

CHEMICALLY MODIFIED SURFACES



Edited by Joseph J. Pesek and Ivan E. Leigh

Chemically Modified Surfaces

Edited by

Joseph J. Pesek

San Jose State University, California, USA

Ivan E. Leigh

CertainTeed Corporation, Blue Bell, Pennsylvania, USA



Proceedings of a Symposium on Chemically Modified Surfaces
held in Malvern, Pennsylvania on 16–18 June 1993.

Special Publication No. 139

ISBN 0-85186-595-X

A catalogue record for this book is available from the British Library

© The Royal Society of Chemistry 1994

All Rights Reserved

No part of this book may be reproduced or transmitted in any form or by any means—graphic, electronic, including photocopying, recording, taping, or information storage and retrieval systems—without written permission from The Royal Society of Chemistry

Published by The Royal Society of Chemistry,
Thomas Graham House, Science Park, Cambridge
CB4 4WF

Printed in Great Britain by Bookcraft (Bath) Ltd.

Chemically Modified Surfaces

Preface

The Fifth Symposium on Chemically Modified Surfaces, as with previous symposia in this series, provided a forum for the presentation of new scientific contributions on the chemical modification of different materials, surface characterization, and other topics of current interest. In addition to traditional topics for this series - methods for characterizing oxide surfaces and industrial applications of surface modifications - this symposium featured a plenary lecture on conversion of oxide to hydride surfaces, as well as sessions on modifying polymer surfaces, modifying and characterizing catalysts, and surface studies on membranes and thin films. Publication of this Proceedings of the Chemically Modified Surfaces Symposium enables dissemination to a wider audience of the work presented and discussed at CertainTeed Corporation's Technical Center in Blue Bell, Pennsylvania, June 16-18, 1993.

The organizers acknowledge the cooperation of the participants, particularly those who submitted manuscripts for publication in the Proceedings. Special thanks are extended to session chairpersons, and to CertainTeed Corporation for its support of the Symposium.

Joseph J. Pesek
Ivan E. Leigh

Opening Remarks

Good morning! Welcome to the fifth biennial Symposium on Chemically Modified Surfaces. And welcome to CertainTeed's Leveque Technical Center.

As noted in the fliers that most of you have received over the last months, this Symposium continues the tradition established by Ward Collins and Don Leyden of providing a forum for the presentation of current work on the modification and characterization of surfaces. The topics will vary from meeting to meeting, reflecting the diversity of research areas encompassed by the broader concept "surface chemistry".

Typically, an academic person coordinates the technical program, an industrial person organizes the Symposium. This year Dr. Joseph J. Pesek of San Jose State University arranged the program, and I, with the help of a lot of people here, and thanks to the corporate sponsorship of CertainTeed, have made the meeting arrangements.

As some of you know, it has been touch and go over the last couple of months as to whether we would even hold the Symposium, due to lower than expected registration in the light of a very tight economic climate. Historic Philadelphia is a fitting venue for this year's Symposium, since Joe Pesek and I have felt a little like our Founding Fathers did at Valley Forge in the Winter of 1777! However, it's spring-time again, and we've persevered! Thanks for hanging in there with us. Speaking of Founding Fathers, I'm delighted that Ward Collins is with us today. It's good to see other veterans of this Symposium, along with our newcomers.

I want to acknowledge the support of Maurice Kelley, Manager of Technical Services, and Domenic Tessari, Vice-President of the Insulation Group's R&D Division, for making it possible for the Symposium to come to pass this year. Although we had originally planned to hold it elsewhere, we know you will enjoy the meeting facilities here and your accommodations at the Guest Quarters in Plymouth Meeting. I want to thank Claire Miller, IG R&D's Administrative Supervisor, for coordinating all the arrangements here and at the hotel. Our site manager, Mary Chantry, has arranged for the auditorium facilities as well as for special food services. And many of you have talked with Carolyn Everhardt, who has taken reservations, put together the meeting folders, and handled the multitude of tasks that need to be attended to for a meeting of this kind. She will continue to be our resource person for the duration of the Symposium. Thanks also to Anita Fariello for her help, especially with faxes!

