Grafting of Phosphonate Groups on the Silica Surface

and Characterization with Spectroscopic Methods

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ABSTRACT

The research presented here describes the synthesis and characterization of the phosphonate modified silica gel via the grafting approach. A new approach for the regioslective synthesis of ready-to-graft silylated phosphonates via the catalytic hydrosilylation reactions between the phosphonate with an olefin moiety and the alkoxysilane was developed. The one-step and multiple-step grafting processes were studied by the means of solid state ^{29}Si, ^{13}C and ^{13}P CP/MAS NMR. The mild cleavage of ethyl esters of phosphonate bonded on the silica surface was also investigated.

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LIST OF ABBREVIATIONS

Abbreviation	Description
cm	centimeter, 1×10^{-2} meter
^{0}C	degrees Celcius
CP/MAS	Cross Polarization with Magic Angle Spinning
Et	ethyl
g	gram
Hz	Hertz
J	coupling constant (in Hz)
kHz	kilohertz, 1×10^{3} Hertz
m	meter
Me	methyl
mg	milligram, 1×10^{-3} gram
min.	minute
ml	milliliter, 1×10^{-3} liter
mol	mole
M	mole per liter
mmol	millimole, 1×10^{-3} mole
MS	Mass spectroscopy
m/z	mass to charge ratio
nm	nanometer, 1×10^{-9} meter
NMR	Nuclear Magnetic Resonance

ppm	parts per million
s	second
THF	tetrahydrofuran
μg	microgram
μs	microsecond
δ	chemical shifts (in ppm)

Chapter One

Silica Gel and Its Surface

Because of useful properties such as high thermal, mechanical, chemical stability and high surface area[1], silica gel has many important applications in a number of fields on both laboratory as well as industrial scale such as selective adsorbents in chromatography, catalysis and polymer reinforcement. In most of these applications, silica gel is used as support materials, taking advantage of its surface properties.

Silica gel is made through sol – gel process, which is the most documented method for the preparing of silica. Generally speaking, this method involves five steps: 1) Hydrolysis of alkoxysilanes in the presence of acid as a catalyst,

$$RSiX_3 + 3H_2O \longrightarrow RSi(OH)_3 + 3HX$$
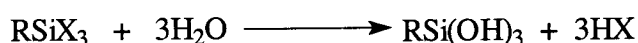
where X can be a hydrolytic labile group such as halide, alkoxy, acyloxy, etc and R can be the same group as X or any functional organic group. 2) Condensation or polymerization to form three dimensional siloxane networks.

$$nRSi(OH)_3 \longrightarrow (RSiO_{3/2})_n + (3/2)nH_2O$$
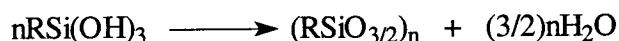
3) Gelation, the sol –gel conversion, as the polymeric network extends through the total volume, the sol thickens to a gel. 4) Aging, the gel is kept in contact with the pore–filling liquid and its structure and properties keep changing as a function of time. 5) Drying to remove the pore – filled liquid. Silica gel is usually classified according to the way in which it is dried. Xeroges is a gel from which the liquid medium has been removed resulting in a compressed structure and reduced porosity. Aerogels is a special form of

xeroges, from which the liquid has been removed in such a way as to prevent any collapse or change in the structure. Chung[2] et al's research shows that, in the manufacturing process, variables such as quantity of water usage, temperature, pH, choice of catalyst etc. and their corresponding magnitudes can dramatically change silica gel's surface properites including surface area, pore volume, average pore size and the number of silanol groups on its surface.

The term surface will be understood to mean the boundary of the nonporous solid phase[1]. By custom, the "surface" usually means the boundary that is impervious to nitrogen, the adsorbate most commonly used to measure the surface area. However, there are micropores into which water can penetrate, but not nitrogen. Since the area in micro-pores is difficult to define, the "surface" will generally be understood to mean that which is measured by the usual BET method of nitrogen adsorption. The BET (Brunauer-Emmet-Teller) method without doubt is the most widespread method in determining the specific area of solid substrates. It is based on a kinetic model of surface of the adsorption process by Langmuir, in which the surface of the solid is regarded as an array of ad-sorption sites.[3] But Langmuir's model is too complex to serve any practical purpose. Brunauer, Emmet and Teller made some simplifying assumptions to derive their famous BET equation:

$$\frac{P}{v_a(P_o-P)} = \frac{1}{v_m C} + \frac{(C-1)P}{v_m CP_o}$$

Where v_a is the number of moles adsorbed per gram adsorbent at gas pressure P, v_m is the monolayer capacity of surface, P_0 is the saturation pressure and C is the BET constant.

Using the monolayer capacity, the specific surface area (S_{BET}) can be easily calculated,

according to:

$$S_{BET} = v_m \, a_m \, N_A \cdot 10^{-20} \qquad (m^2 \cdot g^{-1})$$

With N_A the Avogadro number ($6.02 * 10^{23}$ molecules.mole^{-1}) and a_m the molecular

cross-sectional area of the gas molecule.

The ultimate particles which make up the silica can be regard as polymers of silicic

acid, consisting of interlinked SiO_4 terahedra.[4]At the surface, the structure terminates in

either a siloxane group (-Si-O-Si-) with the oxygen on the surface, or one of several

forms of silanol groups, e.g. single silanols (*Si-OH) or geminal/vicinal silanols [*Si-

(OH)$_2$]. In aqueous solution, monosilicic acid molecules might condense with the surface

to give attached silicon atoms with two or even three attached hydroxyl groups.
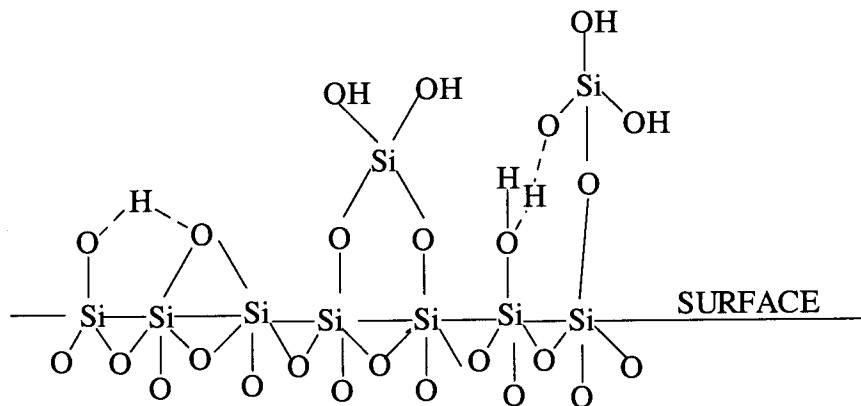
Figure 1

As shown in Figure 1, the silica surface consists of a combination of different types of

silanol groups and of siloxane bridges whose relative concentrations depend on the

calcination temperature as well as ambient humidity and storage time. Branda and coworkers[3] showed that the distribution of silanols on the silica surface are random by simulations based on the dehydration of crystalline β-crystaobalite. Single and geminal silanols on the silica surface can be linked through hydrogen bonds depending on the distance between the silanols and the local geometric structure. According to Vasant and coworkers[4], hydrogen – bonded silanols (vicinal silanols) can be further divided into weakly and strongly bonded silanols. The weakly bonded silanols, called internal or intraglobular silanols, occur in almost all kinds amorphous silica. These silanols in the silica matrix are believed to be inaccessible to water even through the distinction between inter and surface silanols is usually ambiguous. Hydrogen – bonded water or physisorbed water can be adsorbed onto all types of surface silanol groups. After removal of water from the silica surface, the surface reactions between the functional precursor and the silica will depend, among other factors, on the silanol concentration.

The silanol group content of silica can be determined by several different chemical or physical methods[4]. Root and coworkers[5] recently reported a simple and inexpensive physical method. They determined the total silanol group content of the silica by dynamic thermogravimetry (TG). The total number of hydroxy groups in silica is calculated from the entire second weight loss, which starts from the point where all physisorbed water is removed and ends at the point of highest temperature reached in the measurement. After comparing result of TG method with those of solid state NMR spectroscopy method[6, 7, 8], which is a well established method and more complicated and expensive, they claimed that, in most cases, the results of these two methods were in a good agreement, especially when the TG is operated under 550 ^{0}C.

Unfortunately, this method developed by Root and coworkers is unable to distinguish between the surface and bulk hydroxy groups. Zhuravlev[9] reported a method to determine the silanol number on the surface. His measurements were performed using a deuterium exchange method with mass spectrometric analysis. The deuterium exchange method showed the advantage that only surface hydroxyls can enter into the reaction of isotopic exchange and that structural water or intraglobular hydroxyls do not. According to Zhuravlev, the surface concentration of hydroxyl groups (silanol number), α_H, expressed in OH groups per nm^2, is determined as

$$\alpha_H = \delta_{OH} * N_A * 10^{-21} S^{-1}$$

where δ_{OH} is the concentration of hydroxyl groups (mmol.g^{-1}), and S is the specific surface area (m^2.g^{-1}). Based upon more than 100 samples, regardless of the origin and structural characteristics (specific surface area, type of pores, pore size distribution etc.) of the sample, Zhuravlev found that the silanol number for a fully hydroxylated silica is between 4.2 – 5.7 OH groups per nm.

Chapter Two

Chemically Modified Silica

Applications of pure silica are based on porosity, active surface, hardness, thixotropic and viscous characteristics. When the chemical structure of the silica surface is altered, these properties may be combined with specific chemical or physical interaction capacities. During the past 20 years, there has been an explosion of research based on combining or "immobilizing" a potentially useful chemical moiety (e.g. a catalytic center reaction center, or separation environment) on a silica surface[4]. The use of modified silica for applications such as high performance liquid chromatography (HPLC), and gas chromatography (GC) has been extensively investigated[10-12]. Indeed, it is from these systems that a major contribution towards the various techniques of modifying silica gels has arisen.

Recently, the research of using silica- supported reagents as alternatives to more traditional reagents and catalysts has seen increasing interest in green chemistry[13]. Some of the major goals of green chemistry are to increase process selectivity, to maximize the use of starting materials (aiming at 100% atom efficiency), to replace stoichiometric reagents with catalysts, and to facilitate easy separation of the final reaction mixture including the efficient recovering and recycling of reagents/ catalysts[14]. The use of solid catalysts can go a long way to achieving these goals[15]. Polymer – supported solid catalysts have been widely used[16], although they can suffer from limited thermo–oxidative stability. An emerging area of research which seeks to retain the green benefits of heterogenisation and enhanced activity and/or product selectivity while avoiding the drawbacks of catalyst instability and limited reusability, is the development and use as

catalysts of mesoporous inorganic support materials with chemically bound active

centers. The mesoporous nature and high thermal and chemical stability make silica a

potential promising replacement for traditional polymer–supported catalysts and reagents.

There are a variety of methodologies in which organic functionalities can be

chemically attached to a silica surface. Generally, these methods can be divided into three

groups: 1. Grafting, through the reaction between organosilanes or organic molecules and

the silica surface functional groups (usually silanols, Si-OH), 2. Chlorination of the silica

surface followed by reaction of Si-Cl with an appropriate functional molecule/ reactant

(usually a Grignard reagent), 3. Sol – gel process, incorporation of functional groups via

sol–gel methodology followed by (where necessary) post modification.

1. Grafting:

As previously mentioned, modification of silica gels has been developed mainly for

chromatography applications. The first method was developed by Halasz and Sebastian[17]

in 1969. This involved treating an aliphatic alcohol with the silanol groups of the silica

gel (Figure 2), resulting in the formation of a Si-O-C bond.
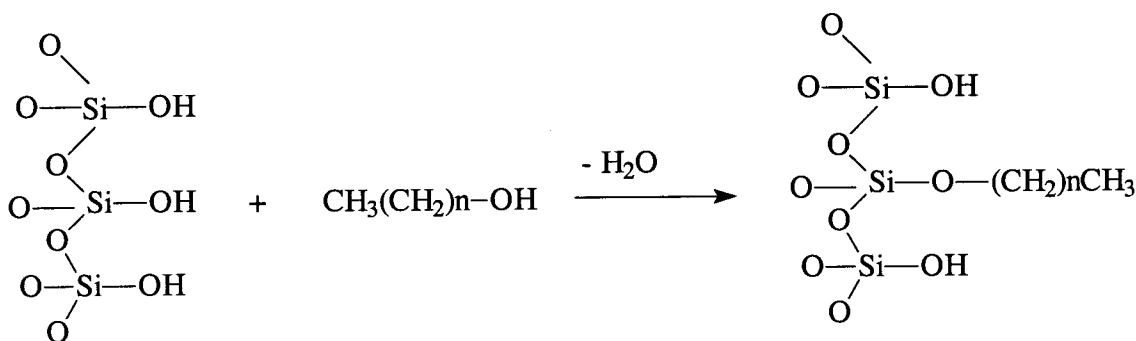
Figure 2   silica gel modification with aliphatic alcohols

Despite exhibiting some good separations in HPLC, this bond is not stable and readily

cleaved under water especially acidic or basic elution conditions[18-20].

An alternative methodology is to treat the surface hydroxyls with organosilanes to

yield an Si-R functonality attached to the silica through an Si-O-Si (siloxane) linkage

(Figure 3), which is more thermally and chemically robust than the Si-O-C bond.
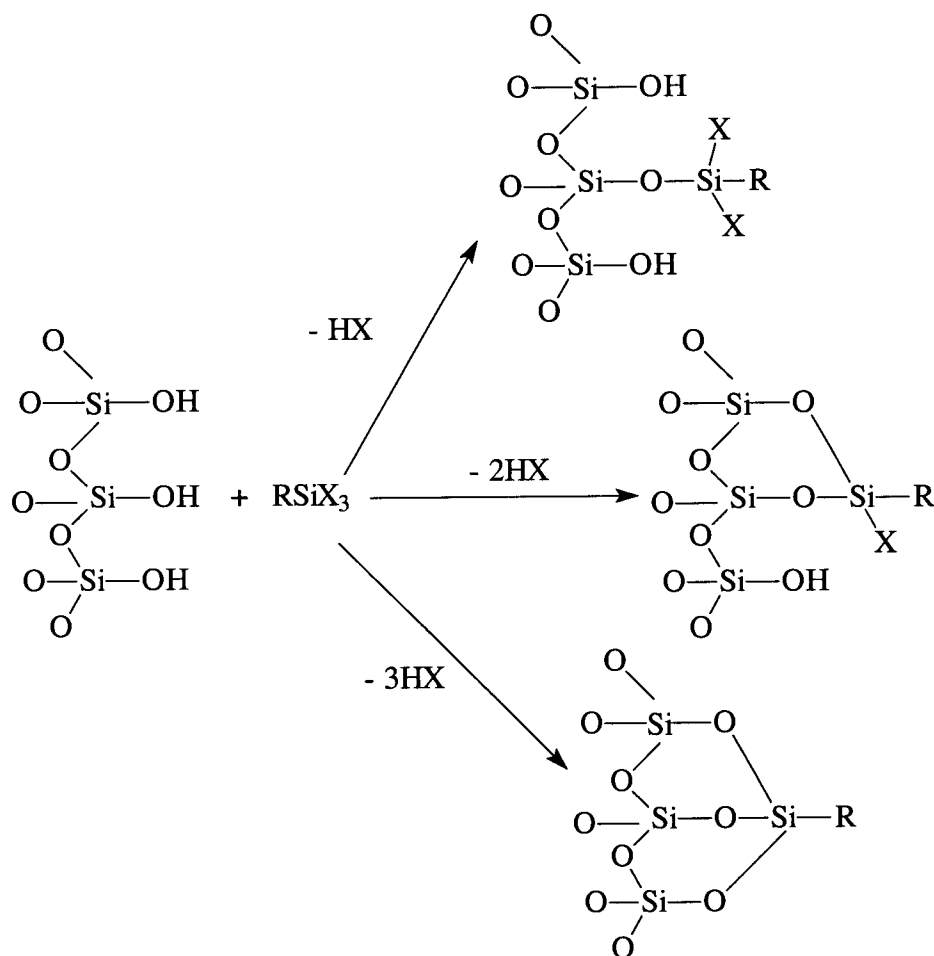
Figure 3 Simplified grafting reaction at a silica surface

In the above scheme, a functional group, X is a leaving group such as halide, amine,

alkoxy or acyloxy. Trialkoxysilanes are the most popular ones, especially the methoxy-

and ethoxy-silanes due to their greater reactivity. When trialkoxysilanes are reacted with

silica, an organic layer is formed on the silica surface via so–called polymeric bonding.

The thickness of this organic layer may vary according to the reaction conditions.

Because of difficulties associated with control of the polymerization process, this method

frequently results in irreproducible phase thickness. Another drawback is the formation of

several surface species resulting from binding via one, two or three Si-O-Si groups as

shown in Figure 3.

When a monofunctional silane (e.g. monomethoxy- or monochlorosilane) is used, only

a single surface – silane linkage is possible and, consequently, an intrinsically

reproducible monolayer can be formed (Figure 4).
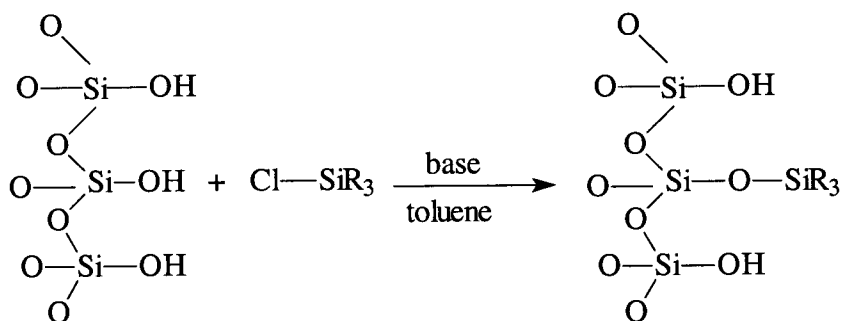
Figure 4 Formation of monolayer

2. Surface chlorination and subsequent displacement

Despite the increased thermal and chemical robustness of the Si-O-Si bond

(compared to Si-O-C), it is still observed that the Si-O-Si bond can be cleaved at elevated

temperatures or under moderately acidic or alkaline elution conditions. An alternative is

to form very strong Si-C bonds on the silica surface. Halasz and Sebastian[17] also

developed a method in which the silica gel was first chlorinated using thionyl chloride.

