57.8%, respectively.

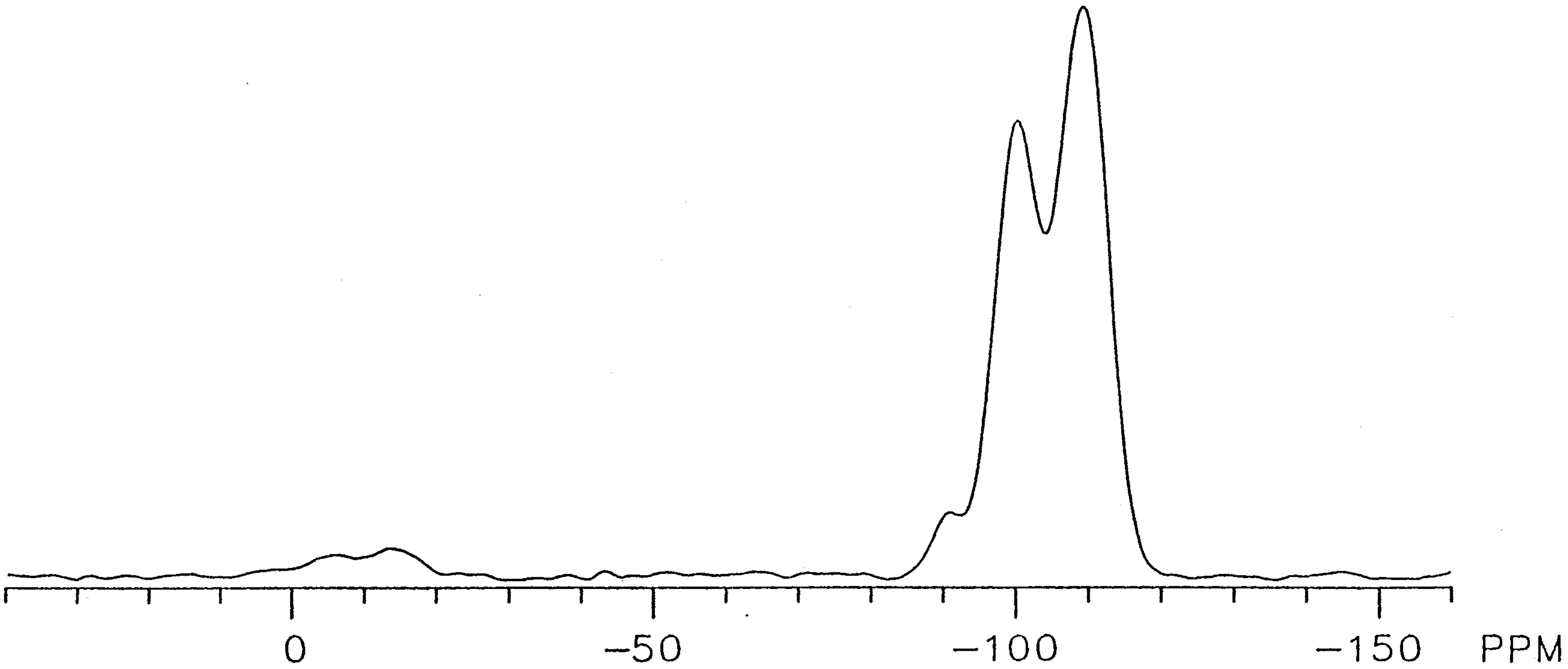
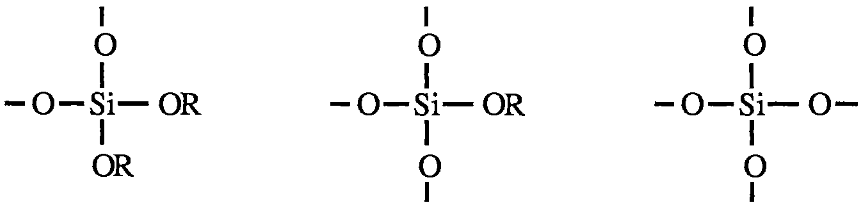


Figure 2. Quantitative ^{29}Si NMR spectrum of colloidal silica **1a**.

Table III. Elemental Analyses and Densities of Colloidal Silicas.

Sample	%C (mg-atom/g)	%H (mg-atom/g)	Density, g/mL
1a	2.47 (2.06)	1.49 (14.8)	2.06
1e	2.53 (2.11)	1.28 (12.7)	2.01
1g	2.25 (1.87)	1.36 (13.5)	2.02



Q_2 Q_3 Q_4

Figure 3. Types of silicon present in colloidal silica. R = Et, H. All other O-atoms are bound to Si.

From the ^{29}Si NMR of **1a**, there are 0.46 RO groups/SiO_2. The elemental analysis of **1a** in Table III shows 1.03 mequiv ethoxy/g. From this a silanol content of approximately 6.0 mequiv/g can be calculated. From surface silanol concentrations reported for silica (6.3-10.0 μmol silanol/m^2),[16] **1a** is expected to have only 0.42-0.67 mequiv/g of surface silanols and ethoxy groups. The remaining 6.3-6.6 mequiv/g must be buried inside the bulk silica.

TGA and mass spectral analysis have also shown ethoxy content in all colloidal silica samples. When **1a** was heated at 20 °C/min, approximately 4.25% of its weight was lost between 70 °C and 200 °C. The mass spectra of the volatilized compounds showed that this weight loss was mainly due to ethanol (Table IV). As the sample is heated from 200 °C to 900 °C, silicon-containing species are driven off, and the total weight loss was 8.79% when heated from room temperature to 900 °C. Colloidal silica samples **1e** and **1g** gave very similar TGA thermograms with the weight loss below 200 °C and total weight loss being 5.80% and 10.29% for **1e** and 4.83% and 8.17% for **1g**.

Amorphous bulk silica possesses a density of 2.20 g/mL.[17] However, the buried hydrocarbon in these samples has lowered the density to 2.01-2.06 g/mL (Table III). This is close to the value of 2.04-2.10 g/mL reported previously by Bogush, Tracy, and Zukoski.[12]

Using the density of 2.06 g/mL and particle diameter of 57.7 nm for **1a**, a surface area of 50.5 m^2/g is calculated assuming smooth spheres. A surface area of 67.4 m^2/g was actually measured by BET nitrogen adsorption. This higher than expected surface area could be due to a rough surface or to the particles being slightly porous. The pore size distribution, determined by BET nitrogen desorption on the dry powder, is shown in Table V. The pores of >60 nm diameter are due to spaces between loosely packed particles. The major fraction of the pore volume occurs in the 10-30 nm diameter range. This pore volume accounts for a porosity of 45.9% in the bulk sample. Random close packing of spheres gives a porosity of 46%.[18] Therefore, we have attributed this pore volume to

Table IV. Mass Spectra of Volatile Compounds from Heating Silica **1a**.[a,b]

Formula	m/e found	m/e calc.	Intensity
Temp = 80 °C			
C_2H_4O	44.0091	44.0262	36
C_2H_5O	45.0612	45.0341	100
SiO_2H	61.0297	60.9745	47
Temp = 250 °C			
C_2H_3	27.0496	27.0235	63
CHO	29.0006	29.0027	45
C_2HO	41.0216	41.0027	100
C_2H_3O	43.0471	43.0184	73
C_2H_5O	45.0612	45.0341	36
C_3H_5O	57.0699	57.0341	68
C_2H_3OSi	71.0821	70.9953	47
$C_2H_3O_2Si$	87.0287	86.9902	30
$C_3H_5O_2Si$	101.0419	101.0059	17
$C_4H_5O_3Si$	129.0624	129.0008	15
Temp = 460 °C			
$C_3H_5O_2Si$	101.0366	101.0059	96
$C_4H_3O_3Si$	127.0392	126.9851	37
$C_6H_6O_4Si$	170.0551	170.0035	100
$C_8H_{12}O_4Si$	200.0665	200.0505	76
$C_7H_7O_5Si_2$	227.0703	226.9831	19

Table IV (Continued)

---

[a]Heating rate = 20 °C/min. [b]Mass spectra of vaporized compounds was obtained by electron impact ionization.

Table V. Pore Size Distribution of Silica **1a**.

Pore Diameter, nm	Pore Volume, mL/g
>60	0.098
60-40	0.004
40-30	0.006
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.

interstices between the packed particles. There is almost no significant porosity in the 2-10 nm range. Thus, there is no measured pore volume from this experiment which is attributed to porosity. However, this measurement only goes down to 2 nm. Van Helden, Jansen, and Vrij[4] have reported measuring <1.2 nm diameter ultramicropores in 21 nm particles prepared by the same method. Our experiment would not detect pores in this size range.