You should each have a meeting folder. In addition, writing supplies (pads of paper, pens and pencils) are available. In the folder you will find the meeting program and abstracts. We should have an attendance list later on - probably tomorrow. For those curious about what CertainTeed does, there's a "fact sheet" included. Also some fliers from VSP, who put out the Journal of Adhesion Science and Technology. Their books in honor of Drs. Pluedemann and Fowkes should be of particular interest to this group.

If you'll turn to the meeting program and abstracts fascicle now, I'd like to review the events coming up. These are on the yellow pages in that fascicle. For Wednesday - today - we'll be starting in shortly with the plenary lecture. For the remainder of the morning the topic will be "Modification of Polymer Surfaces". After lunch we'll spend the afternoon on "Membranes and Thin Films". There should be ample time for discussion of each presentation, and discussions can be continued informally at break time. Lunches will be held in the Whitpain Room, on the other side of the building. Mrs. Everhardt will be with us at breaks; let her know if you have any special needs. We have a board set up outside the auditorium for messages of a non-emergency nature, as well as sign-up sheets. Also, if you'd like to have dinner with a group of us at the hotel tonight (probably at 6:30), please sign up on that sheet by afternoon break.

Thursday's program includes papers on "Modification and Characterization of Catalysts" in the morning, followed by "Industrial Applications of Modified Surfaces" in the afternoon. If we finish up early, you may wish to go back to the hotel, but be sure to be back for happy hour and our Symposium dinner at six in the Whitpain Room!

On Friday we'll wrap up with the session on Characterizing Oxide Surfaces.

A limo back to the hotel will be available at the end of each meeting day.

It is now my great pleasure to introduce the program chairperson and plenary speaker for the Symposium, Dr. Joseph J. Pesek. Dr. Pesek took his Bachelor's degree in Chemistry from the University of Illinois, and his doctorate in analytical chemistry from UCLA. After teaching at Northern Illinois University, he moved to San Jose State University in 1978 and has been there ever since. He is currently Professor of Chemistry and

Chairperson of the Chemistry Department. From 1991 to the present he has been a Dreyfus Scholar at San Jose State. He has also been Visiting Professor at Ecole Polytechnique in Paris, and at the University of Aix-Marseilles. He was recently in France and Japan on sabbatical. I don't know if he had a chance to drop in on our St. Gobain parent company's R&D facility near Paris, but I can assure him that he would be most welcome to visit there.

Dr. Pesek is at home teaching both analytical and inorganic chemistry, and has given graduate courses in separation methods, NMR, and FTIR as well. Those in the audience who attended 1991's Symposium will recall that Dr. Pesek spoke on the synthesis, characterization, and modification of hydride silica surfaces. Today, his Plenary Lecture will be on Conversion of Oxide Surfaces to Hydride Surfaces. Dr. Pesek ---

Ivan E. Leigh
Blue Bell, Pennsylvania

Contents

Opening Remarks <i>Ivan Leigh</i>	ix
Plenary Lecture - Conversion of Oxide Surfaces to Hydride Surfaces <i>Joseph J. Pesek</i>	1
New Synthetic Methodology for Grafting at Polymer Surfaces <i>David E. Bergbreiter</i>	24
The Synthesis and Properties of Mutually Interpenetrating Organic-Inorganic Networks <i>Bruce M. Novak, Mark W. Ellsworth, and Celine Verrier</i>	41
The Physisorption and Condensation of Aminosilanes on Silica Gel <i>Karl. C. Vrancken, P. Van Der Voort, K. Possemiers, P. Grobet, and E.F. Vansant</i>	46
Extraordinary Thermal Stabilization of Enzymes through Surface Attachment by Covalently Bound Phospholipids <i>K.M.R. Kallury and M. Thompson</i>	58
Ellipsometry, X-Ray Photoelectron Spectroscopy, and Surface Plasmon Resonance as Techniques for the Study of Chemically Modified Surfaces <i>John D. Brennan, R.F. De Bono, Krishna M.R. Kallury, and Ulrich J. Krull</i>	72
Spectroscopy of Evaporated and Langmuir-Blodgett Films of Gadolinium Bisphthalocyanine on Metal Surfaces <i>B. Berno, R. Aroca, and A. Nazri</i>	91
Surface Chemistry of Microporous Manganese Oxides <i>S.L. Suib, H. Cao, and W.S. Willis</i>	101
High Temperature Sorbents for Oxygen Supported on Platinum Modified Zeolites <i>Pramod K. Sharma</i>	109