The Si-Cl functions on the silica surface can then be treated with organometallic regents

(usually, a Grignard regent) to form Si-C bond (Figure 5)[10, 21].
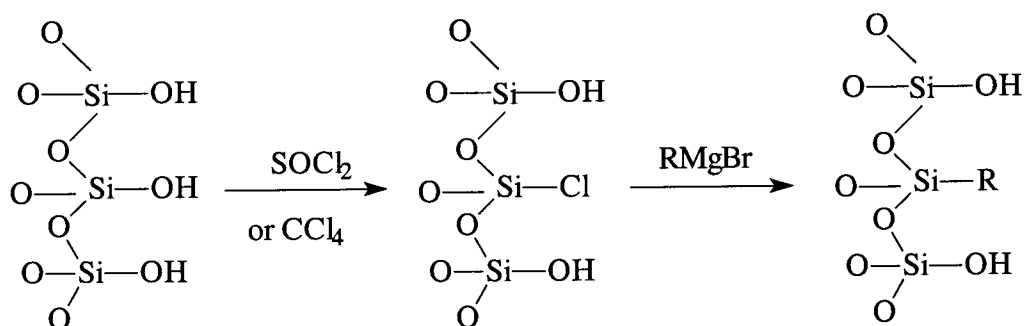
Figure 5 Chlorination of silica surface and then treated with a Grignard reagent

In principle, this method provides a closer attachment and a more stable bonded phase

than that obtained by the corresponding Si-O-Si linkage. However, the wide usage of this

method to modify silica substrate has been hindered by several factors. One factor is that

the preparation of the alkylation reagent (usually very strong nucleophile) may interfere

with the functionalities that will be immobilized on the silica, which limits the

functionality that can be attached. Only a very limited number of functionalities can be

present in the halide compound from which a Grignard reagent can be prepared.

Recently, Maciel and Tao[22] showed that most of the widely used organometallic reagents,

such as organolithium and Grignard reagents, which are sufficiently reactive to attack

Si*-Cl moieties, are able to attack and cleave Si*-O-Si* linkage and cause serious

damage to the silica framework.

3. Sol – gel techniques

All those methods mentioned above try to modify the silica surface properties by

chemically attaching functionalities to the silica surface structure, which is already

formed before the modification process. Those methods are generally known as post-modification methods. In the sol-gel method, the functional groups are incorporated into the silica matrix during the forming of silica gel. This method usually involves the co-polymerization of a silica precursor (typically a tetraethoxysilane, TEOS) with an organoalkoxysilane precursor bearing the functionalities. As mentioned before, this sol – gel process first involves the hydrolysis of alkoxysilanes, then the condensation to form siloxane networks. In order to get a rapid and completed hydrolysis, an acid or a base is usually used. In both cases the reaction occurs by a nucleophilic attack of the oxygen contained on water, to the silicon atom. Mechanisms of both cases proposed by Vansant and coworkers[4] are shown in Figure 6 and Figure 7.
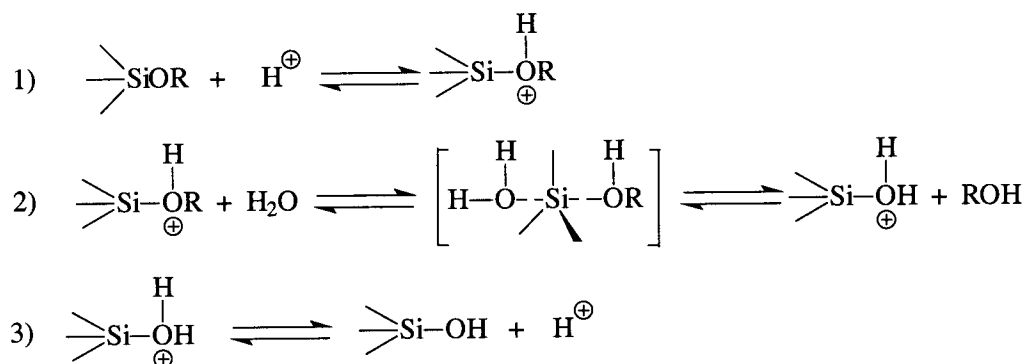
Figure 7 The acid catalyzed hydrolysis of silane ester
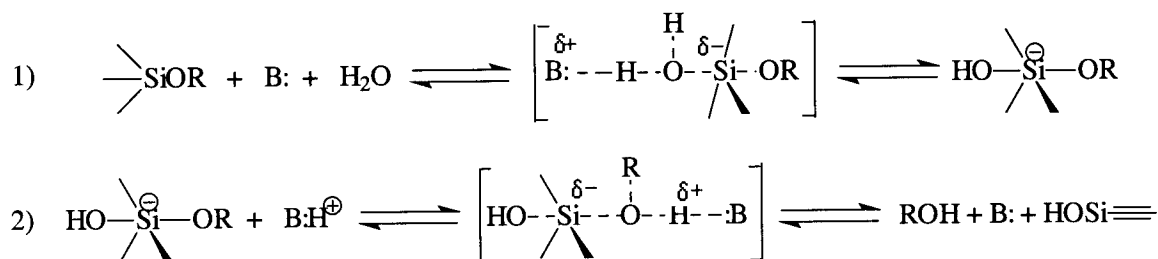
Figure 6 The base catalyzed hydrolysi of silaine ester

With the sol-gel method, high loading of organic functional groups is usually achieved. However, because it is often difficult to control both the surface area and porosity of the final material, access to some of attached functional groups by the desired substrate may be difficult[4].

In 1992, scientists[23-24] at Mobile Oil developed a new family of mesoporous molecular sieves (M41S) by using cationic surfactants as templates around which the sol – gel process took place. Removal of the templates resulted in materials with high surface area and a regular array of pores. This technique was initially developed for the preparation of purely inorganic materials. Recently, this methodology has been extended to incorporate organomodified materials[25-29]. Unlike previous sol – gel materials, the templated materials possess very high surface area and more regular pore structure, which allows greater access of reactants to the active sites. The general preparation of procedure for these materials is shown in Figure 8.

RSi(OEt)₃   +   Si(OEt)₃ $\xrightarrow[\text{2) Template extraction}]{\text{1) Template}}$
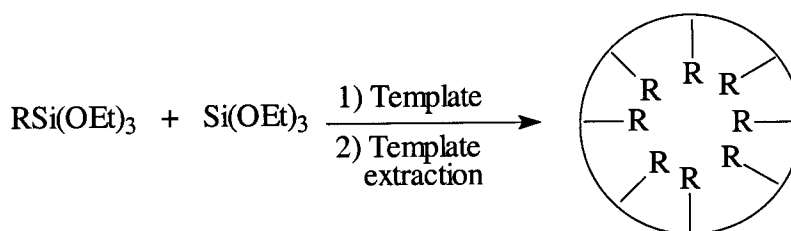
Figure 8 Preparation of organofunctionalised silicas via templated sol - gel method

Chapter Three

Modification of Silica with the Phosphonate Group

and Hydrolysis of Phosphonate Ester

Phosphonates have proven to be useful building blocks in the preparation of hybrid organic – inorganic materials[30-32]. Recently, the potential applications of silica based materials with covalently bonded phosphonate functionality have generated great interests. It has been reported that these materials already find use in ion detection[33], syntheses of self – assembled mono and multilayers[34-36], in catalysts[37-39], and in the preparation of chromophore films with second order nonlinear optical (NLO) properties[40-42].

Generally speaking, there are two main approaches to attach phosphonate functionalities to the silica surface. The first is through catalyzed gelations, to incorporate the phosphonate groups into the silica matrix during the preparation of silica gel. The second is grafting, through reactions between phosphonosilanes with proper leaving groups such as halides or alkoxyl groups and silica surface functional groups (usually silanols, Si-OH). Because of the electrophilic nature of the phosphorus atom of phosphonates, it is usually applicable to immobilize phosphonate groups on silica surface via chlorination–alkylation approaches (alkylation reagents are usually very strong nucleophiles).

In 1996, Cardenas and coworkers[43] initially reported the HF- catalyzed gelation of phosphoethyltriethoxysilane and studied the process by ^{29}Si and ^{31}P solid state NMR. Carbonneau and coworker's[44] recent publication described the gelification of the same precursor using NH_4F as a nucleophilic catalyst (Figure 9).

$$(EtO)_3-Si-CH_2CH_2-\overset{\overset{\displaystyle O}{\|}}{P}-(OEt)_2 \quad + \quad xSi(OEt)_4 \xrightarrow[\text{2) Gelation}]{\text{1) Hydrolysis}} xSiO_2, O_{1.5}SiCH_2CH_2\overset{\overset{\displaystyle O}{\|}}{P}(OEt)_2$$

$$x = 1 \text{ to } 20$$
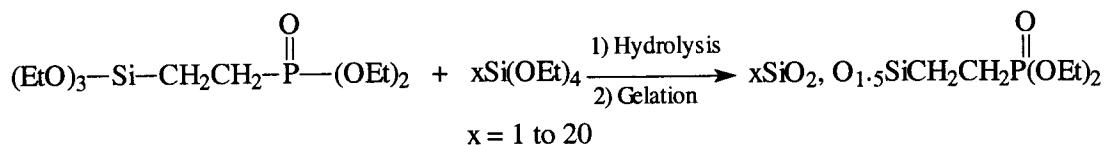
Figure 9 Gelification of (diethoxyphosphonoethyl) triethoxysilane

Theoretically, the sol–gel method can achieve high loading of organic functional groups, however Lanneau and coworkers reported that the carbons of organic moiety were not detected by CP MAS ^{13}C NMR. This fact suggested that a significant number of organic functional groups might be "buried" into the bulk of silica gel and might not be accessible as active sites for surface reactions.

Chevalier and coworkers[45] covalently grafted phosphonate groups onto the silica surface for applications in Ca^{2+} ion sensitive field – effect transistors. The grafting process involved the reaction of phosphonate functionalized chlorosilane with silanol groups on the silica surface (Figure 10). Unfortunately, no ^{13}C and ^{31}P solid state NMR date were reported to support the success of grafting.
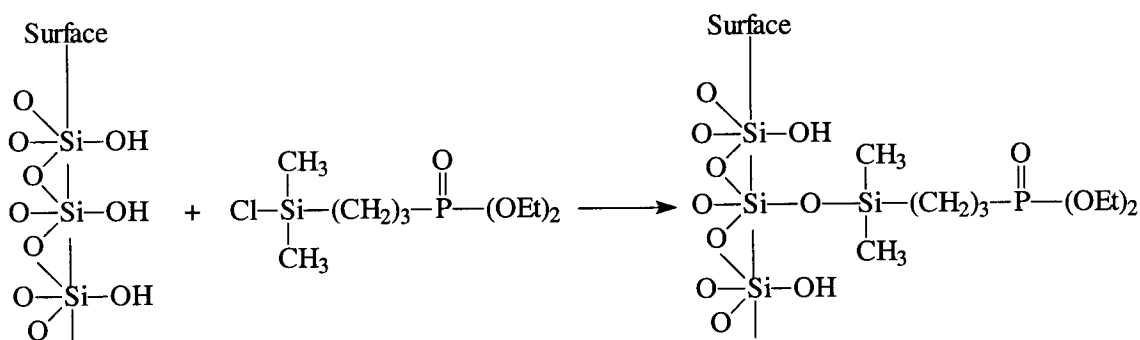
Figure 10 Grafting (diethoxyphosphonobutyl) chlorosilane on to silica surface

According to Chevalier and coworkers, the mechanism of the grafting of chlorosilane on surface silanols could involve the nucleophilic attack at the silicon atom of the

chlorosilane by the oxygen atom of the silanol group. The leaving group, Cl‾, is released

and a siloxane (Si-O-Si) bridge is formed between the surface and the graft.

As shown above, one of the important steps in both approaches is the preparation of

the proper silylated phosphonate precursor. One of the popular methods of the synthesis

of a silylated phosphonate group involves radical addition of HPO(OEt)₂ to the allyl or

vinyl silane precursors in the presence of a radical initiator (usually a peroxide). Sullivan

and coworkers[39] used this method in their preparation of a new solid catalyst at yields of

55% (Figure 11).

$$
EtO-\underset{\underset{OEt}{|}}{\overset{\overset{O}{\|}}{P}}-H \quad + \quad (EtO)_3SiCH_2CH=CHCH_2Si(OEt)_3 \quad \xrightarrow[140\ ^0C,\ 18\ h]{(t\text{-}Bu)OO(t\text{-}Bu)} \quad (EtO)_3SiCH_2\overset{\overset{\overset{O}{\|}}{\underset{|}{P}-OEt}}{\underset{}{}}CHCH_2CH_2Si(OEt)_3
$$
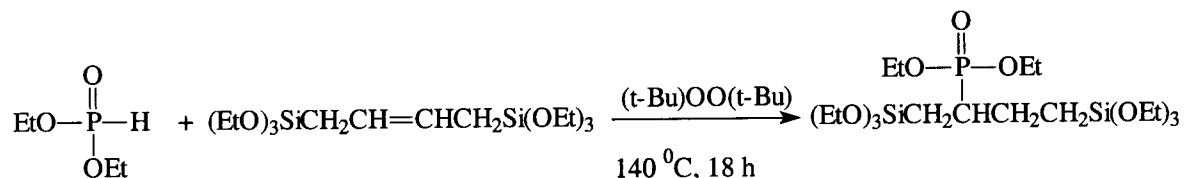
Figure 11 Radical addition of HPO(OEt)₂ to 1,4-bis(triethoxysily)But-2-ene

Chevalier and coworkers[45] developed another approach for the synthesis of a silylated

phosphonate. In their approach, the diethylphosphonate was first prepared by Michaelis-

Abuzov reaction of triethylphsphite with allyl bromide (Figure 12), then the phosphonate

was silylated via catalyzed hydrosilylation (Figure 13).

$$
RBr \; + \; P(OC_2H_5)_3 \longrightarrow Br:[\; CH_3CH_2-O-\underset{EtO\;\;\;\;\;OEt}{\overset{}{P}}-R\;] \longrightarrow (EtO)_2\overset{\overset{O}{\|}}{P}R \; + C_2H_5Br
$$

R = allyl group
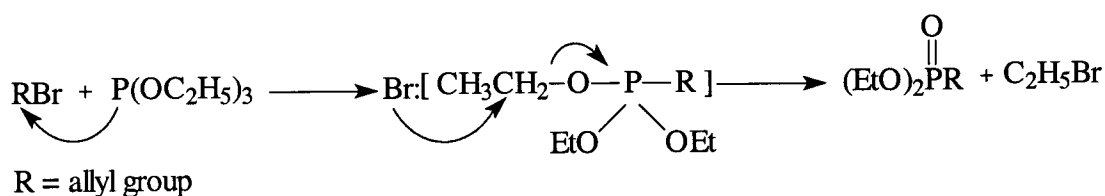
Figure 12 Preparation of allyldiethoxyphosphonate
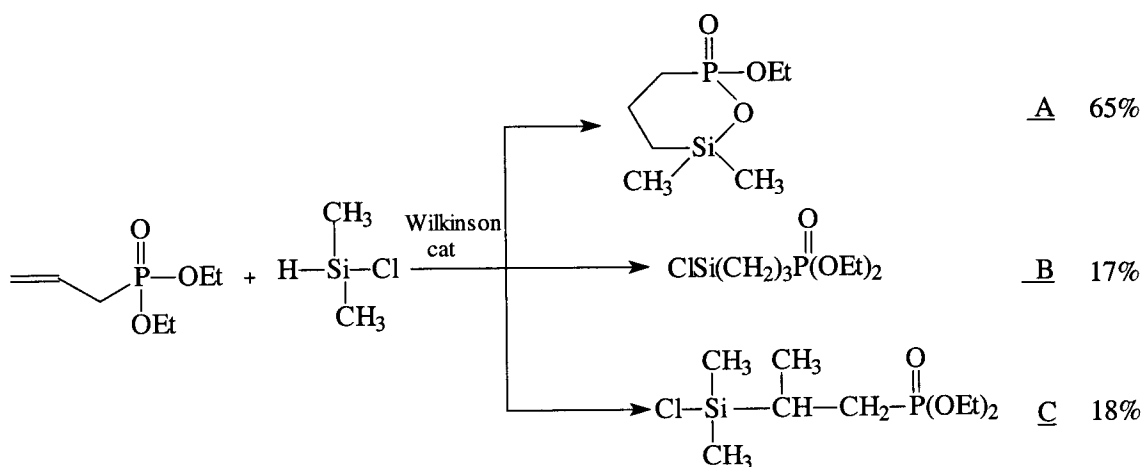
Figure 13 Preparation of silylated phosphonate via hydrosilylation

As shown in Figure 13, Chevalier group found that a mixture was obtained and the yield of the target product (product B) was poor. The product A, product of the intramolecular side reaction, was actually the principle product, which suggested that there was a chemical incompatibility with the presence of the chlorosilane group and a phosphonate group on the same molecule. The hydrosilylation in the β-position instead of expected terminal attack in the α-position also took place, which suggested that the Wilkinson catalyst might not have regioselectivity in the hydrosilation reaction.