Steric Stabilization. In order to sterically stabilize mercaptopropylsilica, adsorption of poly(ethylene glycol) (PEG) or poly(vinylpyrrolidone) (PVP) was first attempted. Polymer molecular weights used were 600-6,800 and 10,000-40,000 for PEG and PVP, respectively. After the tetraethyl orthosilicate hydrolysis reaction had run for 5 h, these polymers could be added as ethanolic solutions to stabilize the silica. Polymer addition was followed by addition of mercaptopropyltrimethoxysilane. Thus, this gives a possible one-pot synthesis of stabilized mercaptopropylsilica. If the polymer solution was added after less than 5 h of particle growth, stable colloids were not formed (Table VI).

With PVP, a dispersion was achieved which was stable (where stability is defined as the length of time before any precipitation is observed) for four months using a polymer MW of 40,000 and 0.47 g PVP/g SiO_2. As the MW or amount of polymer was reduced, the dispersion stability decreased (Table VI). PEG has limited solubility in ethanol and the maximum amount of polymer which could be used was 0.2 g PEG/g SiO_2. No stable dispersions were found in the range of 0.02-0.2 g PEG/g SiO_2.

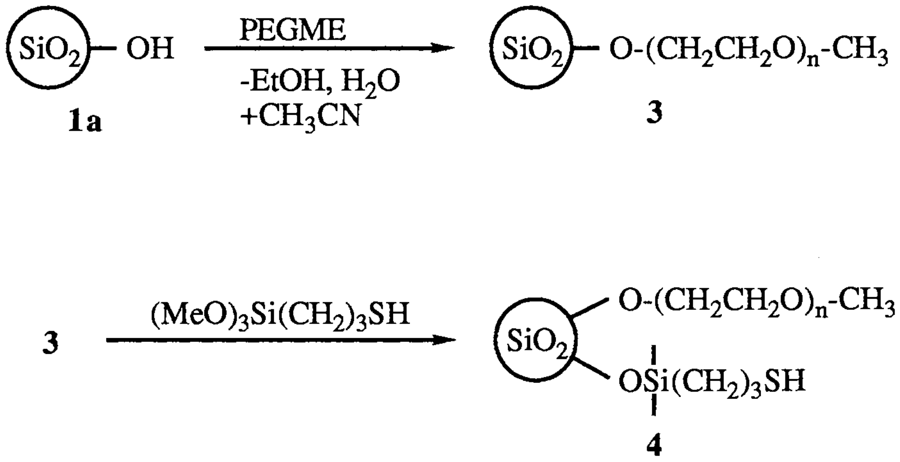
These results show that steric stabilization can be used in a one-pot synthesis of mercaptopropylsilica giving stable dispersions in ethanol, water, and acetone. However, when the PVP-stabilized silica was precipitated by centrifugation, and the free polymer removed by decanting off the clear solution above the particles, the silica could not be redispersed, showing that much of the polymer does not adsorb but remains free in solution. Because all of the polymer does not adsorb, a large amount of added polymer is necessary for stabilization to occur.

Table VI. Stability of Mercaptopropylsilica with Added Poly(vinylpyrrolidone) (PVP).

MW of PVP	g PVP/g SiO_2	Stability (days)
10,000	0.0236	2
10,000	0.236	1
40,000	0.0236	0
40,000	0.108	0
40,000	0.236	42
40,000	0.470	115
40,000	0.235[a]	0
40,000	0.235[b]	21
40,000	0.235[c]	25

[a]PVP was added after tetraethyl orthosilicate had hydrolyzed for 1.0 h. [b]PVP was added after tetraethyl orthosilicate had hydrolyzed for 2.0 h. [c]PVP was added after tetraethyl orthosilicate had hydrolyzed for 3.0 h.

Scheme 1. Steric stabilization of mercaptopropylsilica by PEGME ester.



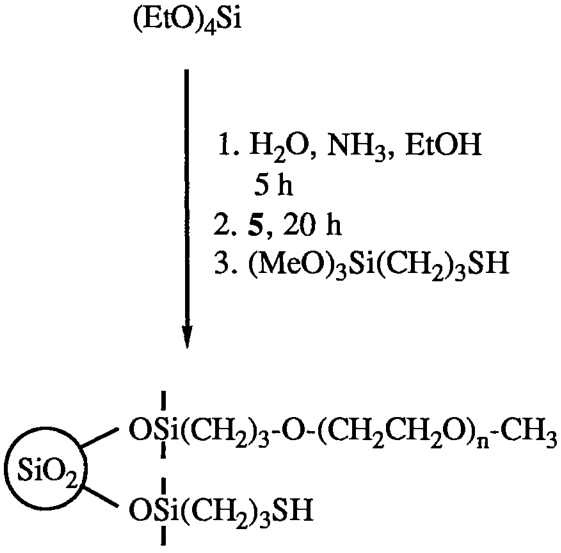
A possible way to reduce the amount of polymer required for stabilization is to bind the polymer chains to the surface in some way. Initially, poly(ethylene glycol monomethyl ether) (PEGME) was covalently bound to the surface as an ester, giving a stabilized silica which could then be reacted with mercaptopropyltrimethoxysilane (Scheme 1). The surface esterification was done by adding PEGME to **1a**. The water and ethanol were then distilled away and replaced with acetonitrile, keeping a constant volume of dispersion throughout the process. Since water, ethanol, and acetonitrile form a ternary azeotrope (72.9 °C), the water and ethanol could be completely removed by this process, giving colloidal silica esterified with PEGME, **3**. Mercaptopropylsilica could then be added directly to this dispersion in acetonitrile to give **4**.

The most stable dispersions of **4** were formed by adding 0.021 g PEGME/g SiO_2 (MW of PEGME = 1,900) and 0.25 mmol mercaptopropyltrimethoxysilane/g SiO_2. This gave stabilities of 6 and 10 weeks in acetonitrile and water, respectively. As the amount of polymer was increased or decreased in the range of 0.01-0.10 g PEGME/g SiO_2 or as the amount of mercaptopropyltrimethoxysilane added to the reaction was increased, the stability of the dispersion decreased.

We were encouraged from these results, which show that small amounts of polymer can be used for steric stabilization of mercaptopropylsilica. However, there are several problems with this method. The most stable dispersions are obtained when 0.25 mmol silane/g SiO_2 is added to the reaction. Even when water was added to the reaction in an attempt to drive this reaction to completion, it gave only 0.10 mmol/g of bound mercaptopropyl groups. This is less than a monolayer, suggesting that these particles may still be partially charge stabilized. This method also gives PEGME attached through a silicate ester linkage, which can be hydrolyzed.[9] Since we are using these dispersions in water, this is a great disadvantage. Loss of the polymer from the silica surface by hydrolysis could be the cause of precipitation of the colloids after 10 weeks. Finally, our goal was to develop a one-pot synthesis of stabilized mercaptopropylsilica which does not require solvent changes. These goals are not met by this technique.

Attachment of a trimethoxysilyl endproup to PEGME would allow it to be reacted directly with silica in ethanol, giving the one-pot synthesis, while at the same time giving a more stable siloxane linkage. Three different methods were attempted for introducing the trimethoxysilyl endgroup onto PEGME. The first method involved preparing the mesylate of PEGME and reacting it with aminopropyltrimethoxysilane. In three attempts, this method gave a hydrolyzed and crosslinked polymer which was insoluble in all solvents. In the second method, the sodium salt of PEGME was reacted with chloromethylphenylethyltrimethoxysilane. The ^1H NMR spectrum shows that the silane was bound to the polymer, but it also shows a large amount of unreacted chloromethyl at 4.55 ppm, suggesting that the alkoxide may be attacking at silicon and displacing methoxide rather than reacting with the chloromethyl group. In the third method (Equation 7), the sodium salt of PEGME was formed and reacted with iodopropyltrimethoxysilane. This method was successful giving a

$$\begin{array}{c}
\mathrm{CH_3\text{-}(OCH_2CH_2)_n\text{-}OH} \\
\Big\downarrow \begin{array}{l} \text{1. NaH} \\ \text{2. } \mathrm{I(CH_2)_3Si(OCH_3)_3} \end{array} \\
\mathrm{CH_3\text{-}(OCH_2CH_2)_n\text{-}O(CH_2)_3Si(OCH_3)_3} \\
\mathbf{5}
\end{array} \qquad (7)$$



6

(8)

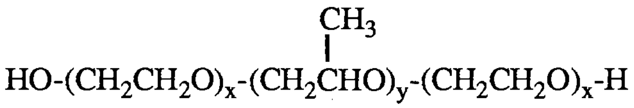
yield of 76% with PEGME of MW = 1,900. When the MW was increased to 5,000, the yield dropped to only 20%. So only **5** derived from PEGME with a MW of 1,900 was used in further reactions.