Catalysts for Environmental Control <i>Ronald M. Heck and Robert J. Farrauto</i>	120
Mechanism of Surfactant-Assisted Increase in Coal Liquefaction Yields <i>Gregory S. Hickey and Pramod K. Sharma</i>	139
The Effect of Glass Fiber Surface Coatings on Fiber Strengths and the Distribution of Flaws <i>J.A. Gómez and J.A. Kilgour</i>	151
Stability and Reactivity of Dimethylethoxysilane <i>Richard E. Johnson and Douglas I. Ford</i>	164
Molecular Dynamics of Liquid Chromatography: Chain and Solvent Structure Visualization <i>Mark R. Schure</i>	181
^2H and ^{13}C NMR Studies of Reversed Phase Liquid Chromatographic Stationary Phases: Solvation and Temperature Effects <i>K.B. Sentell, D.M. Bliesner, and S.T. Shearer</i>	190
Spectroscopic and Chromatographic Characterization of a Self-Assembled Monolayer as a Stationary Phase <i>M.J. Wirth and H.O. Fatunmbi</i>	203
FTIR Study of Adsorption at the Silica/Solution Interface: Interaction of Surface Sites with Carbonyl Groups <i>J.-M. Berquier</i>	210
Subject Index	221

Plenary Lecture

Conversion of Oxide Surfaces to Hydride Surfaces

Joseph J. Pesek

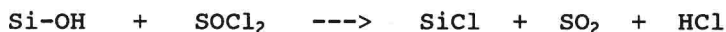
DEPARTMENT OF CHEMISTRY, SAN JOSE STATE UNIVERSITY,
SAN JOSE, CA 95192, USA

Oxides, particularly silica, being ubiquitous in nature have been used in many important chemical applications such as catalysts as well as separation media for various forms of chromatography^{1,2}. In most applications the essential feature of the oxide material is its surface. The surface activity and chemistry of any oxide material is dominated by the presence of free hydroxide groups. While the OH groups often are necessary for certain applications, they can often be detrimental in others. Therefore, a reliable method that can substitute another chemical entity for hydroxide while retaining some form of reactivity should prove useful in a wide variety of applications where an oxide material is desirable.

One such approach for the modification of oxide surfaces involves the conversion of hydroxide groups to hydrides³⁻⁸. For silica this overall process can be described as follows:



One method for accomplishing this conversion involves first chlorinating the surface with an appropriate reagent such as thionyl chloride:



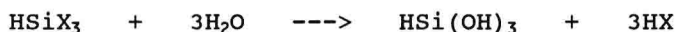
The halogenated surface can then be converted to the desired product via reduction by an inorganic hydride:



Unfortunately this approach (chlorination/reduction) has some serious limitations. First, it is extremely sensitive to moisture in each step and requires appropriate precautions which are both time-consuming and labor-intensive. Second, an efficient condensation apparatus (at dry ice temperature or below) is required to trap the relatively volatile reduction byproducts.