Recently, Carbonneau and coworkers[46] reported a new approach to prepare silylated phosphonate precursor via a double Heck cross-coupling reaction procedure. They first prepared ethyl 4- phosphonatomethylstyrene by a nucleophilic displacement reaction at room temperature in 90% yield (Figure14). The styrene with phosphonate functionality was then reacted with an iodo-bromo paradisubstituted arene in the presence of the catalyst Pd(OAc)₂, which made the reaction selective to iodine (Figure 15). The

bromosubstituted intermediate was then silylated by the second Heck reaction with a 4-

trimethoxysilystyrene (Figure 16).
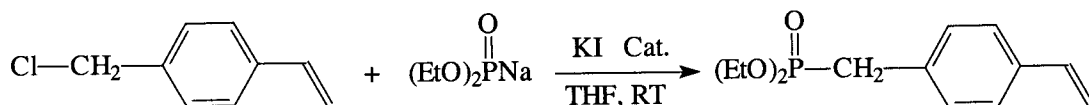
Figure 14 Synthesis of ethyl 4- phosphonatomethylstyrene
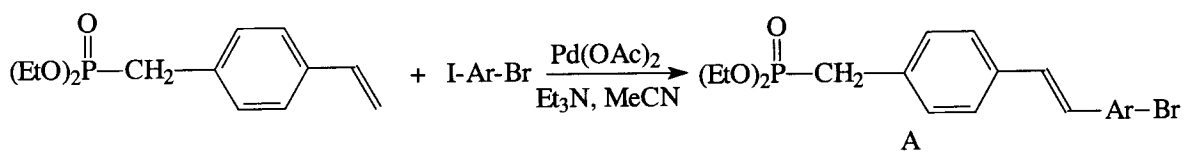
Figure 15 Synthesis of bromosubstituted intermediate, the 1st Heck coupling reaction
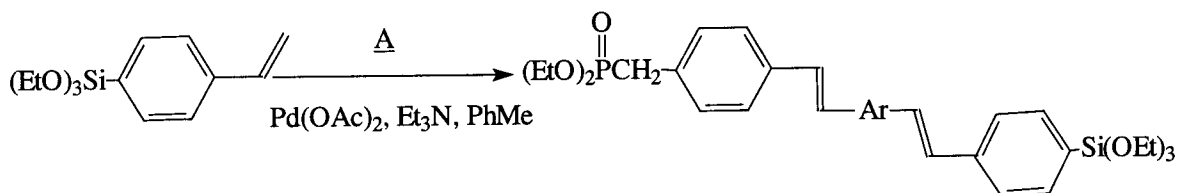
Figure 16 Synthesis of silylated phosphonate procursor, the 2nd Heck coupling reaction

In some potential applications of phosphonates, such as generation of new materials

with NLO properties, self – assembly mono and multilayers and catalysts, the

phosphonate group was first covalently bonded to the silica surface with the silylated end,

then bonded to an oxide (e.g. Al_2O_3, SnO_2, TiO_2) or a metal atom with another end.

Actually, it is the phosphonic acid which can bind to an oxide or a metal atom, not the

phosphonate ester. The phosphonate group was usually protected by forming a

phosphonate ethyl or methyl ester in the processes before it is ready to bind to another

functionality with the free end. To deprotect the phosphonate, the terminal phosphonate

ester must be converted to phosphonic acid group via hydrolysis. The cleavage of diethyl

phosphonate ester in solution was well documented[47-49]. The usual method involved the

reflux of 6 M HCl acid[47]. The mechanism of catalyzed hydrolysis of phosphonate esters

is believed to be similar to that of carboxylic ester (Figure 17).
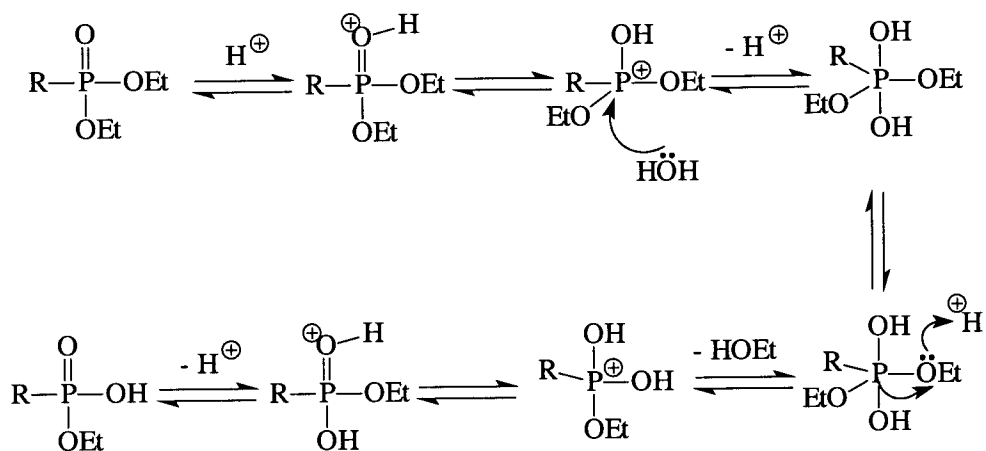
Figure 17 Acid catalyzed hdrolysis of diethyl phosphonte

An alternative method involved first converting the phosphonate alkyl ester to the

more labile trimethylsilyl ester by reacting with TMSI (iodotrimethylsilane) or TMSBr

(bromotrimethylsilane) (Figure 18), then cleaving the trimethylsilyl group away by

hydrolysis or methanolysis at room temperature (Figure 19). Comparing with the reaction

conditions in the catalyzed method, this method was considered to be milder and more

selective.
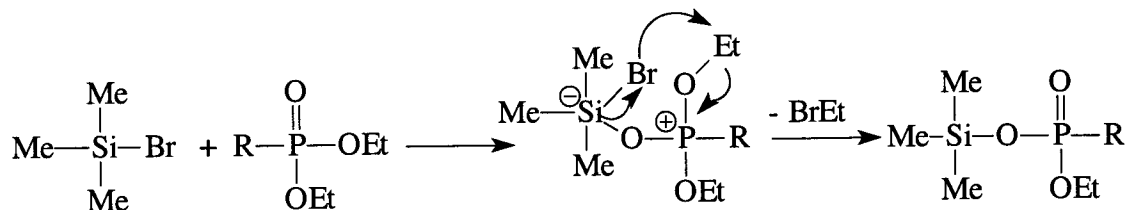
Figure 18 Convertion of phosphonate ethyl ester to trimethylsilyl ester
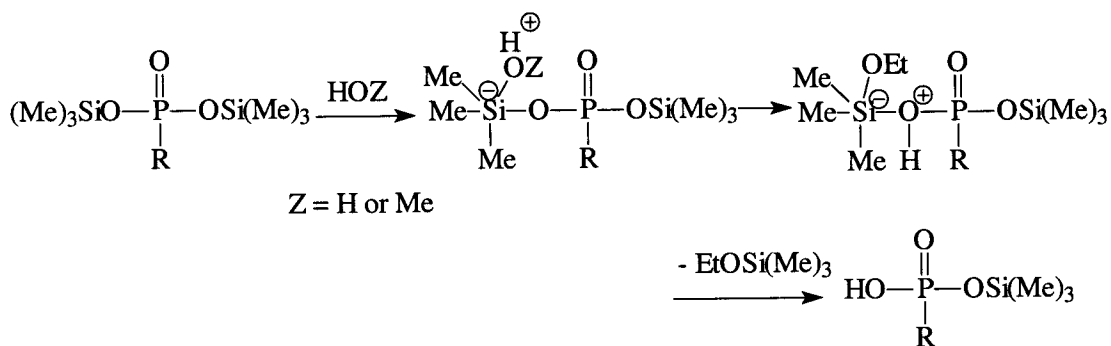
Figure 19 Hydrolysis or metholysis of phosphonate trimethylsilyl ester

However these methods were not necessarily efficient when one of the reagents, the phosphonate, was confined to solid surface as observed by Page and coworkers[50]. In Lanneau and coworkers' recent publication[44], they reported that the tert-butyl phosphonate ester, which was covalently bonded to silica, was readily cleaved away at room temperature and evolution of isobutene was observed.

Chapter Four

Results and Discussions

The phosphonate groups were immobilized on the silica surface by the grafting

method via a one-step approach and multiple-step approaches and these processes were

studied by the means of solid state ^{29}Si, ^{13}C and ^{31}P NMR. The hydrolysis of diethyl

phosphonate ester bonded on silica surfaces was also studied.

4.1. Synthesis of the Diethyl Allyl Phosphonate

The diethyl allyl phosphonate (I) was obtained by the Arbuzov reaction[51] at about 100

^{0}C from triethylphosphite and allyl bromide or chloride for 4 hours (Figure 20).

R = allyl group
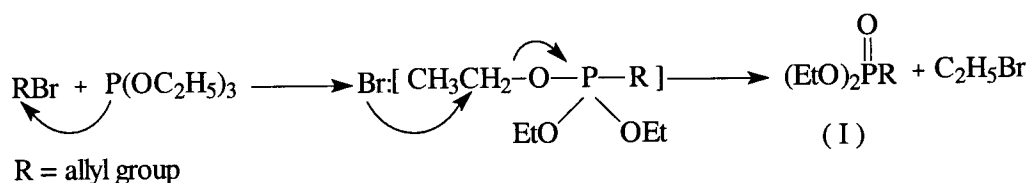
Figure 20 Preparation of allyl diethylphosphonate

Ethyl bromide was removed from the reaction system by distillation during the reaction

in order to minimize the forming of the diethyl ethyl phosphonate. It was believed that

the mechanism of this reaction involved two S_N2 (bimolecular nucleophilic substitution)

reactions in sequence.

The structure of diethyl allyl phosphonate (I) was characterized by the means of ^{31}P,

^{1}H and ^{13}C NMR. The detailed NMR data and assignments for compound (I) are given in

the experimental section
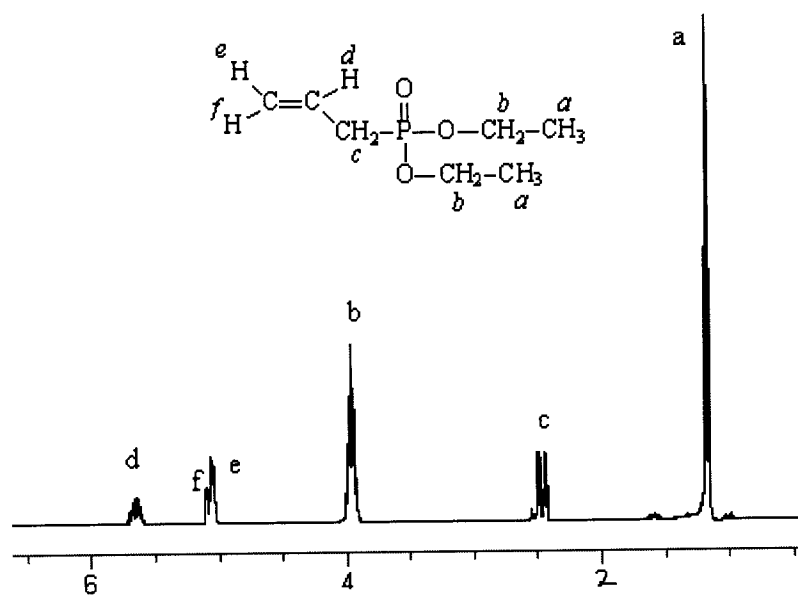
Figure 21 ^{1}H NMR spectrum of the compound (I)
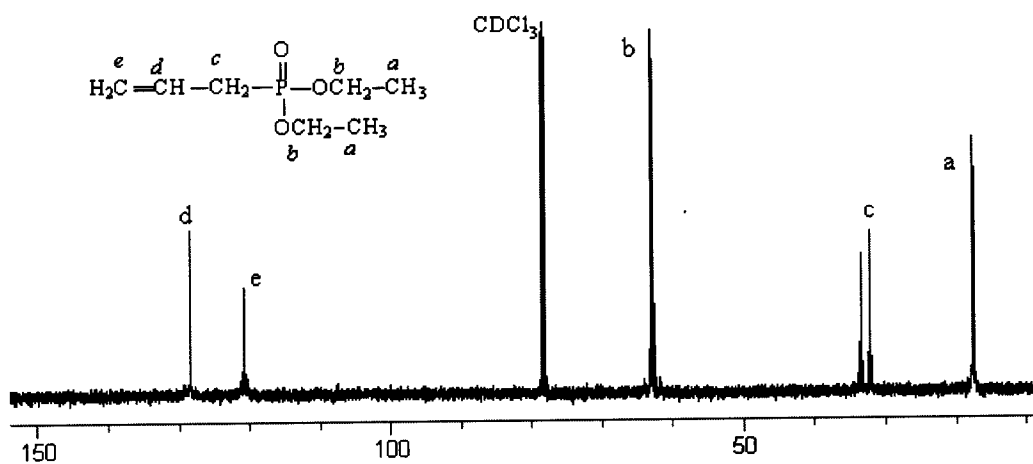
Figure 22 ^{13}C NMR spectrum of the compound (I)

As a result of the presence of the spin 1/2 phosphorus nuclei in the molecule, coupling

between phosphorous and other nuclei was observed. For example, in ^{1}H NMR spectrum

(Figure 21), for protons of methyl group (1.17 ppm) of ethoxy groups, doublet of triplets,

instead of a triplet, was observed as a result of being coupled to phosphorous (J_{HP} = 2.6Hz) (Figure 23).
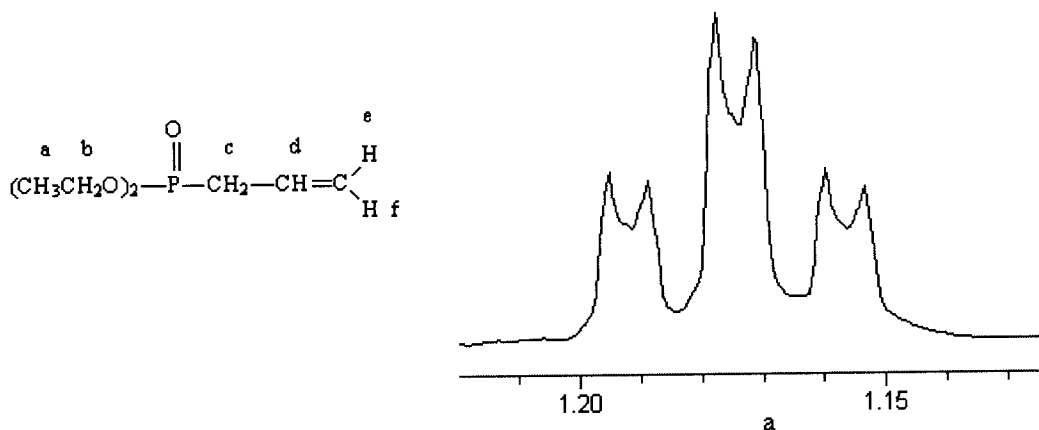
Figure 23 ^{1}H NMR spectrum of H (a) in the compound (I)

In the ^{13}C spectrum (Figure 22), the four doublets (62.94, 62.87 and 17.57, 17.53 ppm) due to the carbon of CH_2 and CH_3 of ethoxy groups experiencing splitting as a result of being coupled to phosphorous (J_{CP} = 6.5 and J_{CP} = 5.9 Hz). Remarkably, allyl carbon (32.3 ppm), which was directly bonded to phosphorous, exhibited appreciable coupling (J_{CP} = 139.0 Hz). Due to incompletely decoupling of the ^{13}C spin from the attached protons, doublet of triplets, instead of doublets, were actually observed (J_{HC} = 26.0) (figure 24). Those large coupling constants, J_{CP}, were indicators of the formation of a phosphorous- carbon bond.
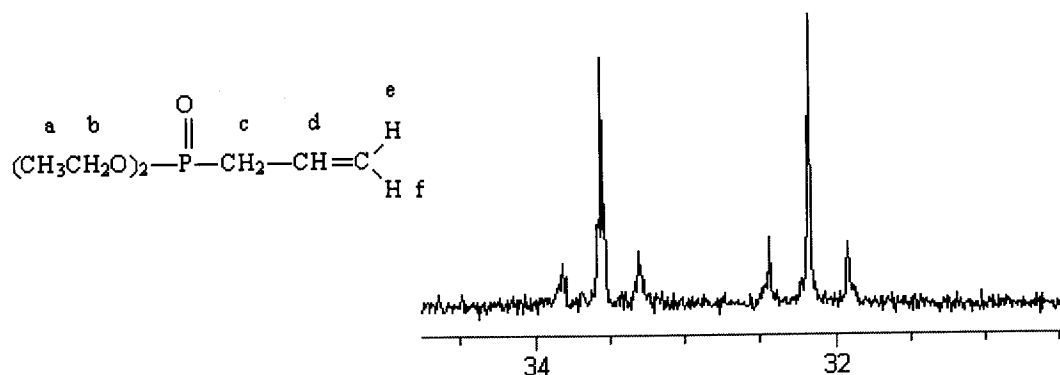
Figure 24 ^{13}C NMR spectrum of carbon (c) in the compound (I)

In ^{31}P NMR of compound (I), a singlet at 27.65 ppm was observed, which agreed with the literature data[43,44].

4.2. Synthesis of Silylated Diethyl Butyl Phosphonate

A one-step grafting process required the synthesis of a bifunctional precursor possessing the phosphonate group at one end and a reactive center towards the silica surface at the other end. In this project, the silane with an ethoxy group was chosen as the reactive center. The ethoxy group would be the leaving group during the grafting reaction with silanol groups of the silica surface. There are a large variety of reactive silanes described in the literature, which differ mainly by the type and the number of their leaving groups[52-54]. The most commonly used reactive silanes have alkoxy, chloro or amino groups as leaving groups. A reactive silane molecule can usually have one to three leaving groups.

Our choice of the monofuctional silane, dimethylethoxysilane, as the reactive silane was led by the objective for this study. One of the important objectives of this project is to further the use of spectroscopic methods for achieving a better understanding of

surface modification of silica via the grafting approach. The problem with the use of

multifunctional silane is that the polycondensation at the surface, which is difficult to

control, usually leads to a thick and ill-defined grafted layer. The choice of a

monofunctional silane is able to avoid this problem and greatly simplify the assignment

of solid state NMR signals. As mentioned before, there is chemical incompatibility with

the presence of the chlorosilane group and a phosphonate group on the same molecule.

According to Chevalier[45], if chlorosilane is used, a mixture will be obtained in the

preparation of ready-to-graft precursor and a cyclic silyl phosphonate, product of the

intramolecular side reaction will be actually the principal product, which means the yield

of target product will very low. To avoid this problem, a monoalkoxy silane was chosen.