Colloidal silica can be prepared and reacted with **5** and mercaptopropyltrimethoxysilane in a simple one-pot synthesis as shown in Equation 8. Using 0.10 g **5**/g SiO_2 gives a dispersion which is unstable in ethanol, but is stable in water for 6 months. This instability in ethanol is expected since PEGME has low solubility in ethanol at room temperature. When dispersed in water, it does not precipitate when added to large amounts of acetone, tetrahydrofuran, 1,4-dioxane, or acetonitrile. However, it precipitates rapidly when 2.0 M NaCl is added due to reduced solubility of PEGME in aqueous salt solution.

Reduced amounts of **5** result in very little or no stabilization. Samples of **6** with 0.02 and 0.10 g **5**/g SiO_2 were found to have 0.62 and 0.61 mmol mercaptopropyl/g by sulfur analysis, showing that the amount of polymer, in the range of 0.02-0.10 g/g SiO_2, has no effect on the surface coverage obtained in this reaction.

An easier method of attaching polymers to colloidal silica is provided by adsorption of polymeric surfactants such as the Pluronic surfactants in Table VII. These surfactants are ABA block copolymers of poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO). When these surfactants are added to a colloidal dispersion in a polar solvent, the PPO segment is insoluble (solubility of PPO having M_n of 2,000 = 0.01 g/100 mL in water at 25 ^oC) and will lie down on the surface of the colloidal particles. The PEO segments are soluble (solubility >100 g/mL in water at 25 ^oC) in most polar solvents and solvation of the polymer chains will cause the PEO segments to extend into solution around the particles (Figure 4), thus, giving steric stabilization.

Table VII. Structures of Pluronic Surfactants.



$$\mathrm{HO{-}(CH_2CH_2O)_x{-}(CH_2\underset{}{\overset{\overset{\displaystyle CH_3}{|}}{C}}HO)_y{-}(CH_2CH_2O)_x{-}H}$$

		MW of Segments		
Surfactant	Total MW	PEO	PPO	%PEO
F38	4700	1880	940	80
F68	8400	3360	1680	80
F87	7700	2695	2310	70
P105	6500	1625	3250	50

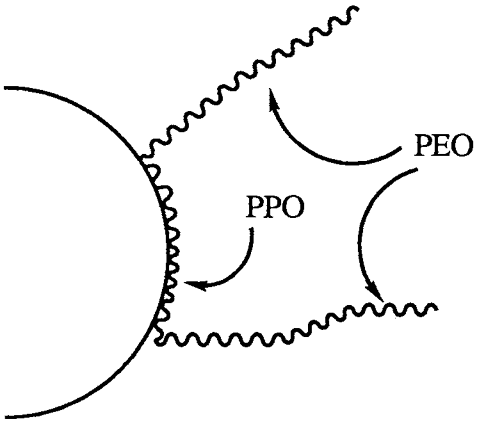
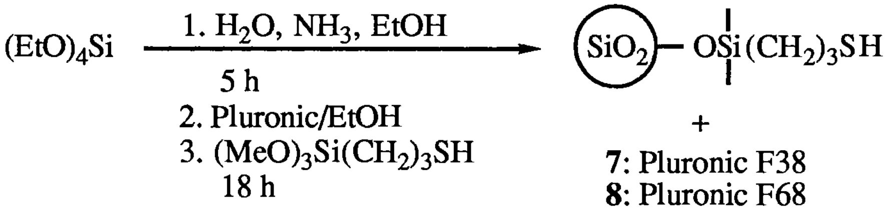


Figure 4. Adsorption of Pluronic surfactants to colloidal silica in water.

The synthesis of stabilized mercaptopropylsilica becomes even shorter using the Pluronic surfactants (Equation 9) since the polymer does not react with the surface. Tetraethyl orthosilicate is hydrolyzed in water, ammonia, and ethanol as before. After 5 h, the surfactant is added as an ethanolic solution to provide steric stabilization, and it is followed immediately by addition of mercaptopropyltrimethoxysilane. This gives a synthesis which is complete within 24 h, less than half the time required for previously used syntheses.



(9)

7: Pluronic F38
8: Pluronic F68
9: Pluronic F87
10: Pluronic P105

The stabilities of dispersions **7-10** in ethanol and water are shown in Tables VIII-XI. In ethanol, only short-term stabilities (≤14 days) are obtained from Pluronics F38, F68, and F87, which contain either 70% or 80% PEO. With ≥0.125, 0.063, and 0.063 g surfactant/g SiO_2 for F38, F68, and F87, respectively, the mercaptopropylsilica precipitates during the reaction. However, by adding 25-50% water and sonicating, these materials were redispersed in most cases. The only exception was with 0.125 g F68/g SiO_2, which formed a gel and could not be redispersed. With Pluronic P105, very stable dispersions are formed in ethanol, with stabilities ranging as high as 3 months using 0.04 g P105/g SiO_2. It is apparent from Tables VIII-XI that the stability of the dispersions in ethanol increases as the PEO content and the MW of the surfactant are decreased.

Dispersions **7-10** were transferred to water by distilling away the ethanol and replacing with water. The colloids precipitated during this process except when the surfactant level approached 0.20 g/g SiO_2. Samples which precipitated during the transfer to water could be redispersed by sonicating for 3-16 h.

Once the dispersions were transferred to water, they all gave stabilities dependent on the amount of surfactant similar to that shown in Figure 5 for Pluronic P105. As surfactant is added, the stability increases until it goes through a maximum at 0.025, 0.025, 0.001, and 0.0002 g surfactant/g SiO_2 for F38, F68, F87, and P105, respectively. As the surfactant concentration is increased more, the stability decreases until it reaches a minimum around 0.10 g surfactant/g SiO_2 for all surfactants. After this point, the stability again begins to increase.

The dispersion stability in water is again dependent on the surfactant composition. In general, stability increases with decreasing PEO content and MW of the surfactant.

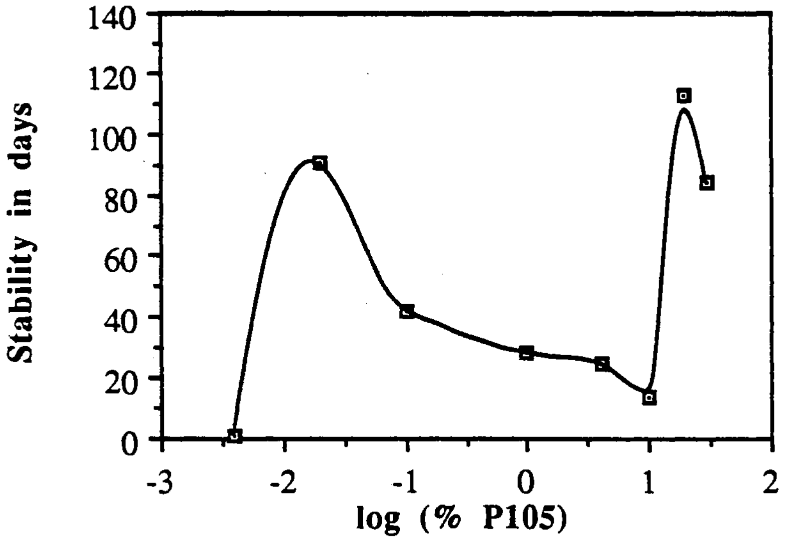


Figure 5. Stability of mercaptopropylsilica in water vs. log (% P105) where % P105 = g P105/g SiO_2 x 100.

Table VIII. Stability of Mercaptopropylsilica with Pluronic F38.

Dispersion	g polym/g SiO_2	Stability, d in ethanol	Stability, d in water	Sonication time for redispersion[a]
7a	0.0004	3-4	2	<3 h
7b	0.0002	3-4	5	<3 h
7c	0.001	7	14	<3 h
7d	0.00625	7	21	<3 h
7e	0.025	14	21	3-5 h
7f	0.063	4[b]	21	overnight
7g	0.125	unstable[b]	14	overnight
7h	0.19	unstable[b]	56	did not ppt
7i	0.25	unstable[b]	--	--

[a] Sonication time required to redisperse particles in water after they precipitated during the transfer to water. [b] Before transferring these samples to water, enough water was added to the dispersion in ethanol so that it could be redispersed by sonication.

Table IX. Stability of Mercaptopropylsilica with Pluronic F68.