Another synthetic method for the production of

hydride surfaces involves the controlled chemisorption of silanetriol, $\text{HSi}(\text{OH})_3$, the hydrolysis product of a trisubstituted silane, on an oxide surface. The hydrolysis step can be described as follows:



After hydrolysis, the silanetriol is attached to an oxide surface, such as silica, by a series of condensation reactions that also involves cross-linking to adjacent silanols to form siloxane linkages similar to those existing on the substrate surface. Under carefully controlled conditions, this process should result in a monolayer formation on the surface in which the hydroxides are replaced by hydrides:



The basic process involves the same methodology used in typical silane-coupling procedures^{9,10}. Most often the hydride is replaced by an organic moiety and the reaction is then referred to as organosilanization. Organosilanization is the most frequently used reaction for modification of silica, and other oxide surfaces, used in chromatography, capillary electrophoresis, catalysis, and electrochemistry. Therefore, it is essential to evaluate the two approaches for the production of hydride surfaces as well as the ultimate usefulness of these materials as replacements for hydroxide surfaces.

There are several spectroscopic and thermal methods of analysis which can be used to characterize the hydride surface^{5,6,8}. Among the best is diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy. The Si-H stretching frequency for these materials is in the range of 2250-2260 cm^{-1} . This region of the infrared spectrum is generally free of interferences from other absorptions so it provides positive identification for the formation of the hydride surface. Some examples of the use of this method are given in Figure 1 for different sources of native silica. Each group of spectra is a comparison between the native material, the hydride formed from chlorination/reduction and the hydride formed from triethoxysilane (TES) silanization. For all the spectra where the hydride is present, a distinct strong band is seen at about 2259 cm^{-1} which represents the Si-H stretching absorption. In these spectra, as well as those representing silica from other sources, a semi-quantitative evaluation of the extent of hydride formation can be made from the intensity of the Si-H stretching peak. In every case, the intensity of the peak for the hydride formed from the TES reaction is significantly greater than for the peak in the spectrum of the material formed in the chlorination/reduction process. Another feature of the DRIFT spectra which should be noted involves the isolated-silanol absorption

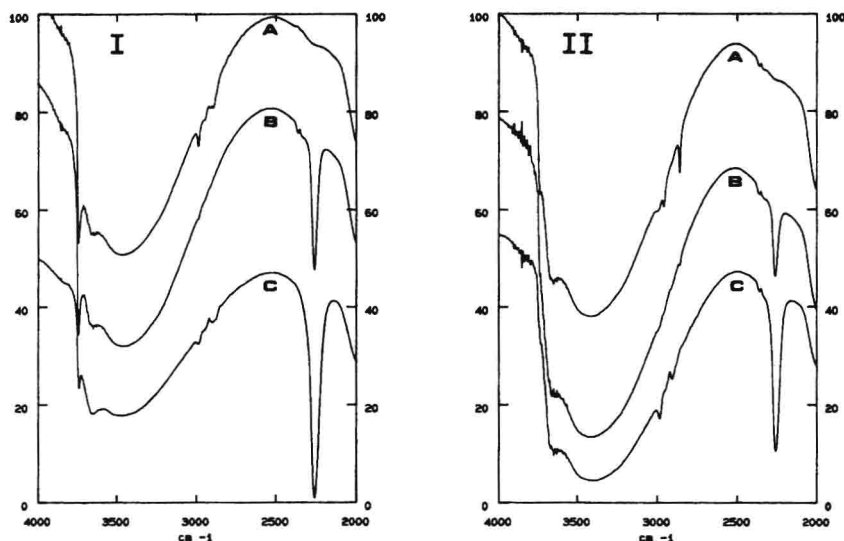


Figure 1 Partial Drift Spectra of hydride modified silicas: (I) Partisil-40; (II) Vydac TP. Curves: (A) native silica; (B) chlorination/reduction product; (C) TES silanization product

band at 3739 cm^{-1} . Again in every case the intensity of this band is lower for the hydride material formed from the TES reaction. This is an important feature since isolated silanols are mainly responsible for both poor chromatographic and electrophoretic performance when certain solutes such as bases are separated by these methods.