The silylated diethyl butyl phosphonate, compound (II), was prepared by

hydrosilylation of allyl diethylphosphonate with dimethylethoxysilane in the presence of

the catalyst (Figure 25).

$$CH_2=CH-CH_2-\overset{\overset{\displaystyle O}{\|}}{P}-(OEt)_2 \quad \xrightarrow[\text{Cat.}]{\overset{\displaystyle Me}{\underset{\displaystyle Me}{\overset{|}{H-Si-OEt}}}} \quad EtO-\overset{\overset{\displaystyle Me}{|}}{\underset{\displaystyle Me}{Si}}-(CH_2)_3-\overset{\overset{\displaystyle O}{\|}}{P}-(OEt)_2$$

(II)
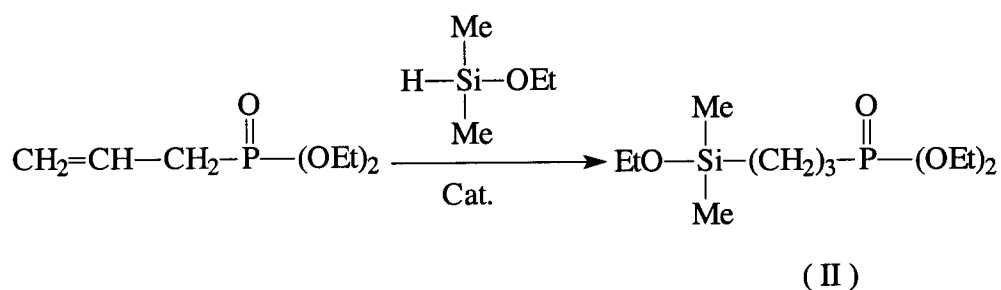
Figure 25 Synthese of the silylated phosphonate

I n general, due to the fact that relatively few reactive functionalities interfere with the

catalytic olefinic addition, the hydrosilation reaction has been considered as a very

versatile method to form Si-C bond. Hydrosilylation is generally carried out in the

presence of a transition-metal catalyst. A variety of inorganic and organic transition-

metal complexes have been found to be very effective catalyst in hydrosilation reaction, such as chloroplatinic acid in a 2-propanol solution (known as "Speiers" catalyst) and well known Wilkinson's catalyst (tris(triphenylphosphine) chlororhodium(I)). Some of these catalysts showed very poor regioselectivities, as observed by Chevalier[45]. Laub and coworkers[55] reported that dicyclopentadieneplatium(II) chloride had very good regioselectivity in hydrosilylation and the principle product was an anti-Markovnikov adduct. Our study confirmed Laub and coworkers' report and high yield (72%) of the silylated diethyl butyl phosphonate was obtained.

In both the ^{13}C and ^1H NMR of the silylated diethyl butyl phosphonate, extensive coupling observed was a result of the spin ½ phosphorous nuclei present in the molecule. In the ^{13}C NMR spectrum (figure 26), the three methylene groups in the bridge between phosphorous and silicon were observed as two doublets of triplets (16.8 ppm, J_{CP}= 4.6 Hz and 29.8 ppm, J_{CP}= 138.3 Hz) and a multiplet (12.0-12.2 ppm, J_{CP}= 16.0 Hz). The two
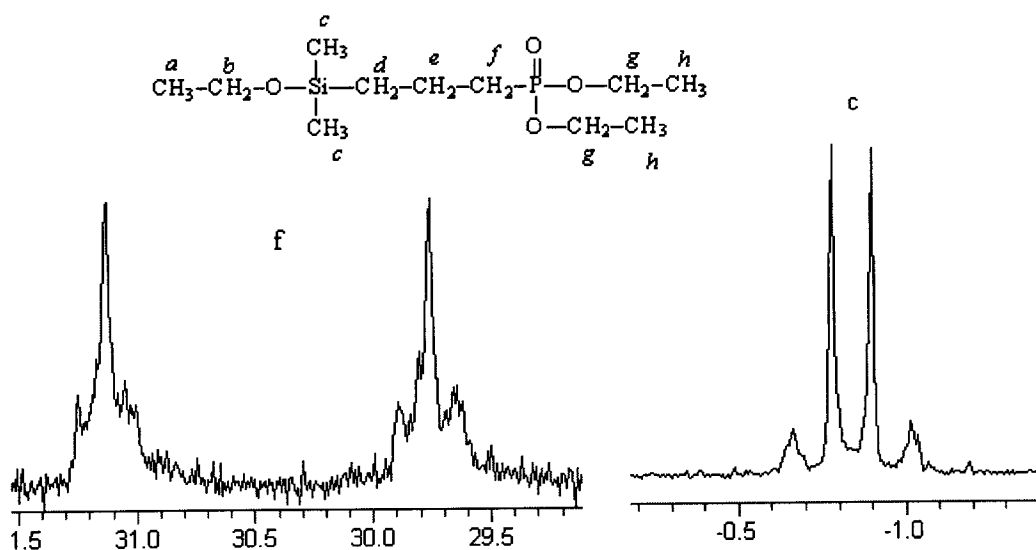
Figure 26 ^{13}C NMR spectrum of carbon (f) and carbon (c) in the compound (II)

methyl groups attached to the silicon were found as a quartet (- 0.78 ppm, J_{CH} = 11.6 Hz) and did not show splitting patterns due to carbon –phosphorous coupling, which suggested that the C-P coupling range in the compound (II) might be just at three bond distance.

In the ^{1}H NMR of compound (II), extensive H-P coupling patterns were also observed. In particular, methylene protons in the ethoxy group phosphonate ester were observed to be uniquely split by phosphorous to give a pair of overlapping 1 : 4 : 6 : 4 : 1 quintets, J_{HP} was about 10 Hz.
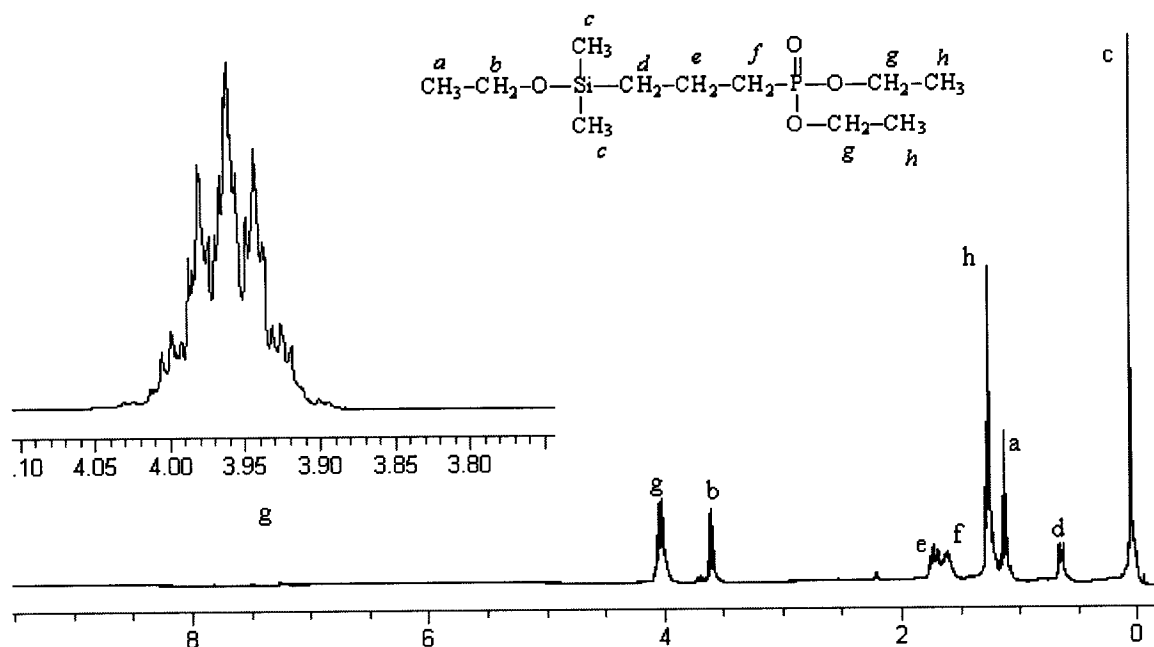
Figure 27 ^{1}H NMR spectrum of the compound (II) and of its carbon (g)

The structure the silylated diethyl butyl phosphonate was also verified by MS. The Mass spectrum was obtained with a HPLC/MS mass spectrometer. The ionization method used was electron-spray ionization (ESI). The molecular ion (m/z 282) was not observed in the mass spectrum. The principle peak observed was 237.2 (m/z). The mass

spectroscopic data suggested that the cleavage of O-Si bond might be involved in the fragmentation of molecular ion of the silylated butyl diethylphosphonate (Figure 28), which was expected because tertiary silicon cation was known to be very stable in the gaseous phase.

$$CH_3-CH_2-O-\overset{+}{\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}}-(CH_2)_3-\overset{\overset{O}{||}}{P}(OEt)_2 \longrightarrow \overset{+}{\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}}-(CH_2)_3-P(OEt)_2 + EtO^\bullet$$
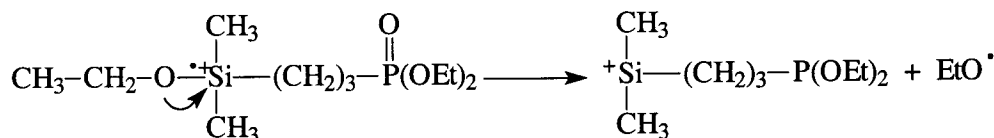
Figure 28 Fragmentation of molecular ion of the silylated butyl diethylphosphonate

4.3 Grafting of Silylated Phosphonate to the Silica Surface

One-Step Grafting Approach, Synthesis

The compound (II), silylated diethyl butyl phosphonate, was directly grafted to the silica surface through siloxane linkage (Si-O-Si) to give Sample B. The siloxane linkage was formed by catalytic silylation reaction of the silanol group from silica surface with the ethoxy group at the silyl end of the compound (II) (Figure 29).
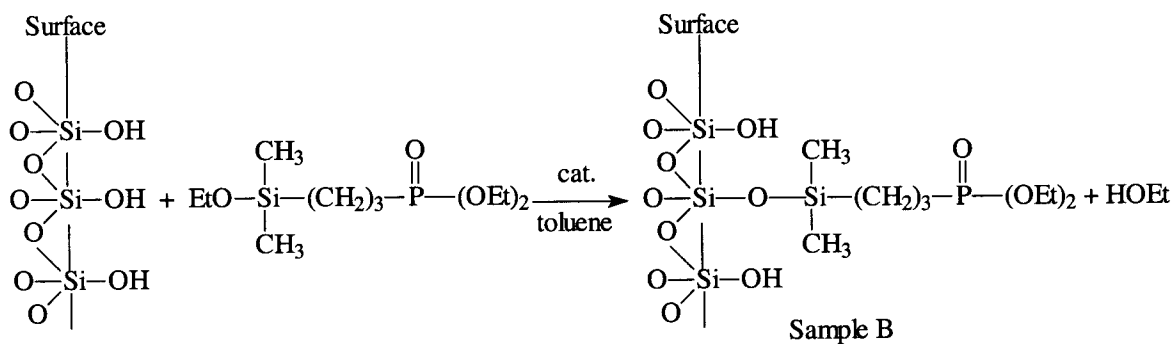
Figure 29 Grafting the compound (II) on to the silica surface

There were several different opinions about the mechanism of the silylation reaction

between the alkoxysilane and silanol groups on silica surfaces. Blitz and coworkers[56]

believed that alkoxysilane might chemically bond to the silica surface only if water was

present at the interface. In another words, they believed the alkoxy group of alkoxysilane

must be converted to hydroxy group by hydrolysis before the silylation reaction on the

silica surface could take place, which implied that the silylation reaction on the silica

surface was actually the analogue of gelation reaction in the sol-gel process. They also

reported that the direct silylation reaction on the silica surface could happen in fully dry

condition if ammonia was present as a catalyst and proposed the following mechanism

for the ammonia catalyzed silylation[57] (Figure 30).
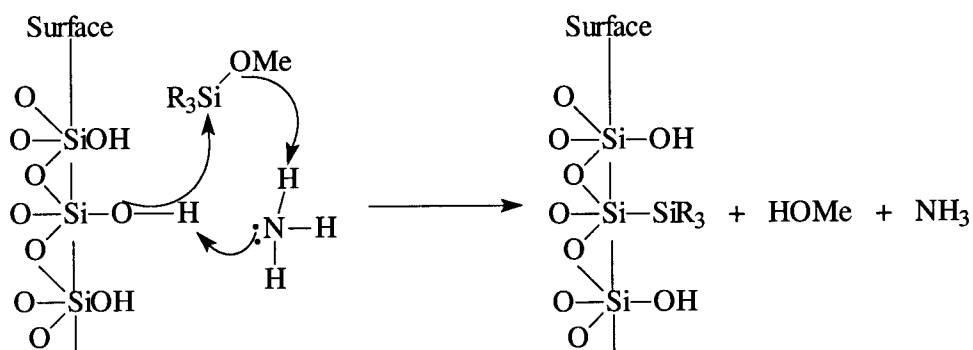
Figure 30 Ammonia-catalyzed silylation reaction

Recently, Berouet and coworkers[58] reported that they successfully grafted

polyisoprene terminated with trialkoxysilane functionality onto the silica surface in fully

dry condition without using any catalysts and spectroscopic data were provided to

support their success.

In this study, the surface silylation reaction was carried out by refluxing the compound

(II), silylated diethyl butyl phosphonate, with silica gel in toluene in the presence of

pyridine as a catalyst. All the reagents were carefully redistilled or dried before use and

the reaction was carried out under argon atmosphere in dry glassware. After the grafting

process, the silica modified with phosphonate group, sample A, was characterized by

solid state ^{29}Si, ^{13}C and ^{31}P CP/MAS NMR. The NMR data will be discussed in detail

further below. All the data proved that the siloxane linkage was formed between the

precursor, compound (II), and silicon atoms on the silica surface and the precursor was

chemically attached to the silica as a monolayer. Based on our experimental results, we

believed that the nucleophilic substitution mechanism proposed by Chevalier and

coworkers[45] might be correct here. According to Chevalier, the mechanism of the grafting

of chlorosilane on surface silanols could involve the nucleophilic attack at the silicon

atom of the alkoxysilane by the oxygen atom of silanol group. Then the leaving alkoxy

group was released and a siloxane bridge was formed between the surface and the graft

(Figure 31).
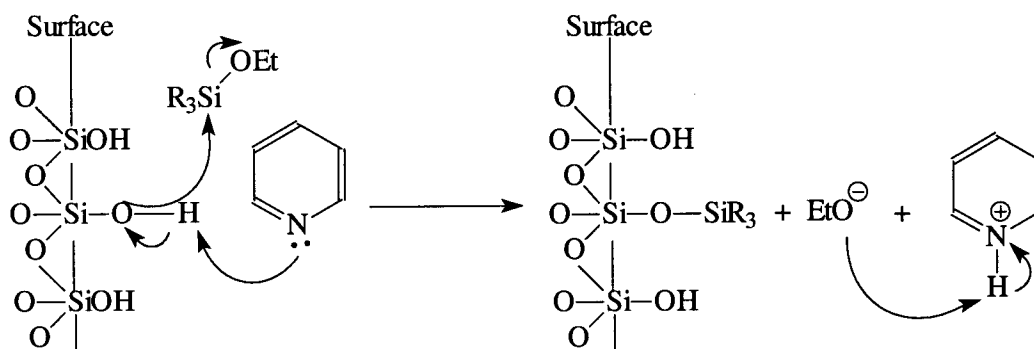
Figure 31 Pyridine-catalyzed silylation reaction (S$_N$)

One-Step Grafting Approach, CP/MS NMR

The silica gel used as a substrate in this project was obtained from Aldrich (100A, surface area $300m^2.g^{-1}$). Sample A was obtained by washing the received silica gel in 0.10 M HCl acid, to get rid of trace metal that might be introduced during manufacturing and dried under vacuum before use. The ^{29}Si CP/MAS NMR spectrum (Figure 32) of the sample A, silica gel before grafting, showed two signals at −100.5 ppm and −110.1 ppm, which were respectively assigned to silicon of single or free silanols (designated[59, 60] Q_3) and silicon of siloxane groups (designated Q_4).
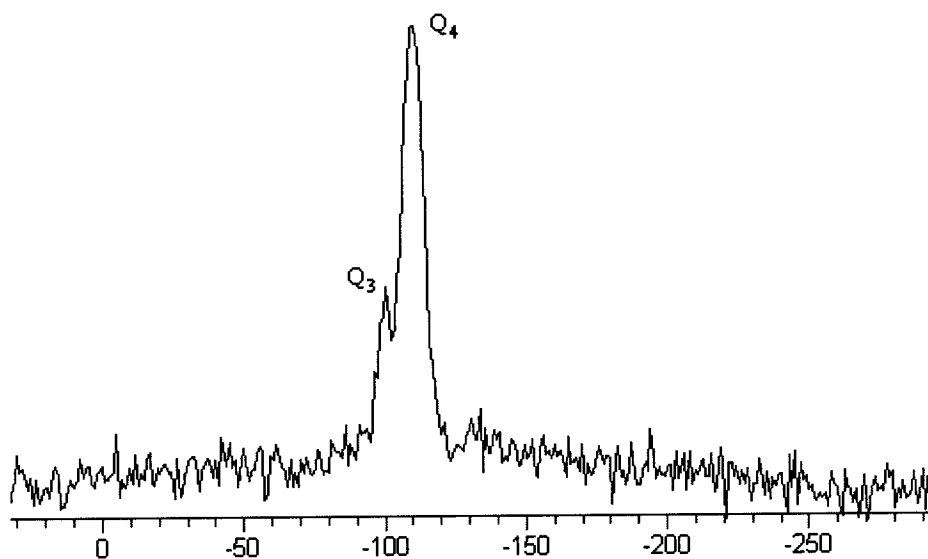
Figure 32 ^{29}Si CP/MAS NMR spectrum of the sample A

Q_2 geminal and vicinal silanol groups were not observed, which might be due to variables in manufacturing process, such as quantity of water usage, temperature and pH, especially the temperature in dry processes.