Dispersion	g polym/g SiO_2	Stability, d in ethanol	 in water	Sonication time for redispersion[a]
8a	0.001	3	10	<3 h
8b	0.00625	3	14	<3 h
8c	0.025	1	14	3-5 h
8d	0.063	unstable[b]	14	overnight
8e	0.125	unstable[c]	--	--
8f	0.19	unstable[b]	42	did not ppt
8g	0.25	unstable[b]	42	did not ppt

[a] Sonication time required to redisperse particles in water after they precipitated during the transfer to water. [b] Before transferring these samples to water, enough water was added to the dispersion in ethanol so that it could be redispersed by sonication. [c] Precipitated during reaction and could not be redispersed.

Table X. Stability of Mercaptopropylsilica with Pluronic F87.

Dispersion	g polym/g SiO_2	Stability, d in ethanol	 in water	Sonication time for redispersion[a]
9a	0.00004	2-3	14	5 h
9b	0.0002	14	14	5 h
9c	0.001	7	70	overnight
9d	0.00625	4[b]	21	overnight
9e	0.025	2[b]	2	overnight
9f	0.063	unstable[b]	2	overnight

[a] Sonication time required to redisperse particles in water after they precipitated during the transfer to water. [b] Before transferring these samples to water, enough water was added to the dispersion in ethanol so that it could be redispersed by sonication.

Table XI. Stability of Mercaptopropylsilica with Pluronic P105.

Dispersion	g polym/g SiO_2	Stability, d in ethanol	in water	Sonication time for redispersion[a]
10a	0.00004	2-3	1	1 h
10b	0.0002	14	91	1 h
10c	0.001	21	42	1 h
10d	0.01	63	28	<3 h
10e	0.04	86	25	3 h
10f	0.10	69	14	overnight
10g	0.20	66	120	did not ppt
10h	0.30	56	84	did not ppt

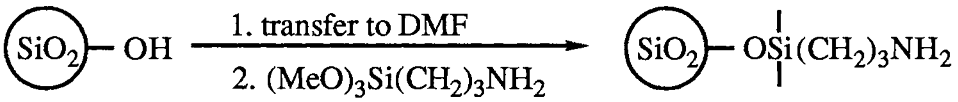
[a] Sonication time required to redisperse particles in water after they precipitated during the transfer to water.

Table XII. Surface Coverages of **7-10** Determined by Sulfur Analysis.

Dispersion	%S (mg-atom/g)	% reaction[a]
10b	3.31 (1.03)	98
9c	2.80 (0.87)	83
10g	2.63 (0.82)	78
7d	2.55 (0.80)	76
8b	2.44 (0.76)	72
10f	1.88 (0.59)	56

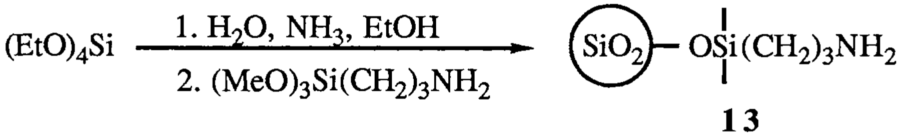
[a] % reaction is based on %S calculated from g S/(g SiO_2 + g $Si(CH_2)_3SH$) where g SiO_2 is the amount of silica that would be formed if all tetraethyl orthosilicate is completely hydrolyzed and g $Si(CH_2)_3SH$ assumes that the ethoxy groups on mercaptopropyltrimethoxysilane are completely hydrolyzed and the silane is all bound to the surface.

Table XII shows the mercaptopropyl surface coverage, determined by elemental analysis, for some of these dispersions. The final stability of the dispersion appears to have a large effect on the surface coverage obtained. Dispersion **10b** is the most stable and has a surface coverage of 1.03 mequiv/g, corresponding to 98% binding of the added mercaptopropyltrimethoxysilane. Dispersions **9c**, **7d**, and **8b** have intermediate stabilities and gave 72-83% binding of the silane. Dispersion **10f** is a sample at the minimum in stability for P105 and only 56% of the silane was bound. This suggests that there may be some particle clustering during the reaction, reducing the surface area which is readily available. The one exception to this trend is **10g** which has a stability close to that of **10b** but has lower surface coverage. But **10g** contains approximately 1000 times as much surfactant as **10b**, and surface coverage by the surfactant may decrease the surface area available for reaction with mercaptopropyltrimethoxysilane.



$$\text{SiO}_2\text{—OH} \xrightarrow[\text{2. (MeO)}_3\text{Si(CH}_2)_3\text{NH}_2]{\text{1. transfer to DMF}} \text{SiO}_2\text{—OSi(CH}_2)_3\text{NH}_2 \quad (10)$$

1a **12**



$$(\text{EtO})_4\text{Si} \xrightarrow[\text{2. (MeO)}_3\text{Si(CH}_2)_3\text{NH}_2]{\text{1. H}_2\text{O, NH}_3\text{, EtOH}} \text{SiO}_2\text{—OSi(CH}_2)_3\text{NH}_2 \quad (11)$$

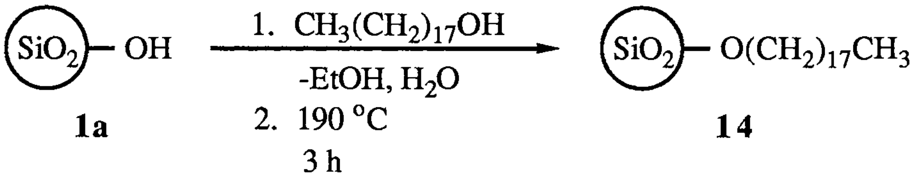
13

Aminopropylsilica. One method for preparation of aminopropylsilica is shown in Equation 10. This method is the same as the procedure reported in Chapter II for mercaptopropylsilica. Colloidal silica is formed in ethanol, transferred to DMF, and functionalized with aminopropyltrimethoxysilane to give **12**. N analysis shows 0.81 mequiv/g of bound aminopropyl.

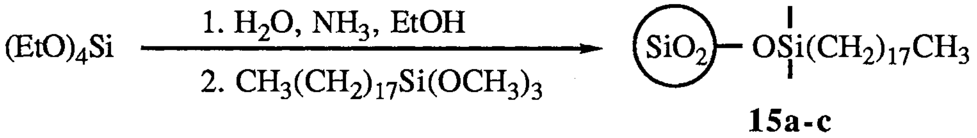
An easier synthesis of aminopropylsilica is given in Equation 11. It is a one-pot reaction for preparation of colloidal silica and modification with aminopropyltrimethoxysilane giving a surface coverage of 0.64 mequiv aminopropyl/g by N analysis.

In both syntheses, only 15-20% of the aminopropyltrimethoxysilane is bound to the silica. The remainder is removed by washing during the isolation of the silica. Because of this, 4.0 mmol/g of added aminopropyltrimethoxysilane is needed in the reaction to give surface coverages comparable to that obtained by adding 1.0 mequiv/g of other silanes. Apparently, aminopropyltrimethoxysilane reacts with the silica surface more slowly than other silanes.

Both of these methods give very stable dispersions in ethanol and the silica can be readily transferred to water. These ethanolic dispersions are not precipitated by adding acetone, acetonitrile, tetrahydrofuran, dimethylformamide, 1,4-dioxane, ethyl ether, toluene, or 2.0 M NaCl. They are precipitated by acidifying to pH 1.0 with 1.0 M HCl and adding acetone or by adding 1.0 M $CaCl_2$. Dispersion **12** is precipitated rapidly by adding a few drops of 1.0 M $CaCl_2$. Dispersion **13** precipitates slowly overnight after adding a four-fold excess (by volume) of 1.0 M $CaCl_2$. When the $CaCl_2$ was removed by washing with water, **12** and **13** began to redisperse even without agitation.



(12)



(13)

Octadecylsilica. Stabilization of colloidal silica in nonpolar solvents can be achieved by functionalizing with C_{18} chains. When the method previously reported by van Helden, Jansen, and Vrij[4] was repeated (Equation 12), a silica containing 6.65% C (5.54 mg-atom/g) resulted. It is stable in benzene, toluene, cyclohexane, and chloroform. Quantitative ^{13}C NMR showed 1.29 mequiv ethoxy/g and 0.19 mequiv C_{18}/g.

This method requires an approximately 40-fold excess of octadecanol and the reaction workup reported by van Helden requires several long ultracentrifugation steps. We found that the excess octadecanol could be removed by washing with 1,4-dioxane, and <5% of the octadecylsilica is lost in the process. Dioxane is a solvent for octadecanol, but it is not a good enough solvent to disperse the octadecylsilica. This provides a much easier method to purify the octadecylsilica.