Another useful spectroscopic method for characterizing modified surfaces is cross-polarization magic-angle spinning (CP-MAS) NMR. It is possible to make the same comparison using Si-29 CP-MAS NMR between the native silica, the chlorination/reduction product and the TES reaction product that was done by DRIFT. Figure 2 shows an example of such a comparison using the same batch of native silica. The peaks observed in the spectrum for the native material (A) are those which have been reported previously for many types of silica. They include the peak representing the siloxanes [Q_4 , $\text{Si}^*(\text{OSi}\equiv)_4$] at -110 ppm , single silanols [Q_3 , $\text{HOSi}^*(\text{OSi}\equiv)_3$] at -100 ppm and geminal silanols [Q_2 , $(\text{OH})_2\text{Si}^*(\text{OSi}\equiv)_2$] at -90 ppm . When the surface is modified by the chlorination/reduction procedure two additional peaks appear in the spectrum (B). These peaks are due to the $\text{HSi}^*(\text{OSi}\equiv)_3$ resonance at -84 ppm and the $\text{HSi}^*(\text{OH})(\text{OSi}\equiv)_2$ resonance at -74 ppm . These same two peaks also appear in the Si-29 CP-MAS NMR spectrum (C) of the hydride product from the TES reaction but are much more intense than in the chlorination/reduction spectrum. As in the DRIFT spectra, it can be concluded from the solid state NMR results that the TES reaction produces a

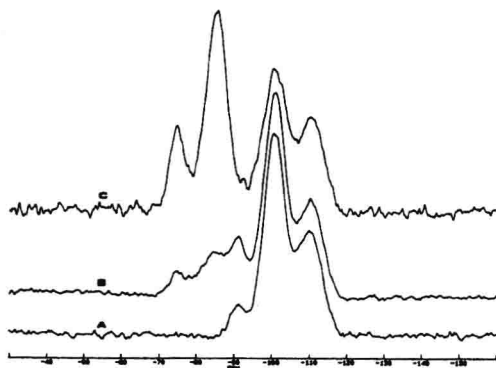
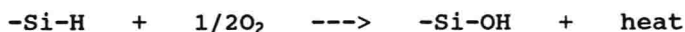


Figure 2 Si-29 CP-MAS NMR spectra of Partisil-40 silicas: (A) native silica; (B) chlorination/reduction product; (C) TES silanization product

higher concentration of hydride on the surface than the chlorination/reduction method.

Further characterization of the hydride material is possible through thermal methods of analysis. Both DSC and TGA can be used to detect the following reaction of the hydride material:



Some examples of typical DSC curves from two sources of native silica are shown in Figure 3. As in the

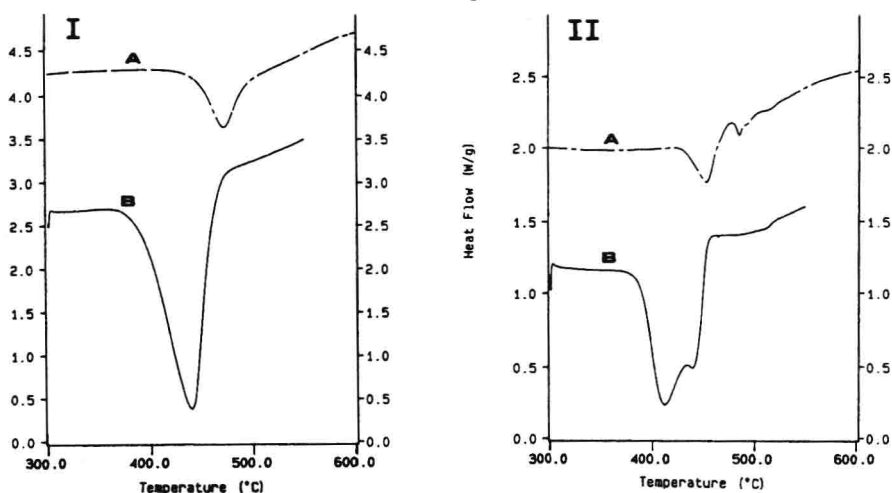


Figure 3 DSC curves of hydride-modified silicas in air: (I) Partisil-40; (II) Vydac TP. Curves: (A) chlorination/reduction production; (B) TES silanization product