Figure 33 showed a comparison of the ^{29}Si CP/MAS NMR spectra for "native" silica,

sample A, and modified silica gel, Sample B.
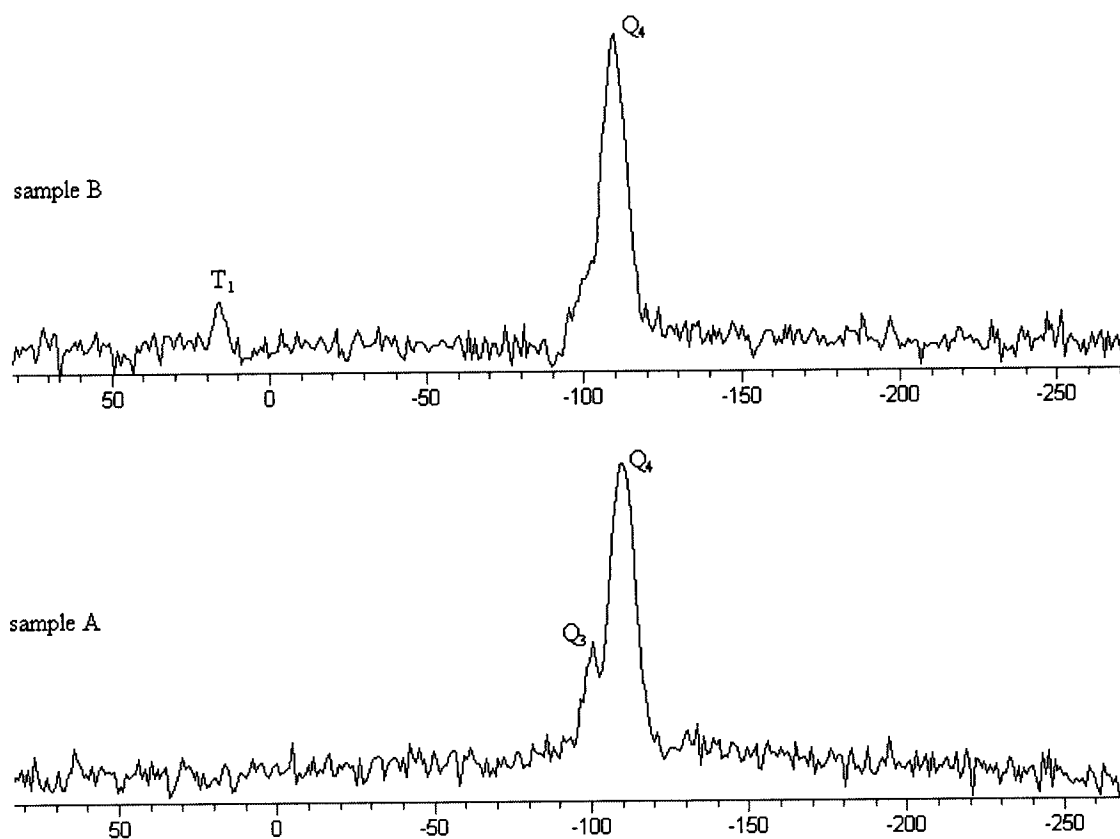
Figure 33 ^{29}Si CP/MAS NMR spectrum of the sample A and sample B

On the spectrum of sample B, two peaks were found. The first one at -110 ppm was Q_4

silicon atoms of siloxane groups on the silica surface which was not modified in the

grafting process. Comparing to the spectrum of "native" silica gel, sample A, an increase

of signals of the siloxane groups was observed. At the same time, it was interesting to see

that Q_3 peak of free silanol groups totally disappeared, which implied that a high loading

of the graft was obtained.

On the spectrum of sample B, two peaks were found. The first one at −110 ppm was

Q_4 due to silicon atoms of siloxane groups on the silica surface, which was not modified

in the grafting process. Comparing to the spectrum of "native" silica gel, sample A, an

increase of signals of the siloxane groups was observed. At the same time, it was

interesting to see that Q_3 peak of free silanol groups totally disappeared, which implied

that a high grafting loading might be obtained. The second peak at 13.6 ppm was

assigned to T_1 due to silicon atoms directly bonded to phosphonate group via siloxane

linkage, which proved that the silica surface was chemically modified by the phosphonate

functional group.

Figure 34 ^{13}C CP/MAS NMR spectrum of the sample B

The sample B, silica gel obtained after grafting of dimethylethoxysilyl-terminated

phosphonate, was also characterized by means of ^{13}C CP/MAS solid state NMR. The

assignments of the corresponding chemical structure are shown on the spectrum given in

Figure 34. The most upfield signal (δ -0.42 ppm) is assigned to the carbon of the methyl

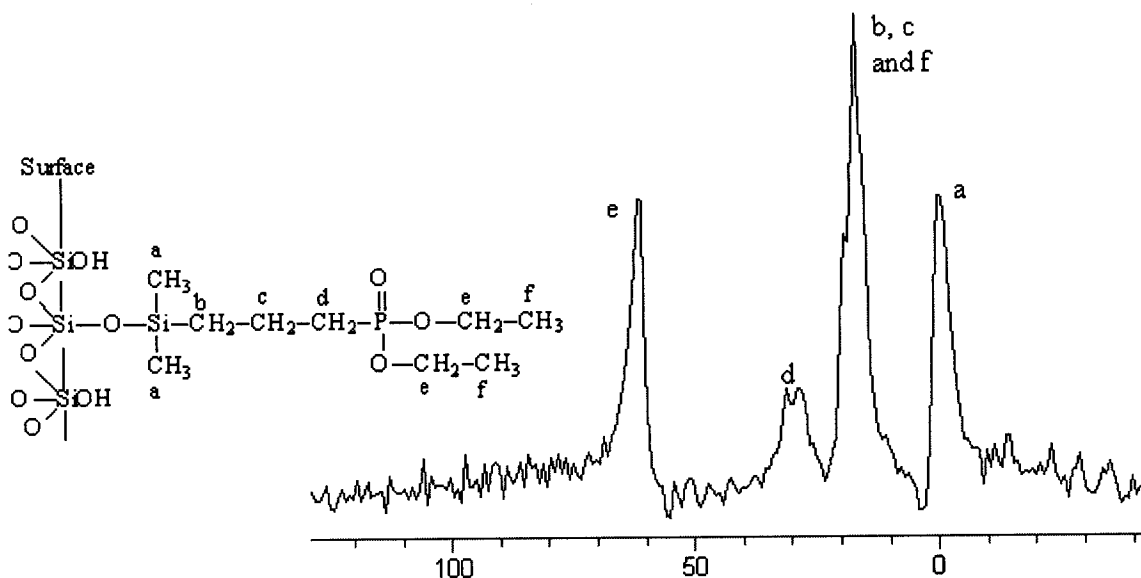groups directly attached to silicon. The broad overlapped peak roughly in the range δ 2.7-20.4 ppm is assigned to the carbon of the bridging methylene groups (carbon b and c) between phosphorous and silicon and methyl groups in the phosphonate ester. It is very interesting that the bridging methylene group directly attached to the phosphorus is found as a doublet (δ 30.8 and 28.2 ppm, $J_{CP} = 134.1$ Hz) due to the extensive carbon-phosphorus coupling. This has not been described in the literature, at least to our best knowledge. The most downfield signal (δ 61.2 ppm) is assigned to the carbon of the methylene groups in the phosphonate ester.

A good similarity between the chemical shifts of the carbons from the grafted structure and those of the carbons from the precursor, the silylated phosphonate, was observed. For example, the bridging methylene group directly attached to phosphorus was observed as a doublet (δ 31.1 and 29.8 ppm, $J_{CP} = 138.3$ Hz) in the spectrum of ^{13}C solution NMR of the precursor and was also observed as a doublet (δ 30.8 and 28.2 ppm, $J_{CP} = 134.1$ Hz) in the spectrum of the ^{13}C CP/MAS solid state NMR of the grafted structure.

In the ^{31}P CP/MAS solid state NMR spectrum of sample B, two phosphorous resonances were observed (Figure 36) at 32.5 ppm and 25.7 ppm. The resonance at 32.5 ppm is very close to that in the precursor compound (δ 32.3 ppm), both attributed to the fragment $-(CH_2)_3PO(OCH_2CH_3)_2$. The much lower intensity resonance at 25.7 ppm was not observed in the spectrum of the precursor. Sullivan and coworkers[61] also noticed this phenomenon in their experiment of modifying the silica surface by sol-gel process. They monitored the sol-gel process by ^{31}P NMR and found that the second signal around 24 ppm did not appear in the free-flowing sol mixture or gelification reaction. They reported
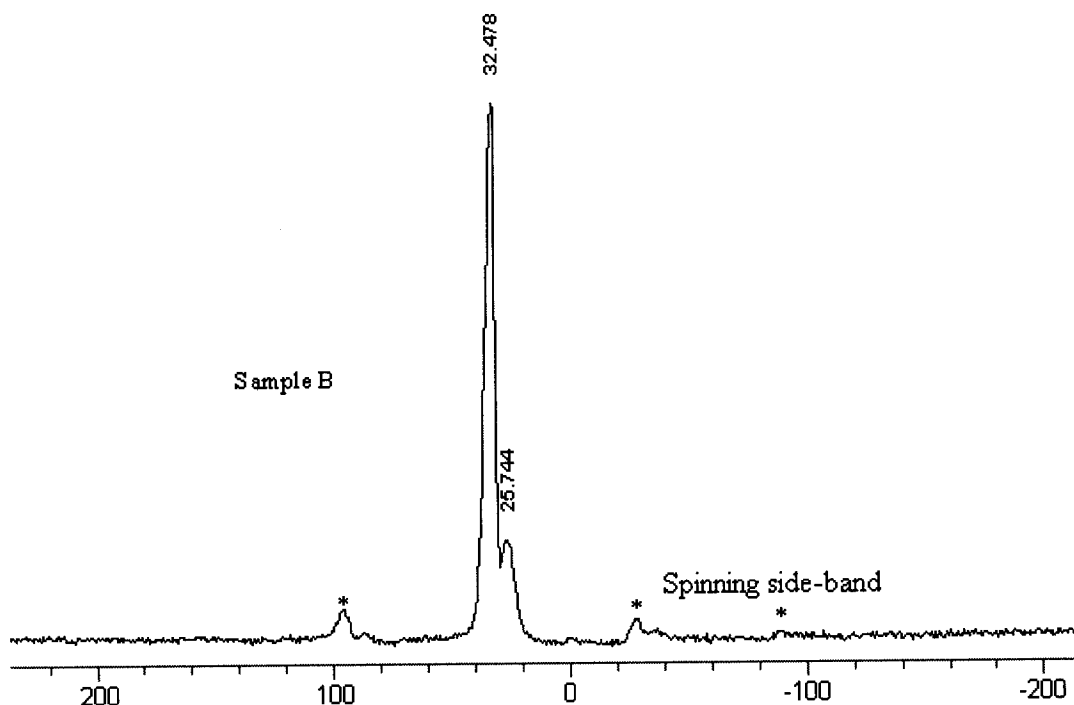
Figure 35 ^{31}P CP/MAS NMR spectrum of the sample B

that the second peak was observed only after the sample was further processed (aging and

drying). They believed that the appearance of the second signal might be a consequence

of surface interaction between the phosphonate groups and the silica framework. They

suggested that some restricted rotation of phosphonate moiety within silica matrix due to

the sol-gel process and/or H-bonding between oxygen atoms of phosphonate moiety and

silanol groups of silica surface might be involved in the appearance of the second peak. It

is the first time that the same phenomenon is also observed in the silica gel modified with

phosphonate groups by grafting process.

4.4. Multiple-Step Grafting Approaches

In order to elucidate the mechanism of the silylation reaction between the

alkoxysilane and silanol groups on silica surfaces, the grafting of the compound (II),

silylated diethyl butyl phosphonate, was carried out in two steps and monitored by solid

state NMR step by step. First, the alkoxysilane with a Si-H moiety was grafted to the silica surface through siloxane (Si-O-Si) linkage via silylation reaction to give the hydride-modified silica gel. Then the allyl dietheylphosphonate was chemically attached to the silica surface through the Si-C linkage via catalytic hydrosilylation reaction as described previously in this chapter (section 4.2.).

For comparison reason, the first step, preparation of hydride-modified silica gel, was carried out in two different approaches: direct silylation reaction between alkoxysilane and silanol groups on silica surfaces (figure 36) and hydrolysis-silylation (Figure 37).
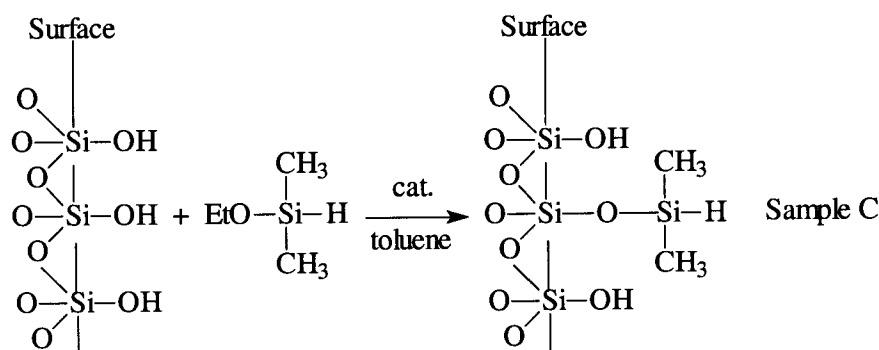
Figure 36 Synthesis of hydride-modified silica via direct silylation reaction
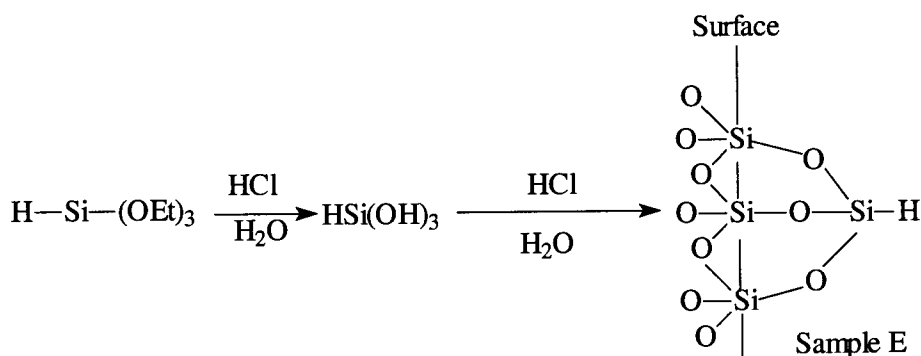
Figure 37 Synthesis of hydride-modified silica via hydrolysis-silylation reaction

As shown in Figure 36, the dimethylethoxysilane reacts directly with the silanol group on silica surfaces to form Si-O-Si bond in the presence of the catalyst, pyridine, in fully dry conditions. Figure 37 shows that the trihydroxy-sustituted silane reacts with silanol groups on the silica surface to form three Si-O-Si bonds via silylation or "condensation" reaction in HCl aqueous solution. Actually, the trihydroxy-substituted silane can use one or two of its hydroxy groups to react with the surface silanols and use the rest of its hydroxy groups to react with other the trihydroxy-sustituted silane. So it is likely that a polymerized random multilayer, instead of a well- defined monolayer, will be formed on the silica surface via the hydrolysis-silylation approach.

CP/MAS NMR

Figure 38 shows a comparison of ^{29}Si CP/MAS NMR spectra for "native" silica (sample A), hydride-modified silica gel via direct silylation (sample C) and via hydrolysis-silylation approach.

Figure 38 ^{29}Si CP/MAS NMR spectra of native silica (sample A), of hydride-modified Silica via direct silylation (sample c) and via hydrolysis-silylation approach (sample E)

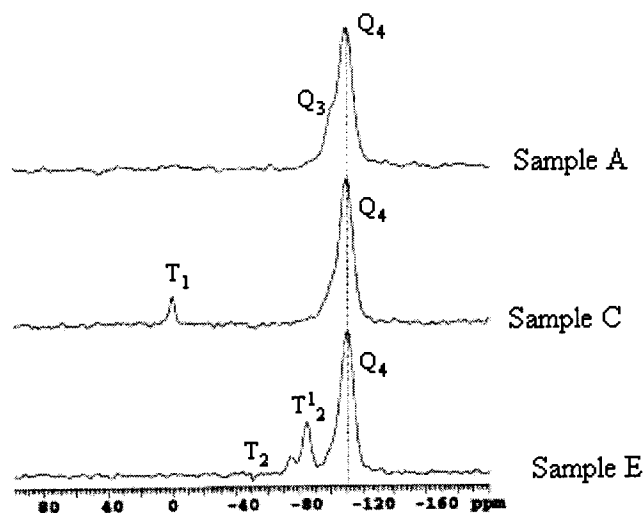As discussed previously (section 4.3.), there are two peaks in the CP/MAS Si^{29} spectrum of native silica gel at -100.5 ppm and –110.1 ppm due to siloxanes (Q_4) and single silanols (Q_3) on the silica surface. Comparing to the spectrum of the native silica gel, the spectrum of hydride-modified silica gel via the direct silylation reaction (sample C) shows that Q_3 peak totally disappeared and a new peak (T_1) appears at 0.04 ppm due to silicon bonded to the dimethylsilane, which constitute the proof of successful grafting. In the spectrum CP/MAS Si^{29} of hydride-modified silica gel via hydrolysis-silylation approach, the disappearance of Q_3 signals is also observed and two new peaks at –84.8 and –74.6 ppm due to T^1_2, silicon bonded to surface silicon and adjacent silane, and due to T_2, silicon bonded to surface silicon via two Si-O-Si bond, respectively. The appearance of T^1_2 and T_2 and disappearance of Q_3 signals prove that the silica surface is chemically modified. Because of steric hinderance, the T_3 peak due to the silicon bonded to three surface silicon atoms at the same time through Si-O-Si linkage is not observed,
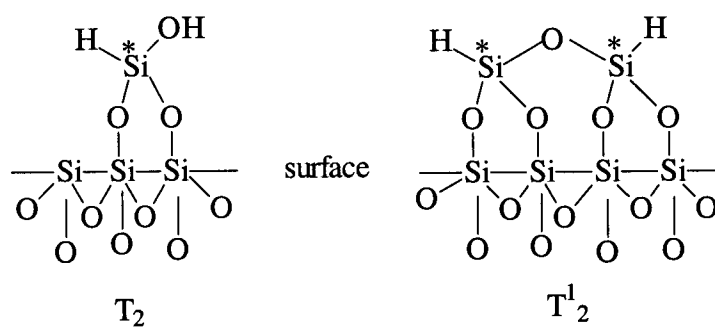
Figure 39 The grafted structure formed at the silica surface via hydrolysis-silylation approach

Which confirms Vangani and Rashit's observation[62] .The grafted structure formed at the silica surface via hydrolysis-silylation approach is shown in Figure 39.