Van Helden's synthesis of octadecylsilica gives C_{18} groups attached as esters which can be hydrolyzed. Van Helden[4] reports that if the dry powder is exposed to air, the atmospheric moisture can hydrolyze the C_{18} esters. This method also requires a multiple step synthesis. In order to improve the synthesis, the one-pot synthesis shown in Equation 13 was developed. During this synthesis, the octadecylsilica precipitates. But unlike mercaptopropylsilica, which formed an undispersible gel when formed in ethanol without a stabilizer, the octadecylsilica was readily redispersable. This is very convenient in the workup of the reaction, because the solvent can be decanted away, the octadecylsilica purified by washing with dioxane, and then redispersed.

Stable dispersions resulted when 0.5 (**15a**) or 1.0 (**15b**) mmol C_{18}/g SiO_2 was incorporated in the reaction. But with 3.0 mmol C_{18}/g SiO_2, the octadecylsilica could not be redispersed. Samples **15a** and **15b** contained 10.03% C (8.35 mg-atom/g) and 16.38% C (13.64 mg-atom/g). Quantitative ^{13}C NMR showed that **15a** contains 0.36 mequiv C_{18}/g and 0.11 mequiv ethoxy/g. Octadecylsilica **15b** contains 0.86 mequiv C_{18}/g and 0.23 mequiv ethoxy/g.

Analysis of Surface Modified Silicas. Quantitative ^{13}C NMR data was obtained using direct polarization and magic-angle-spinning. The %C detected in the samples is compared with results from elemental analysis and ^{13}C NMR obtained using cross polarization in Table XIII. %C from direct polarization NMR is close to that from elemental analysis when errors in drawing the baseline are taken into consideration. With cross polarization NMR, it is clear that not all C in the sample is detected. Figures 6 and 7 show the ^{13}C spectra of octadecylsilica **14** obtained by cross polarization and direct polarization, respectively. The C_{18} is expected to give peaks around 60 ppm (C(1)), 26 ppm (C(2) and C(17)), 30 ppm (C(3) - C(16)), and 12 ppm C(18). The peak at 17 ppm and part of the peak at 60 ppm are due to ethoxy and the peak at 85 ppm is due to the internal standard, delrin. In the cross polarization NMR spectrum (Figure 6), there is no peak at 12 ppm due to the terminal CH_3 of the C(18) chain. By comparing the areas of the peaks

TABLE XIII. %C Determined by Elemental Analysis, Cross Polarization ^{13}C NMR, and Direct Polarization ^{13}C NMR.

Sample	Elem. Anal.	Cross Polarization	Direct Polarization
10b	6.04	4.2	5.2
13	4.07	2.4	3.9
14	6.65	4.4	7.1
15a	10.0	4.0	8.2
15b	16.4	6.9	19.2

at 17 ppm and 60 ppm, the ethoxy contribution to the peak at 60 ppm can be determined, and from this, the peak area due to C(1) of octadecyl can be calculated. When the C(1) peak area in the cross polarization spectrum is compared to the peak area due to C(2)-C(18), it is found that C(1) contributes 1/4 of the total area due to octadecyl rather than 1/18. Apparently, only the carbons having reduced mobility because they are near the silica surface are being detected by cross polarization. When direct polarization is used, C(1) contributes 1/19 of the octadecyl peak area, which is close to the expected value and within experimental error for the peak area determination.

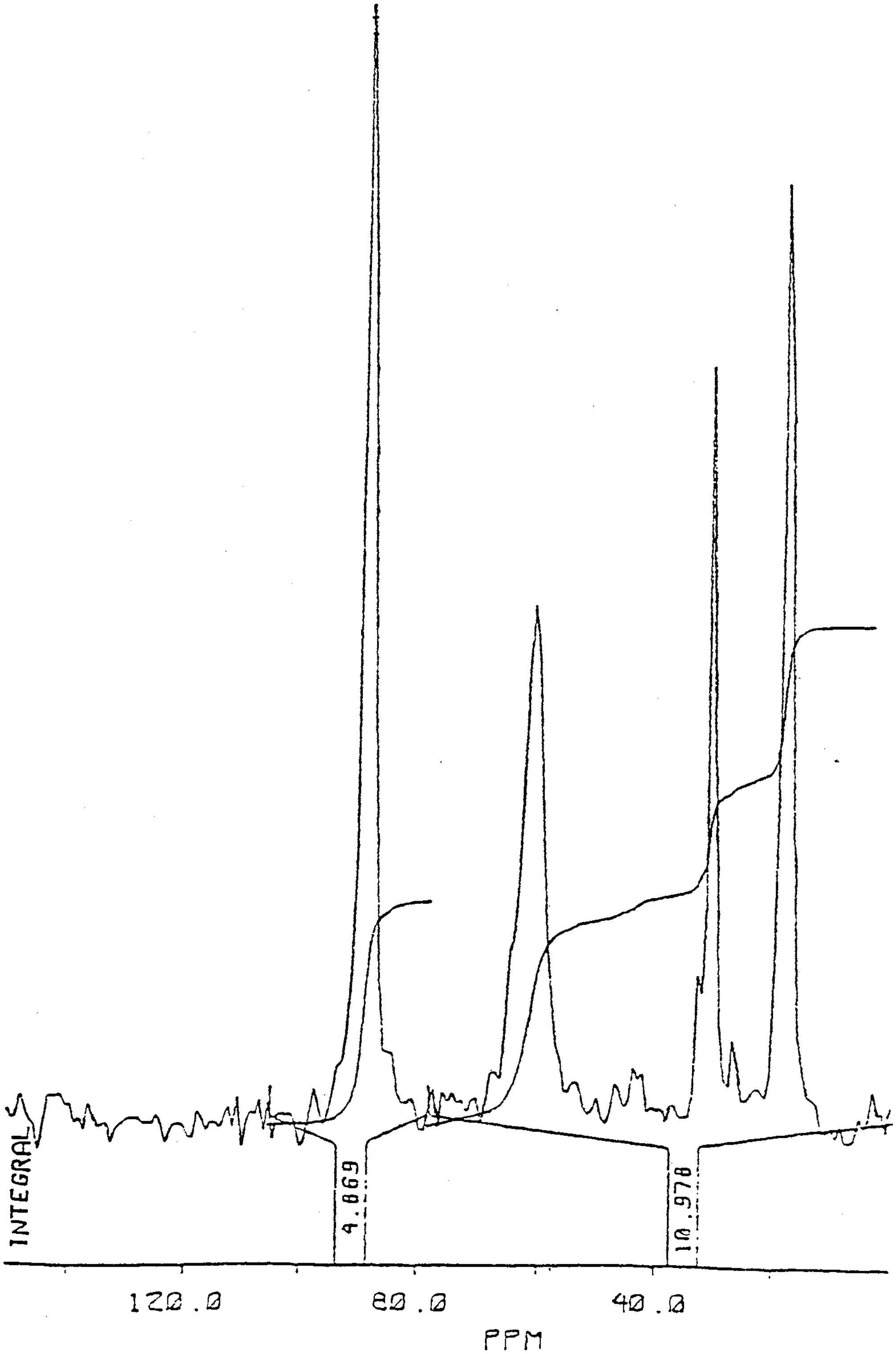


Figure 6. Cross polarization ^{13}C NMR spectrum of **14**.