spectroscopic methods, the DSC peak for the TES reaction is larger than for the corresponding peak from the chlorination/reduction method. There is a slight

displacement (20-30°) of the peak maximum to lower temperature for the TES material. This shift may be due to a slight excess over a monolayer (polymerization) on the surface. For the Vydac material a second peak appears in the DSC curve for both the chlorination/reduction process and the TES reaction. The origin of this second peak is not known but may be the result of a more heterogeneous surface that affects the thermal decomposition process. However, for both types of silicas it is clear that the amount of hydride on the surface is greater for the TES modification method.

Exact quantitative determination of the amount of hydride on the surface can be done by placing the material in a very strong base which will liberate hydrogen gas⁸. The hydrogen gas can be collected and the quantitative measurement is made by peak area determinations from the gas chromatogram. With a good standardization procedure, the precision of the determination is about 2-4% relative standard deviation. Knowing the surface area from BET measurements, the SiH surface concentration can be calculated from the gas chromatographic data. The original SiOH surface concentration can be determined from TGA data on the native material and a comparison between the two surface concentrations, $[\text{SiH}]/[\text{SiOH}] \times 100$, will then allow the determination of the percent of silanols that were converted to hydrides. Some results for these conversion efficiencies on several types of silica using both methods are shown in Table 1. It can be clearly seen from the results in the table that the TES silanization method is superior to the chlorination/reduction procedure on all types of silica. Except for Vydac silicas, this efficiency is generally close to 100% for the TES product. The low values for the efficiency on Vydac silica may be due to a material with many micropores which are not measured by the BET method but contain OH-groups resulting in a low surface area measurement or perhaps strongly adsorbed water which could lead to abnormally high surface-SiOH densities. Either one or a combination of these two situations would lead to a low efficiency determination.

The hydrogen displacement/gas chromatography method (HD/GC) is a rather tedious and time-consuming procedure for the determination of hydride content. Since the area

Table 1 Percent Hydride Modification Efficiencies

silica	chlorination/reduction product	TES silanization product
Partisil-40	24 (18) ^b	97
Partisil-10	23	79
Kromasil-100	23	126
Vydac TP (lot 1)	4	30
Vydac TP (lot 2)	6	35
Nucleosil 300-10	23	92

of the peak in the DSC thermogram is directly related to amount of hydride on the surface, it should be possible to estimate the SiH concentration from this data. A comparison between the DSC peak area and the specific SiH coverage determined from the HD/GC experiment is shown in Figure 4. While there is a high degree of correlation

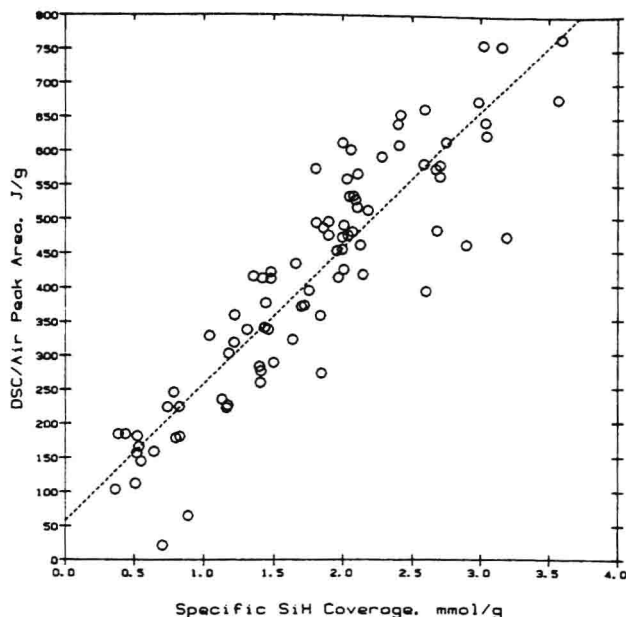


Figure 4 DSC/air peak as a function of surface coverage

between the two measurements, there is a considerable degree of uncertainty associated with the DSC results leading to the scatter in the data. Therefore, the DSC measurement can be used to give a good estimate of the SiH concentration on the surface but for an accurate determination the HD/GC method must be used.