Sample C and E were also characterized by the ^{13}C CP/MAS solid state NMR (Figure 40). In the spectrum of sample C, one peak at 0.98 ppm is observed, which is attributed to
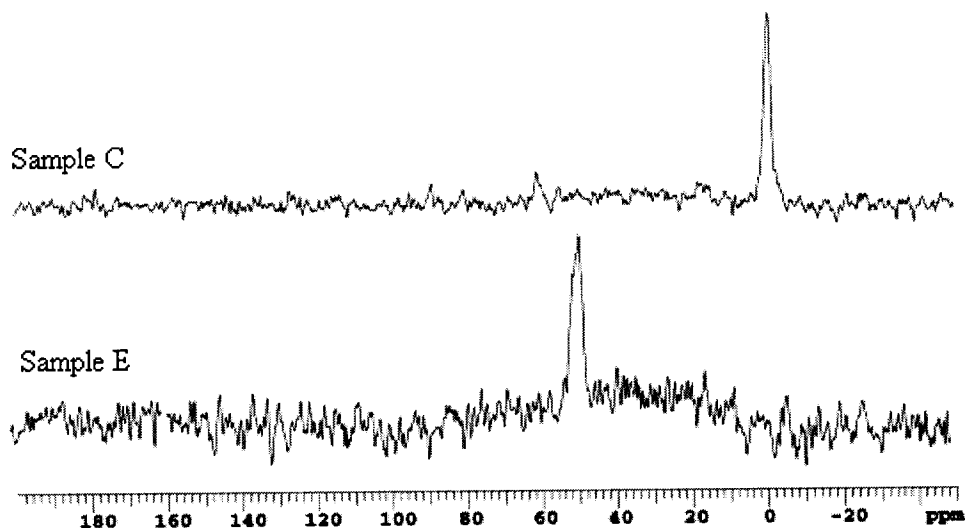
Sample C

Sample E

Figure 40 ^{13}C CP/MAS NMR spectra of hydride-modified silica the sample C via direct hydrosilylation and sample E via via hydrolysis-silylation approach

the methyl groups of the grafted silane moiety. This confirms that the direct silylation grafting process is successful. In the spectrum of sample E, only one peak at 48.5 ppm is observed due to the physically absorbed trace methanol which might be introduced into the grafted structure during the washing process. It was not completely removed even being heated under vacuum, which confirms the expectation that a polymerized random multilayer might be formed on the silica surface. Carbons of ethoxy group of the precursor (triehoxysilane) were not detected, which suggests that the hydrolysis of the precursor was very efficient.

Grafting the Allyl Diethylphosphonate onto the Hydride-Modified Silica Surface, CP/MAS NMR

Allyl diethyl groups were immobilized onto the silica hydride-modified silica surface (sample C and E) through Si-C bonds via catalytic hydrosilation to give sample D and F respectively.
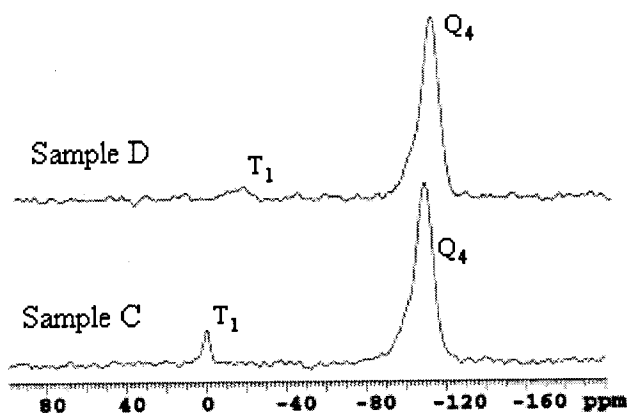
Figure 41 ^{29}Si CP/MAS NMR spectra of hydride-modified silica (sample C) and of phosphonateobonded silica (sample D)

Figure 41 shows a comparison of ^{29}Si CP/MAS NMR spectra for sample C and sample D. The T_1 peak on the spectra of sample C appears at 0.04 ppm, which is attributed to the silicon bonded to the dimethylsilane through one siloxane linkage. Because of the shielding effect of the alkyl group, the T_1 peak on the spectrum of sample D moves towards the upfield and is observed at −16.1 ppm, which proves that the Si-C bond was formed on the silica surface.

A good similarity was observed between the ^{13}C CP/MAS NMR spectra of sample D and of sample B (Figure 42), which is expected. The same grafted structure should be formed on the silica surface because the same processes were used to prepare sample B and D. The only difference is that the same process was carried out in multiple steps in

the preparation of sample D. Comparing with the spectrum of the sample B, a decrease

of the intensities of the corresponding peaks in that of the of sample D are noticed, which

suggests that the loading of the phosphonate group on the sample D's surface is lower

than that on the sample B's surface. This might be due to the lower efficiency of

hydrosilylaion reaction involved in the preparation of the sample D, in which one of the

reagent, silane, was confined on the silica surface.
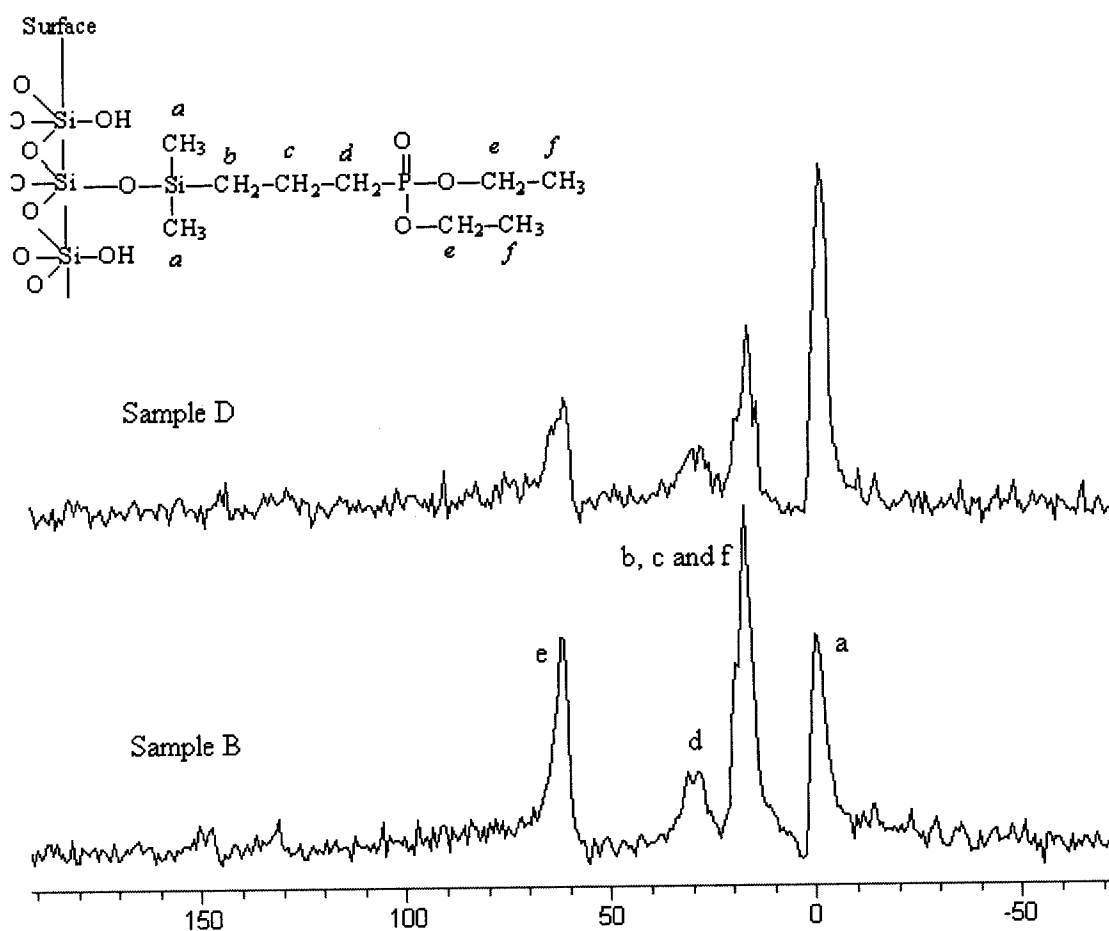

Figure 42 ^{13}C CP/MAS NMR spectra of the sample B and sample D

Figure 43 shows a comparison of ^{29}Si CP/MAS NMR spectra for sample E, hydride-

modified silica gel via hydrolysis-silylation approach, and sample F, silica gel obtained

by attaching the phosphonate group on the sample E's surface via the catalytic
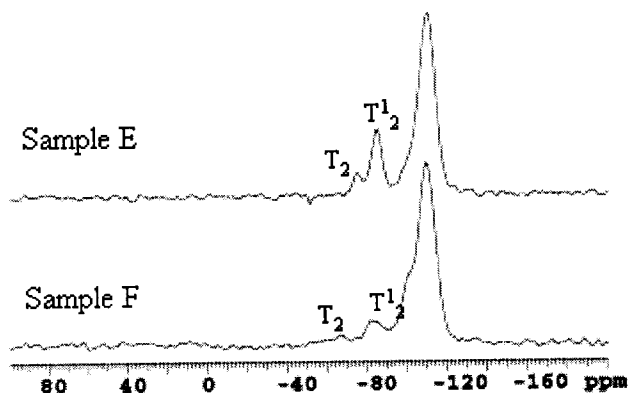
hydrosilylation reaction.

Figure 43 ^{29}Si CP/MAS NMR spectra of the sample E and sample

As discussed previously, two peaks on the ^{29}Si CP/MAS NMR spectra of the sample E

at –84.8 and –74.6 ppm are assigned to T^1_2 and T_2 (Figure 39). After the hydrosilylation

reaction, the protons in the T^1_2 and T_2 structures were replaced by the butyl

diethylphosphonate groups. Because of the shielding effect of the alkyl group, the T^1_2 and

T_2 peaks on the spectrum of sample F moves towards the upfield and is observed at –82.2

and -66.6 ppm, which proves that the Si-C bond was formed on the silica surface.

In the ^{13}C CP/MAS NMR spectrum of the sample F (Figure 45), The broad overlapped

peak roughly in the range δ 15.0-19.8 ppm is assigned to the carbon of the bridging

methylene groups (carbon a and b) between phosphorous and silicon and methyl groups

(carbon d) in the phosphonate ester. The peak at δ 28.3 ppm is assigned to the methylene

(carbon c) which is directly bonded to the phosphorous. The most downfield signal at δ

62.3 ppm is due to methylene groups in the phosphonate ester.
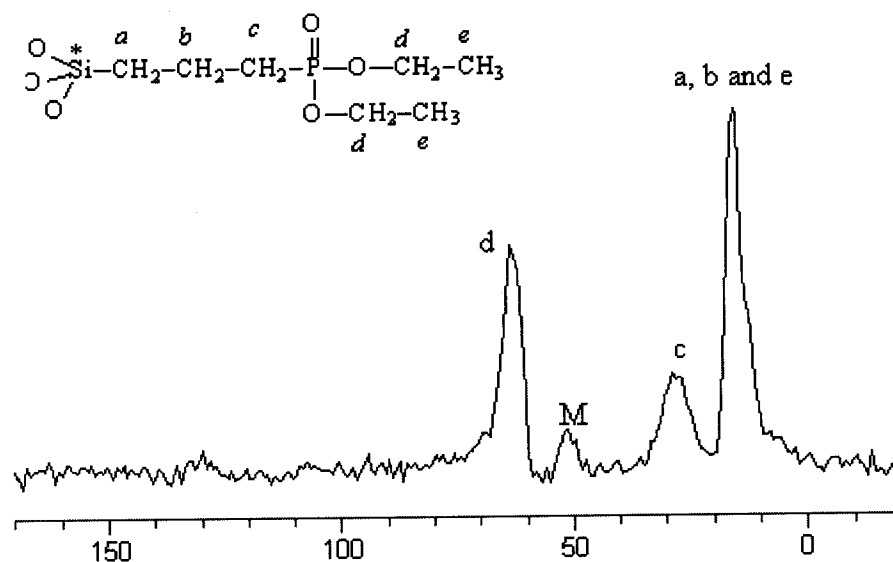
Figure 44 ^{13}C CP/MAS NMR spectrum of the sample F

An unexpected signal (M) is observed at δ 50.8 ppm. It is assigned to the methoxy group which replaced the hydroxy group of the T_2 grafted structure via the nucleophilic substitution reaction during the hydrosilylation process (Figure 45). The appearance of signal M confirms the previous observation that trace methanol has been "buried" in the polymerized multilayer formed via hydrolysis-silylation approach.
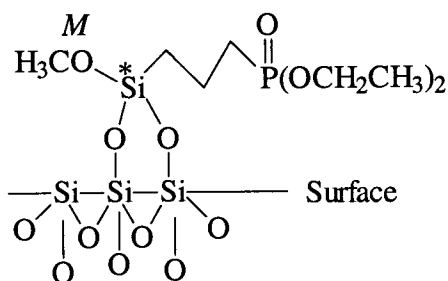
Figure 45 The grafted T_2 strucure on the surface of the sample F

Figure 47 shows a comparison of ^{31}C CP/MAS NMR spectra for sample B, D and F.

The ^{31}P CP/MAS NMR spectra of the sample D and F are noticed to be almost identical

to that of the sample B (discussed in section4.3.2.1), which suggested chemical

environment experienced by the phosphorous nuclei in these materials is almost identical.
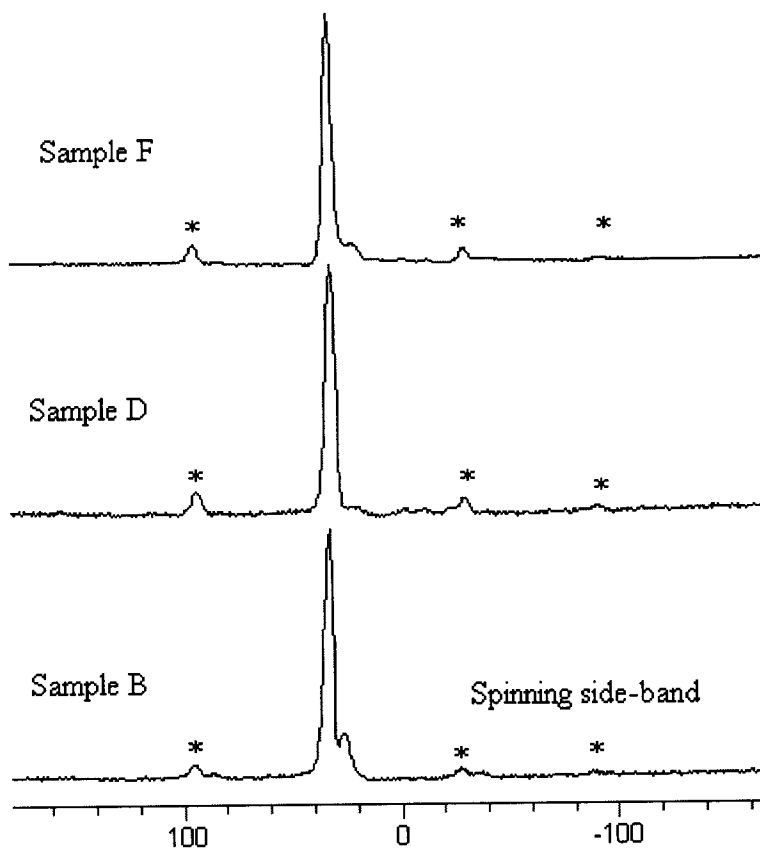
Figure 46 ^{31}P CP/MAS NMR spectrum of the sample B, D and F

The ^{29}Si, ^{13}C and ^{31}P CP/MAS NMR data prove that both multiple-step approaches

are successful.

4.5. Hydrolysis of Ethyl Phosphonate Esters Bonded to the Silica Surface

The ethyl ester of the phosphonate group bonded on the silica surface (sample B) were replaced by trimethylsilyl esters via a nucleophilic substitution reaction with bromotrimethylsilane (TMSBr). The very labile trimethylsilyl esters were then cleaved away by hydrolysis reaction with water at 70 ^{0}C to give the sample G. Initially, the sample G was intended to be characterized by the means of $^{29}$Si, ^{13}C and ^{31}P CP/MAS NMR, but due to the time limit, only the ^{13}P CP/MAS NMR data were collected which is shown in Figure 47.
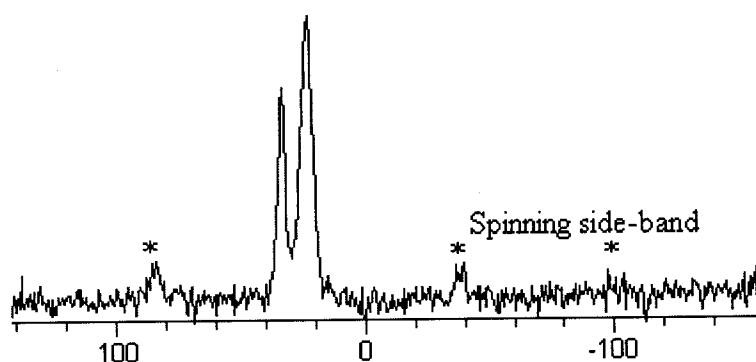

Figure 47 ^{31}P CP/MAS NMR spectrum of the sample G

Two significant signals are observed at δ 33.0 and 22.8 ppm. The peak at δ 33.0 ppm is assigned to the free phosphonic acid. The appearance of the second peak at δ 22.8 ppm is believed to be due to the interaction between the phosphonic acid moiety and silanol groups on the silica surface.