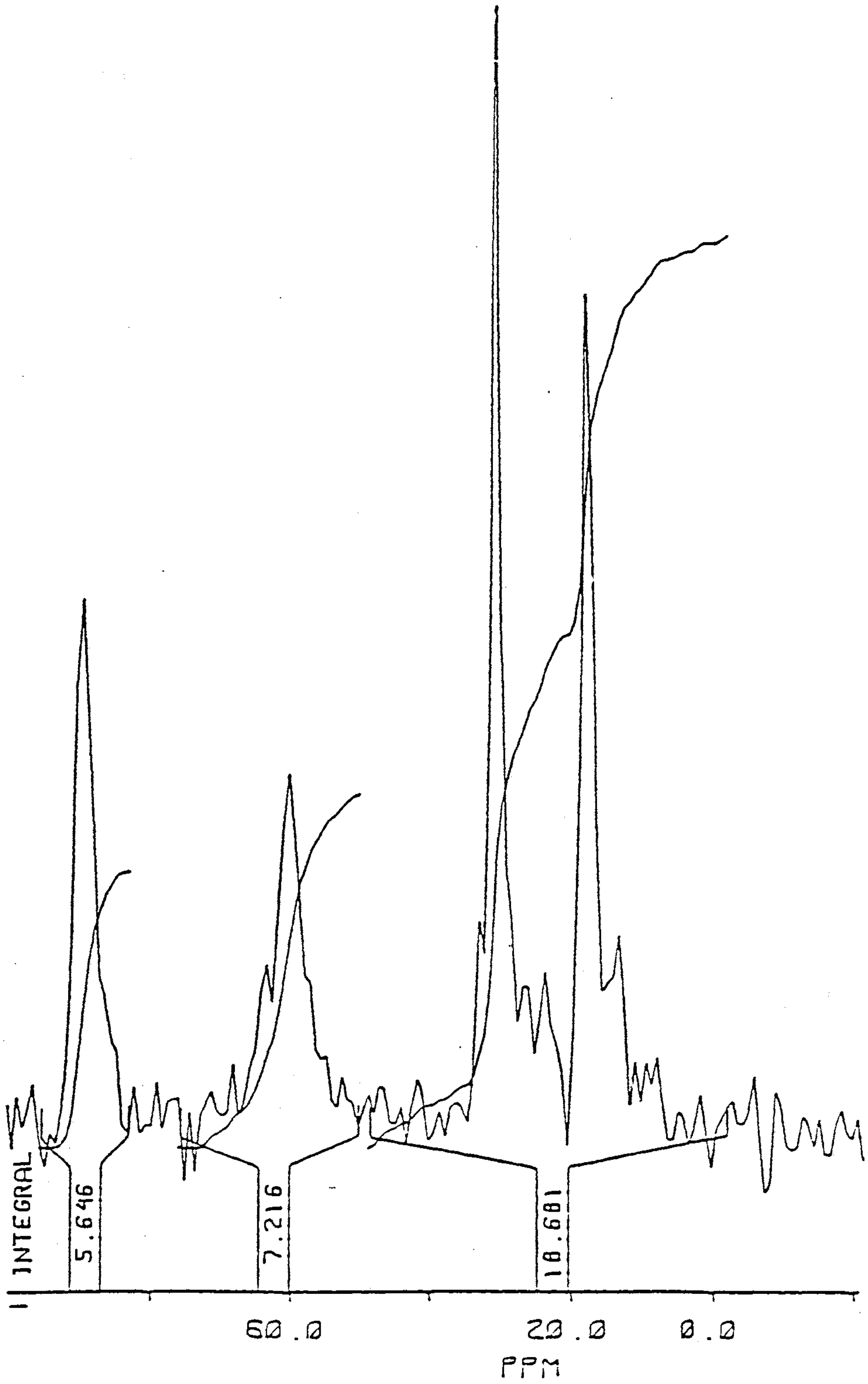


Figure 7. Direct polarization ^{13}C NMR spectrum of **14**.

Table XIV. Quantitative ^{13}C NMR Results.[a]

Sample	Ethoxy	Other
10b	17.8, 61.4 ppm (0.48 mequiv/g)	12.9, 28.6 ppm $(CH_2)_3SH$ (0.90 mequiv/g) 14.3, 31.5, 44.0 ppm $((CH_2)_3S)_2$ (0.22 mequiv/g)
13	---	10.4, 22-27, 36-46 ppm $(CH_2)_3NH_2$ (1.06 mequiv/g)
14	19.1, 60.6 ppm (1.29 mequiv/g)	13.7, 24.1, 32.0, 33.2, 63.5 ppm $C_{18}H_{37}O$ (0.19 mequiv/g)
15a	18.8, 60.6 ppm (0.23 mequiv/g)	15.3, 24.8, 32.3 ppm $C_{18}H_{37}Si$ (0.86 mequiv/g)
15b	19.5, 59.8 ppm (0.11 mequiv/g)	15.8, 24.5, 32.4 ppm $C_{18}H_{37}Si$ (0.36 mequiv/g)

[a] ^{13}C spectra were obtained using direct polarization and magic-angle-spinning.

The results of direct polarization ^{13}C NMR analysis are given in Table XIV. These results show that octadecylsilica prepared from octadecyltrimethoxysilane has a much higher C_{18} surface coverage and lower ethoxy content (Samples **15a** and **15b**) than octadecylsilica prepared by esterifying the surface with octadecanol.

With aminopropylsilica **13**, ^{13}C NMR shows a much higher aminopropyl content than N analysis. There are two possible explanations for this. The NMR spectrum of **13** contains broad peaks due to partial protonation of the amine during the colloid precipitation.[19] These broad lines result in higher error in the peak area determination. Elemental analysis may also contain errors due to incorporation of N into the silica during combustion.

All other NMR analyses in Table XIII are within experimental error of the carbon analysis results. Elemental and NMR analysis of mercaptopropylsilica **10b** gave 1.03 and 1.12 mg-atom S/g, the same within experimental error.

Quantitative ^{29}Si NMR analysis of colloidal silica esterified with octadecanol (**14**) gave 4.3% Q_2, 42.2% Q_3, and 53.5% Q_4 silicon atoms. This is very similar to that found for its precursor, colloidal silica **1a**, with an increase of 4.2% Q_3 and a decrease of 4.3% Q_4, even though **14** was heated to 190 °C during synthesis. TGA shows that a large fraction of the ethoxy content is lost from colloidal silica **1a** when it is heated to 200 °C. But these ^{29}Si NMR results suggest that the octadecanol traps ethoxy and prevents significant loss during the synthesis or the ethoxy groups are driven off to give silanol groups and very little crosslinking to siloxane occurs. Both of these possibilities are consistent with the ^{29}Si NMR spectrum. From the elemental analysis of **1a** and the quantitative ^{13}C NMR spectrum of **14**, the ethoxy contents are 1.03 and 1.29 meqiv/g, respectively. This leads to the conclusion that ethoxy groups are not lost during the synthesis.

^{29}Si NMR shows that when silica is reacted with octadecyltrimethoxysilane to form **15b**, the silica now contains 2.8% Q_2 (-91.3 ppm), 37.3% Q_3 (-100.7 ppm), and 59.8% Q_4 (-110.0 ppm) (Figure 8). This is a slight decrease in Q_2 and increase in Q_4 over the

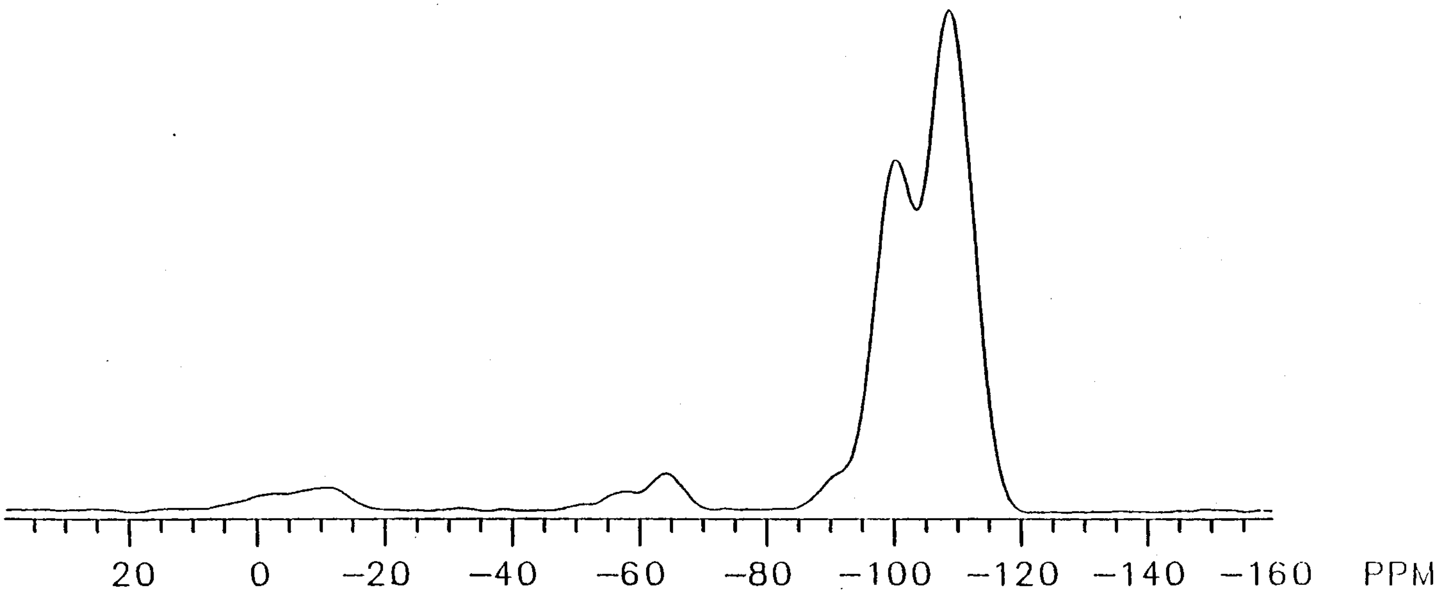


Figure 8. Quantitative ^{29}Si NMR spectrum of **15b**.

unmodified colloidal silica **1a**. This is to be expected since the surface groups are reacting with the trimethoxysilane to increase the number of siloxane bonds. The octadecylsilane is bound to the surface by either one (-50.5 ppm), two (-57.1 ppm), or three (-64.6 ppm) siloxane bonds in relative ratios of 6.9%, 29.6%, and 63.5%, respectively.