In order for the final product to have reproducible properties and for the surface area and pore size to remain the same, it is necessary to control the reaction conditions of the TES silanization so that there is close to a monolayer coverage⁸. If there is less than a monolayer coverage, then a significant number of unreacted silanols will remain. If there is more than a monolayer coverage, then appreciable changes in the surface area and perhaps more importantly the pore size will occur. The primary factors in controlling the TES reaction are solvent, temperature, acid catalyst concentration and TES concentration. From solubility and upper temperature limit considerations, it was determined that dioxane was a suitable solvent for this reaction. Variable temperature studies indicate that as expected the rate of the reaction is accelerated by increasing the temperature so that conditions near the boiling point of

the solvent result in rapid production of the hydride surface. Similarly varying the acid concentration has demonstrated that about 100 mM HCl leads to rapid formation of the product without any significant decomposition. Finally, the concentration of TES is crucial in determining the extent of silanization on the surface. Figure 5 shows the extent of SiH coverage with respect to the concentration of TES for a one-hour reaction time, a 100 mM concentration of HCl using dioxane as the solvent at a temperature near the boiling point (gentle reflux). In both types of silica shown in

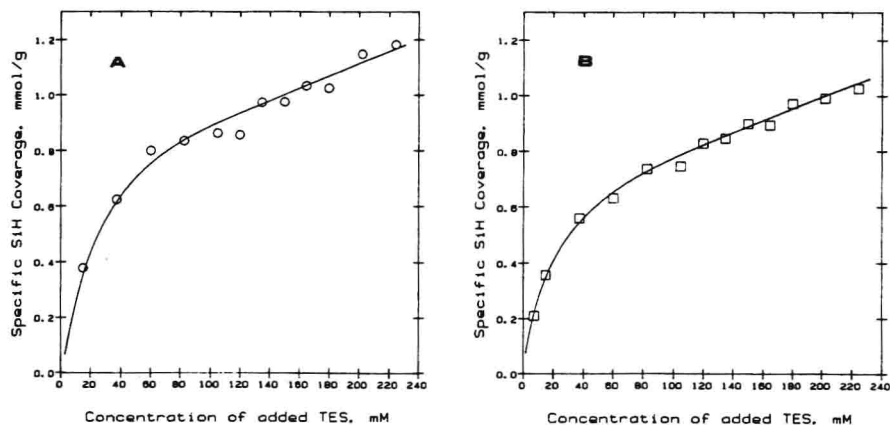


Figure 5 Specific SiH coverage as a function of TES concentration: (A) Vydac TP; (B) Nucleosil 300-10

these examples there appears to be two parts to the reaction curve. An initial rapid portion which reaches a limiting value corresponding to about 8-10 micromoles/m² which is the expected amount expect for monolayer coverage of hydride. The second slower portion of the curve probably corresponds to formation of a multilayer structure of the hydride polymer on the surface. Therefore, from this data it can be concluded that a concentration of about 100 mM TES will produce roughly a monolayer of hydride on the surface in a one-hour reaction time.

While the hydride surface is an interesting material in itself, most applications result from using this product as an intermediate for the attachment of various organic moieties to the surface^{6,7}. This can be accomplished through a heterogeneous-phase hydrosilation reaction such as the following:



The final product has a direct silicon-carbon linkage at the surface which has been shown to be more hydrolytically stable than the Si-O-Si-C linkage which results from organosilanization. The only other approach for making direct Si-C linkages involves two step