Chapter Five

Conclusion

The synthesis of the ready-to-graft phosphonates by the catalytic hydrolysilylation reaction between the alkoxysilane and phosphonate with an olefin moiety afforded excellent yields. The catalyst dicyclopentadienylplatinum (II) chloride showed very good regioselectivity and an anti-Markovnikov adduct was found to be the dominant product.

The solid state CP/MAS NMR data proved that the pyridine-catalyzed grafting processes carried out under fully dry conditions were successful. The CP/MAS data also revealed that the hydrolysis-silylation approach which is similar to the "sol-gel" process would lead to the forming of ill-defined polymerized multilayer on the silica surface. It was noticed that maximum of two alkoxysilyl functions of the same reagent molecule could react with the silanol groups on the silica surface.

In ^{13}C CP/MAS spectra, a good agreement was noted between the chemical shifts of carbons of the starting ungrafted precursors and those of their homologues of the grafted structures. The extensive phosphorus-carbon coupling was observed in both the standard solution NMR and solid state CP/MAS NMR spectra of the phosphonate group.

Based upon the ^{13}P CP/MAS data, the hydrolysis of ethyl esters of the phosphonate group bonded on the silica surface by the TMSBr-hydrolysis method seemed successful.

Chapter Six

Experimental

6.1.1. Materials

Silica gel was obtained from Aldrich (70-230 μm, Surface area 300 $m^2.g^{-1}$). Prior to use, it was washed with hydrochloric acid and dried under vacuum. Allyl bromide, triethylphosphite, dimethylethoxysilane, triethoxysilane, hydrate chloroplatinic acid dicyclopentadiene and bromotrimethylsilane (all from Aldrich, except dimethylethoxy-silane from United Chemical Technologies, Inc., PA) were used as received. All solvents were dried by standard techniques. All glassware was dried under vacuum at 120 ^{0}C for about 6-8 hours before use.

6.1.2. Apparatus and Methods

A Varian Gemini 2000 system was used to collect ^{1}H, ^{13}C and ^{31}P solution NMR data at 400 MHz, 100MHz and 161 MHz, respectively. The solvent used in these operations was CDCl$_3$. The ^{1}H and ^{13}C chemical shifts (δ) were reported in parts per million downfield from TMS (tetramethylsilane). The ^{31}P shifts (δ) were reported in parts per million downfield from phosphonic acid (external standard). The coupling constants (J) were reported in Hz. Splitting patterns for the NMR spectra were labeled as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and dt (douplet of triplets) etc.

A Bruker Daltonics Esquire-LC with Hewlett Packard HP1100 HPLC was used to obtain mass spectra with parameters as follows: direct infusion on Electrospray Ionization (ESI) mode, sample diluted to 0.01mg/mL in methanol and delivered to the flow at 1μl/min., scan begin at 15.00 m/z and scan end at 2200.00 m/z and accumulation time 20000 μs.

Solid-state NMR spectra were obtained using a Varian Unity[plus] 200 (4.7 T)

spectrometer with a Doty Scientific MAS probe. All samples were packed into 7 mm

silicon nitride or zirconia rotors with Kel-F end caps. ^{13}C and ^{31}P spectra were acquired

using a standard CP/MAS (Cross Polarization with Magic Angle Spinning) experiment

(^{i}). ^{13}C NMR spectra were acquired using the following parameters: 5 sec. relaxation

delay, 4.7 μs 90° pulse width, 1 ms contact time, and 5 kHz MAS. Each spectrum was

acquired by co-adding 16k transients. The methyl resonance (δ_{Me} = 17.3 ppm) from a

sample of hexamethylbenzene was used as an external ^{13}C reference. ^{31}P spectra were

acquired using the following parameters; 2 sec relaxation delay, 5.5 μs 90° pulse width, 3

ms contact time, and 5 kHz MAS. Each spectrum was acquired by co-adding 4k

transients. 85% Phosphoric acid (δ = 0 ppm) was used as an external ^{31}P reference. All

^{29}Si spectra were acquired using a standard Bloch decay experiment with following

parameters; 300 sec relaxation delay, 5.5 μs 90° pulse width, and 3 kHz MAS. Each

spectrum was acquired by co-adding 256 transients. Polydimethylsiloxane (PDMS) was

used as an external ^{29}Si reference (δ = -21 ppm). A continuous wave (CW) decoupling

field strength of 55 kHz was used in all experiments.

6.2. Synthesis of Allyl Diethylphosphonate, the Compound (I)

In a three-necked round-bottom flask, equipped with a dropping funnel with a

equalizing tube, a heating mantle, a thermometer, a magnetic stirring device and a

distillation device, 175.0 mL (1 mol, density 0.969 g.mL^{-1}, 98% purity) of

triethylphosphite was introduced. At 80 ^{0}C, 78.70 mL (0.91 mol, density 1.398 g.mL^{-1}, 99% purity) of allyl bromide were added dropwise for about 35 minutes.

The temperature was progressively raised to 100-110 ^{0}C in order to remove the produced ethyl bromide from the reaction system. The reaction then lasted about 6 hours. Allyl diethyl phosphonate, 151.4 grams, was obtained by vacuum distillation, boiling point = 45 ^{0}C at 20 mmHg. The yield was 85 %.

^{1}H NMR (400 MHz) [(C^{1}H$_3$C^{2}H$_2$O)$_2$POC^{3}H$_2$C^{4}H=C^{5}H^{a}H^{b}], (superscripted numbers and letters distinguish hydrogen environments): δ 1.17 (t, 6H, H^{1}, J_{HH} = 7.0 Hz, J_{HP} = 2.6 Hz), δ 2.43 and 2.49 (dd, 2H, H^{3}, J_{HH} = 7.3Hz, J_{HP} = 22.0 Hz), δ 3.92-4.01 (m, 4H, H^{2}), δ 5.04-5.10 (overlapping multiplets, 2H, H$^{5a, 5b}$), δ 5.59-5.72 (m, 1H, H^{4}).

^{13}C NMR (100 MHz) [(C^{1}H$_3$C^{2}H$_2$O)$_2$POC^{3}H$_2$C^{4}H=C^{5}H$_2$], (superscripted numbers distinguish carbon environments): δ 17.58 (dq, C^{1}, J_{CP} = 6.0 Hz, J_{CH} = 10.6 HZ), δ 32.17 and 33.53 (dt, C^{3}, J_{CP} = 139.0 Hz, J_{CH} = 26.0 HZ), δ 62.94 (dt, C^{2}, J_{CP} = 6.5 Hz, J_{CH} = 20.3 HZ), δ 120.50-121.08 (m, C^{5}), δ 128.31 (dd, C^{4}, J_{CP} = 0.2 Hz, J_{CH} = 0.4 HZ).

^{31}P NMR (161 MHz): δ 27.65 (s).

6.3. Synthesis of the Silylated Phosphonate, the Compound (II)

The silylated phosphonate was prepared via a catalytic hydrosilylation reaction between allyl diethylphosphonate, compound (I), and dimethylethoxysilane. The catalyst used in this reaction was dicyclopentadienylplatinum (II) chloride and it was prepared via the method developed by Laub and coworkers[55].

Into a three-necked round-bottom flask, equipped with a dropping funnel with a equalizing tube, a heating mantle, a thermometer, a magnetic stirring device and a reflux

condenser, 16.28 grams (90.9 mmol) of allyl diethylphosphonate, compound (I), and 4

mL of freshly prepared 661.28 µg. mL^{-1} of dicyclopentadienylplatinum (II) chloride

(roughly 100 µg of catalyst per gram of product) solution in THF were introduced. These

olefin/catalyst mixture was heated to about 70- 80 ^{0}C while being magnetically agtated

for 1 hour. Then 13.8 mL (100 mmol, density 0.757 g.mL^{-1}, 99 % purity) of dimethyl-

ethoxysilane was slowly added into the olefin/catalyst mixture for about 30 minutes. The

mixture was refluxed under nitrogen atmosphere at 120 ^{0}C for 48 hours. Then the

resultant mixture was distilled under reduced pressure to yield the silylated phosphonate

(18.5 grams, 72%), compound (II), boiling point 130 ^{0}C at 2 mmHg.

$$H_3C^aH_2C^bO-\underset{\underset{OC^aH_2C^bH_3}{|}}{\overset{\overset{O}{\|}}{P}}-C^cH_2-C^dH_2-C^eH_2-\underset{\underset{C^fH_3}{|}}{\overset{\overset{C^fH_3}{|}}{Si}}-OC^gH_2C^hH_3$$
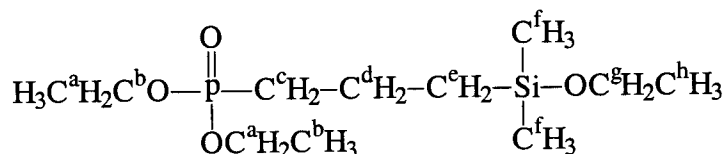
Figure 48 Designation of chemical environments of the silylated phosphonate

^{1}H NMR (400 MHz), (Figure 37, superscripted letters distinguish hydrogen

environments): δ 0.05 (s, 6H, H^f), δ 0.65 (t, 2H, H^e, J_{HH} = 8.3 Hz), δ 1.13 (t, 3H, H^h, J_{HH}

= 7.0 Hz), δ 1.27 (t, 6H, H^a, J_{HH} = 7.0 Hz), δ 1.56-1.77 (overlapping multiplets, 4H, H$^{c,\,d}$),

δ 3.60 (q, 2H, H^g, J_{HH} = 6.9 Hz), δ 4.04 (t, 4H, H^b, JHP = 10 Hz).

^{13}C NMR (100Hz), (Figure 37, superscripted letters distinguish carbon environments):

δ -.90 (s, C^f), δ 17.6 9 (d, C^e, J_{CP} = 5.0 Hz), δ 17.95 (d, C^a , J_{CP} = 7.8 Hz), δ 19.11 and

19.23 (d, C^d, J_{CP} = 16.0 Hz), δ 19.82 (s, C^a), δ 29.76 and 31.32 (d, C^d , J_{CP} = 137.4 Hz),

δ 59.31 (s, C^g), δ 62.48 (d, C^b , J_{CP} = 6.6 Hz).

^{31}P NMR (161 MHz): δ 32.50 (s).

Molecular weight calculated: 282.39 amu, m/z found: [(M – 45 (CH_3CH_2O-)] = 237.2.

6.4. Pretreated Silica Gel, the Sample A

Silica gel was obtained from Aldrich., 70-230 mash, 100A, surface area $300m^2.g^{-1}$.

40 grams of silica gel was acid-washed in 0.10 M HCl for 20 hours at 95 – 100 ^{0}C. After

acid washing, the silica was filtered hot, washed with deionized water, then dried under

vacuum for 24 hours at 130 - 140 ^{0}C.

^{29}Si CP/MS NMR: δ -100.49 (Q_3), δ -110.06 (Q_4).

6.5. Grafting the Silylated Phosphonate Group to Silica Surfaces, the Sample B,

The surface area of sample A was approximately surface area $300m^2.g^{-1}$. According to

Zhuravlev and coworkers' data[9], the silanol number on the surface of fully hydroxylated

silica is between 7.0–9.5 x 10^{-6} $mol.m^{-2}$. According to Snyder[63], due to steric effects,

there will be at most 4.5 x 10^{-6} $mol.m^{-2}$ silanol groups available for reaction with silylated

phosphonate groups.

A mixture of 3 grams of pretreated silica gel, 120 mL toluene, 1 mL of pyridine and 2

grams of the silylated phosphonate (compound II) were placed into a 200ml flask and

refluxed 24 hours at 100 ^{0}C under Argon gas protection. The resulting particles were

filtered hot, washed with toluene, then were placed into 150 mL methanol, heated to

boiling for 10 min., and filtered hot. The final particles were dried in a vacuum oven at

100 ^{0}C for 24 hours.

^{29}Si CP/MS NMR: δ -110.06 (Q_4), δ 13.6 (T_1).

^{13}C CP/MS NMR: δ -0.42, δ 17.21, δ 28.20 and 30.84 (d, JCP = 134.1 Hz), δ 61.24.

^{31}P CP/MS NMR: δ 25.74, δ 32.48.

6.6. Synthesis of Hydride-Modified Silica Gel via Direct Silylation, the Sample C

A mixture of 8 grams of pretreated silica gel, 120 mL of toluene, 1 mL of pyridine and 5 grams of dimethylethoxysilane were placed into a 200ml flask and refluxed 24 hours at 100 ^{0}C under Argon gas protection. The resultant particles were filtered hot, washed with toluene. The resultant powder then placed into 150 ml of methanol, heated to boiling for 10 minutes, and centrifuged hot. The final particles were dried in a vacuum oven at 100 ^{0}C for 24 hours.

^{29}Si CP/MS NMR: δ -110.2 (Q$_4$), δ 0.04 (T$_1$).

^{13}C CP/MS NMR: δ 0.98.

6.7. Synthesis of phosphonate-modified silica by Grafting of Allyl Diethyl-phosphonte onto the Hydride-Modified Silica Gel (the sample C)

A mixture of 120 mL of toluene, 4 grams of ditethyl allyl phosphonate was placed into a 200mL flask with a reflux condenser. The contents were protected from moisture and air with a nitrogen flow. The reaction mixture was heated to boiling. 100 μg of catalyst (dicyclopentadienylplatium (II) chloride) per gram of product was then injected with a syringe as a solution (3 mg.mL^{-1}) in new distilled THF. The mixture was heated to about 70 – 80 ^{0}C while being agitated magnetically for about 1 hour. 3 grams of the hydride-modified silica gel (the sample C) were then slowly added into the olefin / catalyst solution. The mixture was then refluxed for about 36 hours at 100 ^{0}C. After which the mixture was centrifuged and washed with three 50-mL portion of toluene, then placed into 150 mL of methanol, heated to boiling for 10 minutes, and centrifuged hot. After the solvent was removed, the solid was dried under vacuum at 110 ^{0}C for 24 hours.

^{29}Si CP/MS NMR: δ -110.2 (Q$_4$), δ -16.1 (T$_1$).

^{13}C CP/MS NMR: δ -0.40, δ 17.0, δ 28.1, δ 61.24.

^{31}P CP/MS NMR: δ 24.9, δ 33.7.

6.8. Synthesis of Hydride-Modified Silica Gel via Hydrolysis-Silylation Approach, the Sample E

5 grams of pretreated silica gel (sample A), 100 mL of dioxane and 7 mL of 2.3 M HCl (aq) solution were placed in a 3-necked, round bottom flask equipped with a condenser and an addition funnel with equalizing tube. The mixture was heated to about 70 – 80 °C, then 45 ml of 0.5 M triethoxysilane in dioxane solution was added dropwise, over a period of 20-25 minutes. The mixture was then refluxed for about an hour, after which the product was centrifuged and washed consecutively with 50 mL of 20:80 water/THF, THF, and methanol (twice with each solvent). The final product was dried at room temperature and then in vacuum oven at 110 °C for 12-16 hours.

^{29}Si CP/MS NMR: δ -84.8 (T$^1_2$), δ -74.6 (T$_2$).

^{13}C CP/MS NMR: δ 48.5.

6.9. Synthesis of Phosphonate-Modified Silica by Grafting of Allyl Diethylphosphonte onto the Hydride-Modified Silica Gel (the sample F)

2 grams of diethyl allyl phosphonate (compound II) dissolved 75 mL toluene and about 750 μg of catalyst (dicyclopentadienylplatium (II) chloride) dissolved in dry and freshly distilled THF were placed into a 3 neck 200-mL flask equipped with a condenser. The mixture was heated to about 70 – 80 °C while being agitated magnetically for about 1

hour. 3 grams of the hydride-modified silica gel (sample E) were then slowly added into the olefin / catalyst solution. The mixture was then refluxed for about 36 hours at 100 ^{0}C. After which the mixture was centrifuged and washed with three 50-mL portion of toluene, then placed into 150 mL of methanol, heated to boiling for 10 minutes, and centrifuged hot. After the solvent was removed, the solid was dried under vacuum at 110 ^{0}C for 24 hours.

^{29}Si CP/MS NMR: δ –82.2, δ -66.6, δ 110.2.

^{13}C CP/MS NMR: δ 15.0-19.8, δ 28.3, δ 50.8, δ 62.3.

^{31}P CP/MS NMR: δ 23.3, δ 34.0

5.10. Hydrolysis of Ethyl Ester of the Phosphonate Bonded on the Silica Surface TMSBr-Hydrolysis Method

0.50 grams of the sample B was suspended in 2.5 grams of TMSBr (bromo-trimethylsilane) and was refluxed under vigorous stirring at 70 ^{0}C for 72 hours. After evaporation of volatiles, the silica powder was suspended in water in water and refluxed at 90 ^{0}C for 36 hours. Then the resulting powder was centrifuged and dried under vacuum at 110 ^{0}C for 48 hours.

^{31}P CP/MS NMR: δ 33.0, δ 22.8.