Colloid particle sizes are reported in Table XV. It is apparent from this data that incorporation of polymers or trimethoxysilanes after 5 h into the tetraethyl orthosilicate hydrolysis reaction has no effect on the final particle size or monodispersity.

The elemental analyses and densities of the surface modified silicas are shown in Table XVI. The elemental analyses of mercaptopropylsilicas **7d** and **10b** were done at both Galbraith Laboratories and Phillips Petroleum Co. The Phillips analyses used special conditions to insure complete combustion, but they still gave lower %C and %H than the Galbraith analyses, especially with **7d**. However, the sulfur contents are very close. Since the Phillips analyses were done 9 months after the Galbraith analyses, the lower C and H contents may be due to loss of ethanol and water from the silica surface over long periods of time. Sulfur is not lost during storage because the mercaptopropyl groups are less volatile and bound through a more stable siloxane linkage. As expected, the density decreases as the surface coverage increases. All samples in Table XIV have densities that are 0.10-0.15 g/mL less than the density calculated by combining the densities of unmodified colloidal silica (2.06 g/mL) and the silanes bound to the surface. The only exception is **15b**, whose density is 0.25 g/mL less than the calculated density. Bogush, Tracy, and Zukoski[12] previously measured a density of 1.9-1.95 g/mL by helium pycnometry for a sample prepared similarly to octadecylsilica **14**. Moonen, de Kruif, Vrij, and Bantle found a density of 1.77 ± 0.05 g/mL for octadecylsilica possessing a higher carbon content of 8.63%. Our lower density could be due to acetonitrile not penetrating into the sample as well as helium. But as shown in Table XVI, using a less polar solvent, toluene, has no effect on the measured density. If these solvents are not penetrating into the sample, it must be due to their larger size when compared to helium.

TGA analysis of the modified silicas gave thermograms very similar to that for unmodified silica up to approximately 350 °C where a more rapid decrease in weight began, presumably due to loss of surface functional groups. The one exception was octadecylsilica **14**, which had a sharp drop in weight beginning at 240 °C. The TGA thermograms are summarized in Table XVII.

Table XV. Number Average (D_n) and Weight Average (D_w) Particle Diameters of Surface Modified Colloidal Silicas.

Sample	D_n	D_w
Mercaptopropylsilica		
7d	56.9	58.2
8b	59.4	62.4
9c	58.3	59.7
10b	57.5	59.3
10f	62.3	64.4
10g	59.9	61.7
Aminopropylsilica		
12	58.3	59.9
13	58.1	59.5
Octadecylsilica		
14	58.9	62.3
15a	58.2	60.2
15b	59.5	61.1

Table XVI. Elemental Analyses and Densities of Surface Modified Colloidal Silicas.

Sample	%C	%H	%S	%N	Density, g/mL
Mercaptopropylsilica					
7d[a]	6.29	2.17	2.55		1.83
7d[b]	3.59 ± 0.13	1.69 ± 0.04	2.54 ± 0.15		
8b	5.28	2.11	2.44		1.90
9c	5.66	1.89	2.80		1.87
					1.84[c]
10b[a]	6.04	2.06	3.31		1.78
10b[b]	5.77 ± 0.07	1.69 ± 0.01	3.30 ± 0.01		
10f	6.07	1.93	1.88		1.84
10g	7.25	2.25	2.63		1.91
Aminopropylsilicas					
12	6.11	2.29		1.13	1.88
13	3.79	2.04		0.90	1.96
Octadecylsilicas					
14	6.65	2.26			1.75
					1.76[c]
15a	10.03	2.81			1.76
15b	16.38	3.63			1.58
					1.59[c]

Table XVI (Continued)

---

[a] Elemental analysis done at Galbraith Laboratories. [b]Elemental analysis is the average of two runs done at Phillips Petroleum Co. [c]Density was measured by pycnometry using toluene as a solvent. All other density measurements were done using acetonitrile.

Table XVII. TGA Results.

Sample	Weight Loss (%)[a] 30-350 °C	 350-390 °C
Mercaptopropylsilica		
7d	4.66	10.00
8b	4.82	9.03
9c	3.26	8.85
10b	2.63	12.26
10f	3.79	7.31
10g	4.05	12.79
Aminopropylsilica		
12	4.36	9.14
13	4.12	7.27
Octadecylsilica		
14	2.49[b]	11.43[c]
15a	6.25	11.71
15b	4.40	20.72

[a] Heating rate = 20 °C/min. [b] 30-240 °C. [c] 240-900 °C.

DISCUSSION

Colloidal Silica. Stober's synthesis[1] provides an easy method for preparing spherical, monodisperse colloidal silica. The particle sizes in Table XV show that the results of the reaction are reproducible giving approximately the same particle size and size distribution each time. If more spherical or more monodisperse particles are desired, either larger particles can be used or the seed growth technique can be used for preparation of monodisperse smaller particles. The seed growth technique also provides a method for synthesizing dispersions with higher silica contents.

The porosity of colloidal silica is a key question which must be addressed if colloidal silica is to be used as a catalyst support. If the particles are porous, some catalytic sites will be buried inside the pores increasing the mass transfer limitations to catalytic activity. One proposed method for particle formation during this synthesis suggests that initially <10 nm diameter particles are initially formed, followed by coagulation to give the final observed particles. This could produce pores due to interstices between the <10 nm particles. van Helden, Jansen, and Vrij[4] have reported measuring approximately 0.065 mL/g pore volume in 21 nm particles due to ultramicropores of less than 1.2 nm. Bogush, Tracy, and Zukoski[12] have calculated a particle porosity of 11-15% from the density difference of unmodified colloidal silica and colloidal silica esterified with octadecanol to fill any pores. For unmodified colloidal silica **1a** with an average particle size of 57.7 nm and density of 2.06 g/mL, we calculated a surface area of 50.5 m^2/g. The measured surface area was 67.4 m^2/g. This higher than expected surface area suggests that the particles may be porous. BET nitrogen desorption found no pores ≥2 nm in diameter. This still cannot rule out the ultramicropores reported by van Helden, Jansen, and Vrij. However, some of the increased surface area must be attributed to deviation of the particles from smooth spheres. The TEM shows that the particles have rough surfaces which account for some of the increase in surface area. We believe that if the particles are porous, the pores contribute little to the surface area. Therefore, when colloidal silica is used as a catalyst support, most or all of the active sites will be on the outer surface of the silica particles.

There are two proposed mechanisms for growth of colloidal silica particles. LaMer and Dinegar[20] hypothesize that there is a critical silicic acid concentration, C_{SAT}^*, above which particle nucleation occurs. C_{SAT}^* is significantly higher than the saturation concentration, C_{SAT}, above which spontaneous particle growth occurs provided that nuclei are available. Thus, early in the reaction, as hydrolysis of tetraethyl orthosilicate occurs, the silicic acid concentration exceeds C_{SAT}^* and nucleation occurs. After a sufficient number of nuclei are formed, particle growth permanently reduces the silicic acid concentration below C_{SAT}^* and only particle growth occurs after that point. If all nucleation occurs in a short time and all particles grow at the same rate, this would lead to monodisperse particles. Tan, Bowen, and Epstein[21] state that this mechanism explains why the particle size is inversely dependent on the reaction temperature. As the temperature is decreased, the rate limiting hydrolysis step becomes slower. It then takes a smaller number of nuclei to relieve the high supersaturation of silicic acid. Since fewer particles are nucleated, the final particle size must be larger, assuming that all tetraethyl orthosilicate reacts.

A second mechanism for particle growth was proposed by Bogush and Zukoski.[13] In order for colloidal particles to be stable, the interparticle repulsive forces must be larger than the van der Waal's attractive forces. For charged particles, the stability increases approximately linearly with particle size. So as small particles are formed at the first of the reaction, they are marginally unstable and will begin to aggregate in order to lower the interfacial free energy. As large clusters are formed, they will aggregate with freshly formed nuclei until they grow to a colloidally stable size. Since the smaller particles are less stable, they will grow more quickly. The monodispersity achieved in the final particles is thus due to size dependent aggregation rates.

By transmission electron microscopy, Bogush and Zukoski[22] have shown that nucleation occurs for at least the first 30% of the reaction time. For 0.17 M TEOS, 1.3 M ammonia, and 2.0 M water in ethanol, a mixture of large aggregates up to 100 nm in diameter and <10 nm nuclei are observed early in the reaction. As the reaction proceeds, the distribution becomes more narrow until finally monodisperse 200 nm particles are formed.

The rough surfaces in the TEM of small colloidal silica particles support the mechanism of Bogush and Zukoski. However, this aggregation mechanism should give highly porous silica particles due to the interstices between the <10 nm particles. Our results indicate that the particles are either nonporous or only slightly porous. It is possible that the true mechanism is a combination of aggregation and molecular growth, with the particles growing mostly by aggregation of nuclei, but enough reaction is occurring with monomeric silane to fill in the void spaces in the aggregates.

Table III shows that silica **1a** has a slightly higher density than silicas **1e** and **1g**. This difference is slightly greater than the random error in the density measurement. During the synthesis of **1e** and **1g**, higher water and ammonia concentrations were used, increasing the rate of particle growth. If the particles were growing by aggregation of nuclei, rapid particle growth could leave solvent-filled pockets in the interior of the particle. With silica **1a**, particle growth was slower, and the nuclei could rearrange to a more compact formation.

Steric Stabilization. Of the methods used for steric stabilization, adsorption of block copolymer surfactants and binding of trimethoxysilyl terminated PEGME give the shortest syntheses and most stable dispersions of surface modified colloidal silica. Adsorption of homopoplymers requires much more polymer than the other methods. Surface esterification with PEGME requires a longer synthesis and does not give a stable surface linkage. Attachment of trimethoxysilyl terminated PEGME gives a one-pot synthesis of surface modified colloidal silica. The disadvantage to this method is the polymer must react with the surface, increasing the required reaction time.

Adsorption of Pluronic surfactants also gives a one-pot synthesis of surface modified colloidal silica. The synthesis is shorter since the polymer does not react and this method requires the least amount of polymer of any of the attempted methods. Use of Pluronic P105, containing 50% PEO, gives highest stability as well as giving stable dispersions in ethanol, due to increased surfactant solubility in ethanol with higher PPO content. With lower PPO contents, the surfactant solubility in ethanol decreases and colloid stability in ethanol also decreases. The increased stability with lower MW when comparing Pluronics F38 and F68 is probably also due to solubility. The lower MW of F38 gives it more solubility and thus, higher stability. The effect of added polymer on the dispersion stability, shown in Figure 5, has been observed before for sterically stabilized dispersions.[23] Apparently, at low polymer concentrations, virtually all of the polymer adsorbs to the particle increasing the stability. At 0.02% P105, some of the polymer remains free in solution, which is known to decrease the stability of a sterically stabilized dispersion. As the amount of polymer is increased more, it reaches another critical concentration at 10% P105 where the stability again increases. When the unadsorbed polymer was recovered by ultrafiltration from mercaptopropylsilica dispersions containing 10% and 20% P105, it was found that the amount of adsorbed and unadsorbed P105 was 43.0 mg and 32.0 mg, respectively, for 10% P105 and 117.3 mg and 33.7 mg, respectively, for 20% P105. When solutions containing the same amounts of P105, but no silica, were passed through an ultrafiltration membrane, all of the P105 was found in the filtrate. So both dispersions may contain approximately the same amount of unadsorbed polymer. This suggests that virtually all polymer added above 10% P105 is adsorbing to the colloidal particles, building up a thick layer of adsorbed polymer, and increasing the stability.

For steric stabilization of surface modified colloidal silica, using conditions which give the maximum in stability at low polymer concentration (<2% polymer) will leave most of the surface free for surface modification reactions. This method for surface modification of colloidal silica should be useful for a wide variety of functional groups.

Aminopropylsilica. Both methods for preparation of aminopropylsilica give very stable dispersions. At pH <10, protonation of the amines may give a positive surface charge which accounts for the high stability of these dispersions. The one-pot synthesis gives a slightly lower surface coverage than the synthesis in DMF, but it also gives higher stability at least toward added salts. This higher stability and shorter synthesis makes it the method of choice.

Octadecylsilica. The reaction of colloidal silica with octadecyltrimethoxysilane provides several advantages over the octadecanol esterification reaction. It gives a short one-pot synthesis and a simple reaction workup. Surface coverage by octadecyl is 4.7 times greater with the one-pot synthesis and it gives a more stable siloxane linkage. Van Helden[4] reported that the colloidal silica esterified with octadecanol was hydrolytically unstable and our TGA results show it is also thermally less stable than the siloxane linkage. The ester groups are lost at 240 °C and the siloxane linkage is stable up to 350 °C.

REFERENCES

1. Stober, W.; Fink, A.; Bohn, E. *J. Coll. Interface Sci.* **1968**, *26*, 62-69.
2. Brinker, C. J.; Scherer, G. W. *J. Non.-Cryst. Solids* **1985**, *70*, 301-322.
3. Hench, L. L. In: *Ultrastructure Processing of Ceramics, Glasses, and Composites*; Eds: Hench, L. L.; Ulrich, D. R.; Wiley: New York, 1984, pp. 3-5.
4. van Helden, A. K.; Jansen, J. W.; Vrij, A. *J. Coll. Interface Sci.* **1981**, *81*, 354-368.
5. Bridger, K.; Fairhurst, D.; Vincent, B. *J. Coll. Interface Sci.* **1979**, *68*, 190-195.
6. Clark, J.; Vincent, B. *J. Coll. Interface Sci.* **1981**, *82*, 208-216.

7. Edwards, J.; Lenon, S.; Toussaint, A. F.; Vincent. B. *ACS Symp. Ser.* **1984,** *240*, 281-296.

8. Ben Ouada, H.; Hommel, H.; Legrand, A. P.; Balard, H.; Papirer, E. *J. Coll. Interface Sci.* **1988,** *122*, 441-449.

9. Bridger, K.; Vincent, B. *Europ. Polym. J.* **1980,** *16*, 1017-1021.

10. Stejskal, E. O.; Schaefer, J.; Steger, T. R. *Faraday Soc. Symp.* **1979,** *13*, 56.

11. Belton, P. S.; Cox, I. J.; Harris, R. K. *J. Chem. Soc., Faraday Trans. 2,* **1985,** *81*, 63-75.

12. Bogush, G. H.; Tracy, M. A.; Zukoski, C. F. *J. Non.-Cryst. Solids*, **1988,** *104*, 95-106.

13. Bogush, G. H.; Zukoski, C. F. In: *Proceedings of the Third International Conference on Ultrastructure Processing of Ceramics, Glasses, and Composites*; in press.

14. Assink, R. A.; Kay, B. D. *Mat. Res. Soc. Symp. Proc.* **1984,** *32*, 301-306.

15. Kay, B. D.; Assink, R. A. *Mat. Res. Soc. Symp. Proc.* **1986,** *73*, 157-164.

16. Iler, R. K. *The Chemistry of Silica*, Wiley: New York, 1979, p. 631.

17. *CRC Handbook of Chemistry and Physics, 62nd ed.*, **1981,***143*, cmpd. no. s111.

18. Iler, R. K. *The Chemistry of Silica*; Wiley: New York, 1979, p. 483.

19. Caravajal, G. S.; Leyden, D. E.; Quinting, G. R.; Maciel, G. E. *Anal. Chem.* **1988,** *60*, 1776-1786.

20. LaMer, V. K.; Dinegar, R. *J. Am. Chem. Soc.* **1950,** *72*, 4847-4854.

21. Tan, C. G.; Bowen, B. D.; Epstein, N. *J. Coll. Interface Sci.* **1987,** *118*, 290-293.

22. Bogush, G. H.; Zukoski, C. F. In: *Proceedings of the 44th Annual Meeting of the Electron Microscopy of America*; Ed: Bailey, G. W.; San Francisco Press: San Francisco, 1986, pp. 846-847.

23. Vincent, B.; Luckham, P. F.; Waite, F. A. *J. Coll. Interface Sci.* **1980,** *73*, 508-521.

VITA

Rickey Don Badley

Candidate for the Degree of

Doctor of Philosophy

Thesis: COLLOIDAL SILICA: SURFACE MODIFICATION AND CATALYSIS

Major Field: Chemistry

Biographical:

Personal Data: Born in Mooreland, Oklahoma, August 30, 1962, the son of Albert and Frances Badley.

Education: Graduated from Vici High School, Vici, Oklahoma, in May, 1980; received Bachelor of Science Degree in Chemistry from Southwestern Oklahoma State University in May, 1984; completed requirements for the Doctor of Philosophy Degree at Oklahoma State University in May, 1989.

Professional Experience: Teaching Assistant, Department of Chemistry, Oklahoma State University, August, 1984 to May, 1985; Research Assistant, Department of Chemistry, Oklahoma State University, June, 1985 to May, 1989.