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Figure 49 ^{1}H NMR spectrum of allyl diethylphosphonate
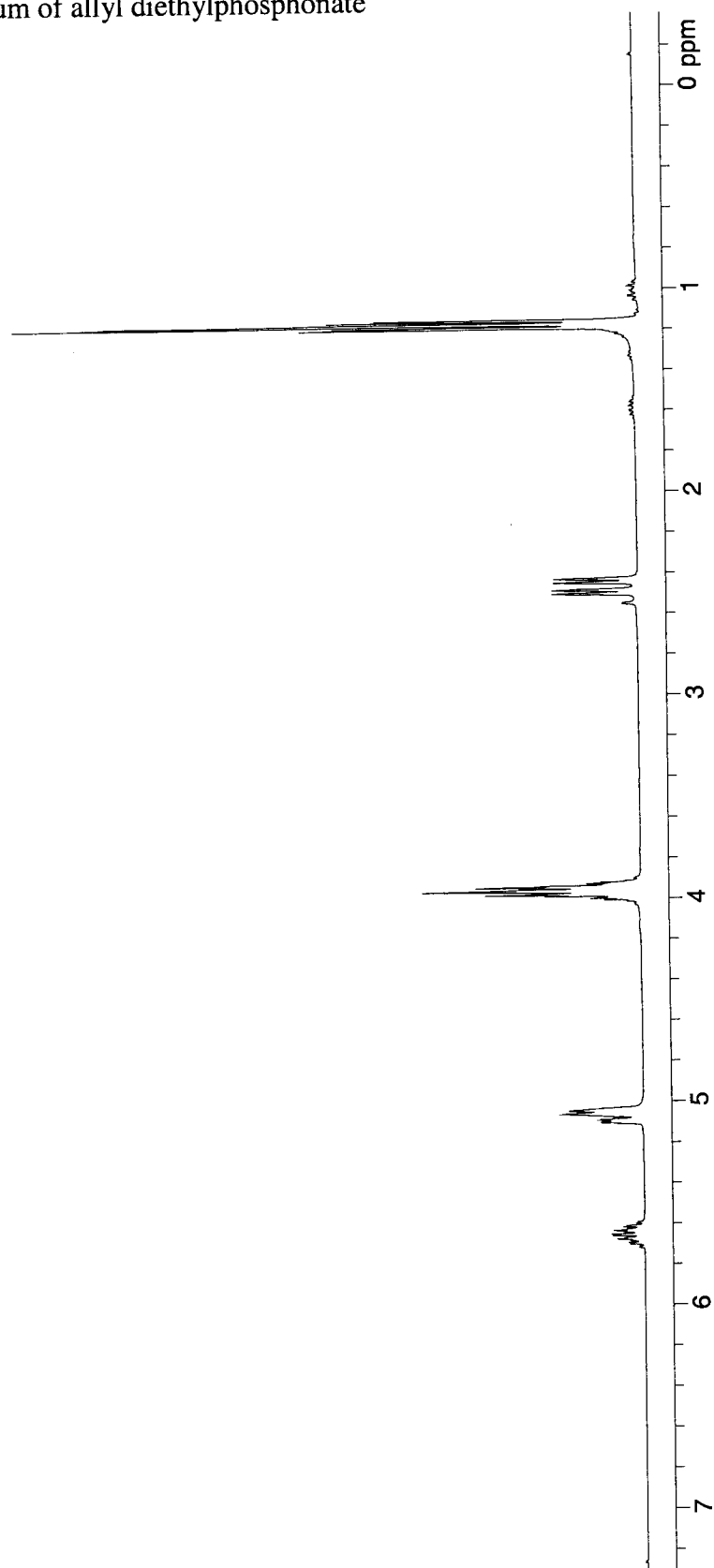
Figure 50 ^{13}C NMR spectrum of allyl diethylphosphonate
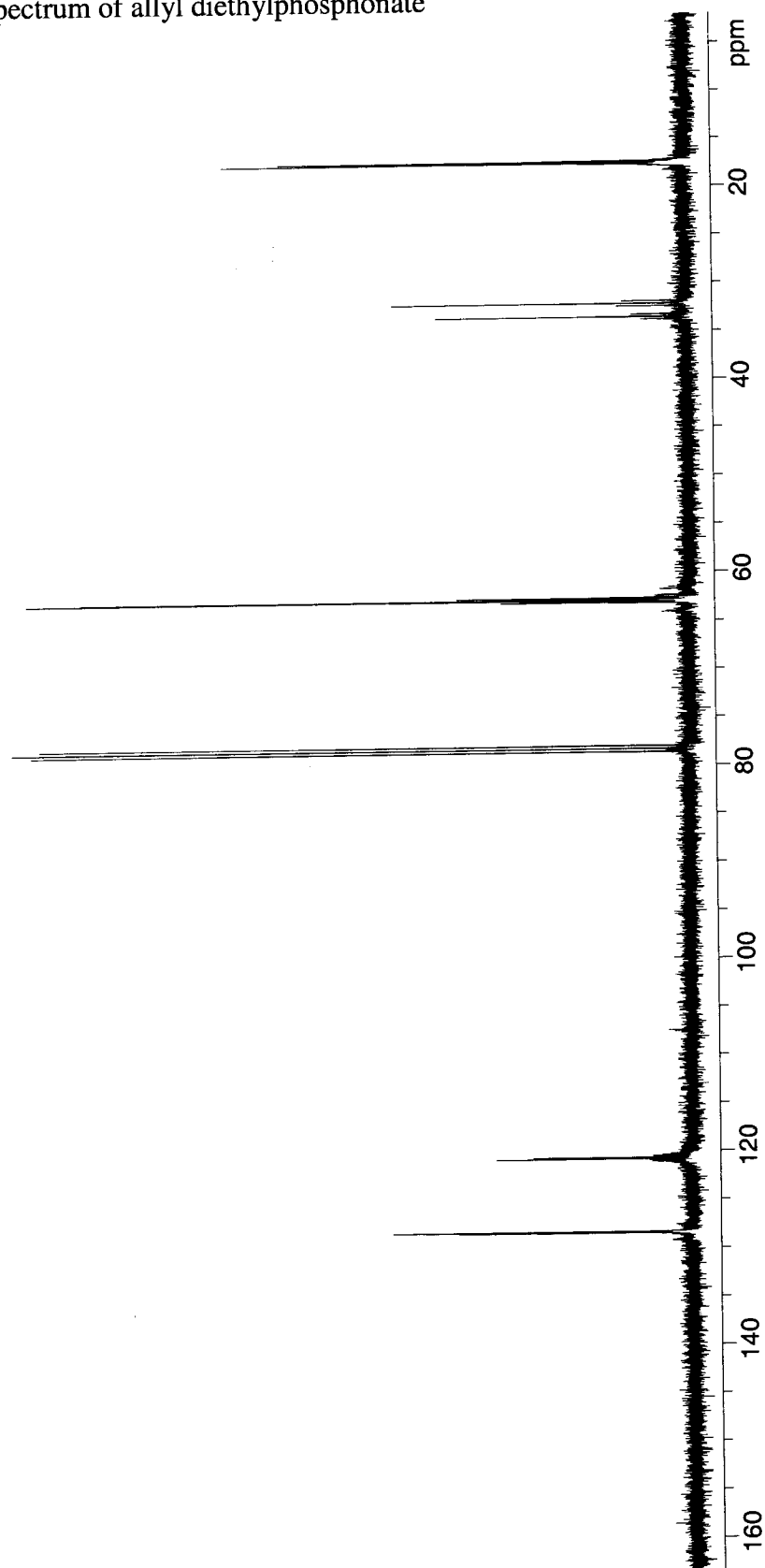
Figure 51 ^{31}P NMR spectrum of allyl diethylphosphonate
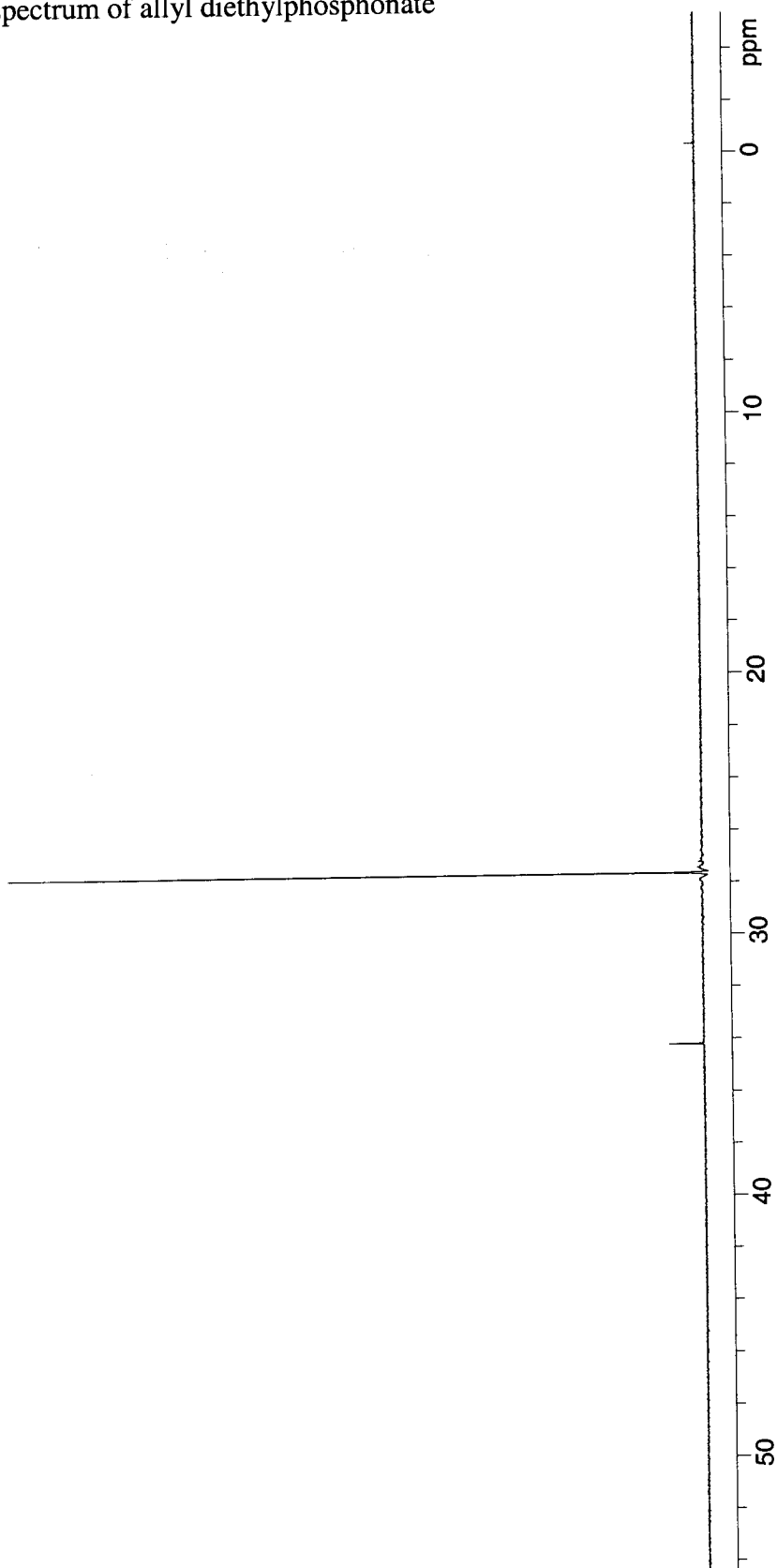
Figure 52 ^{1}H NMR spectrum of (diethylphosphonobutyl)
ethoxymethylsilane

63
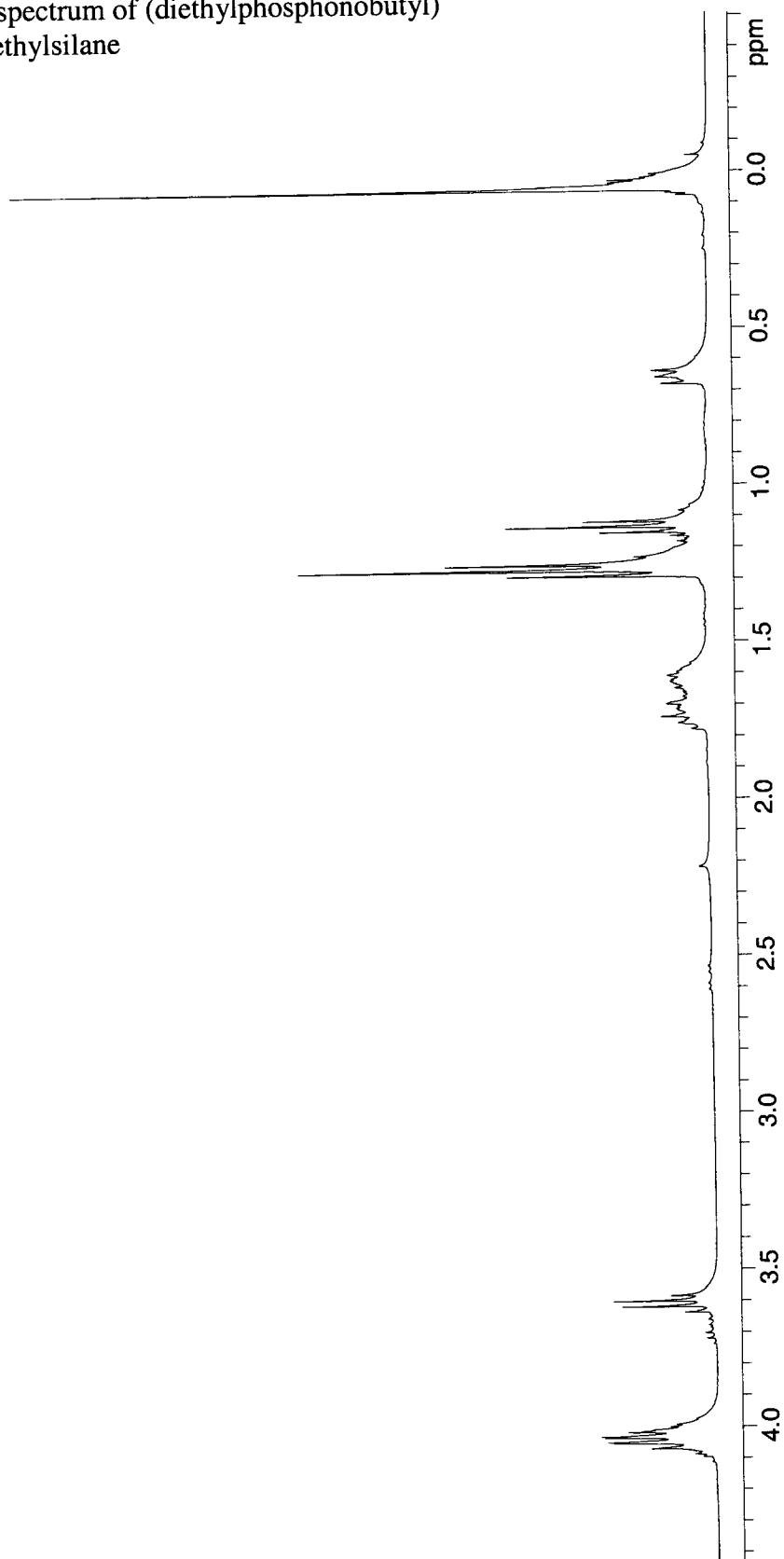
Figure 53 ^{13}C NMR spectrum of (Diethylphosphonobutyl)
ethoxymethylsilane
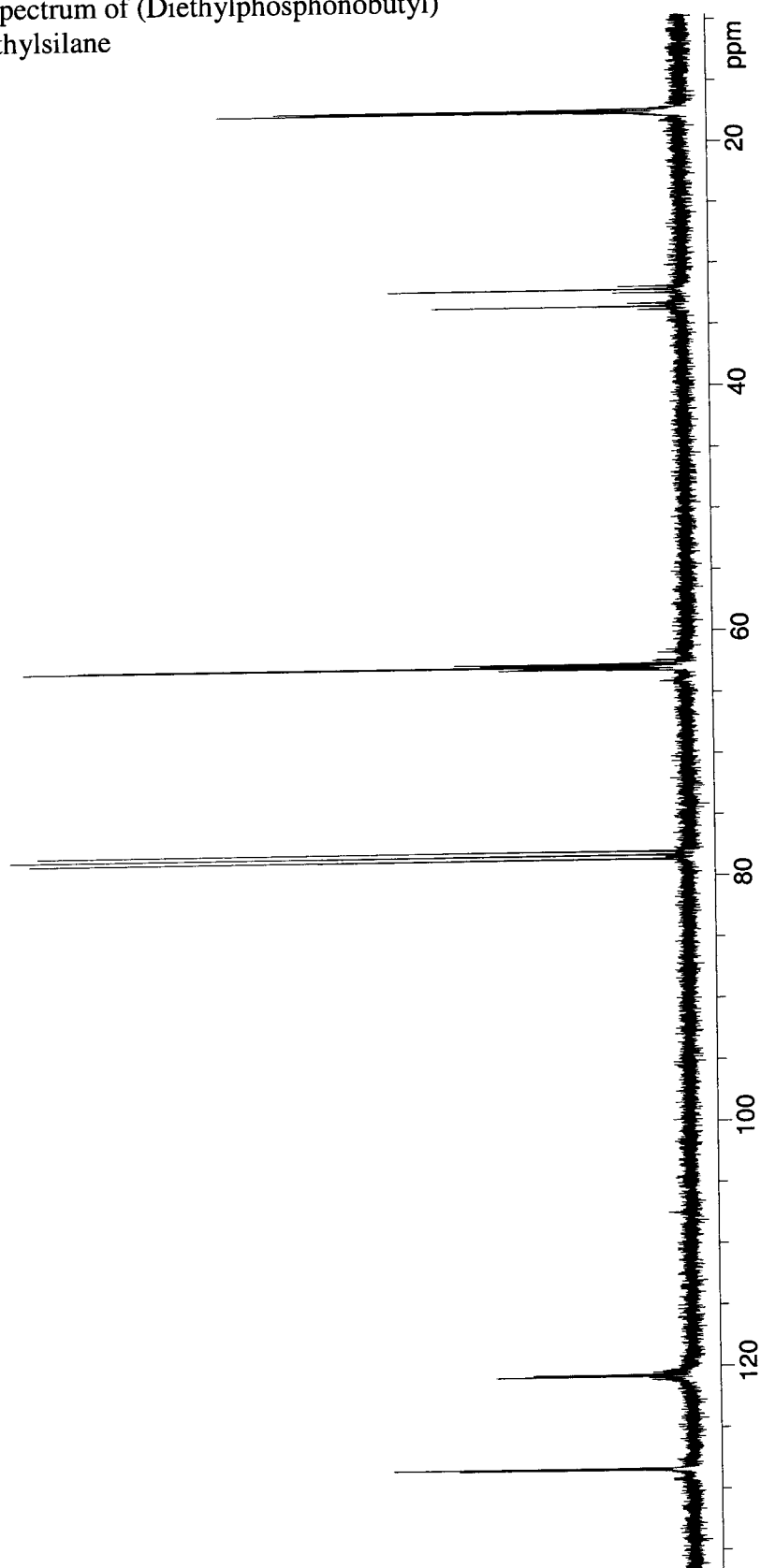
Figure 54 ^{31}P NMR spectrum of (Diethylphosphonobutyl)
ethoxymethylsilane
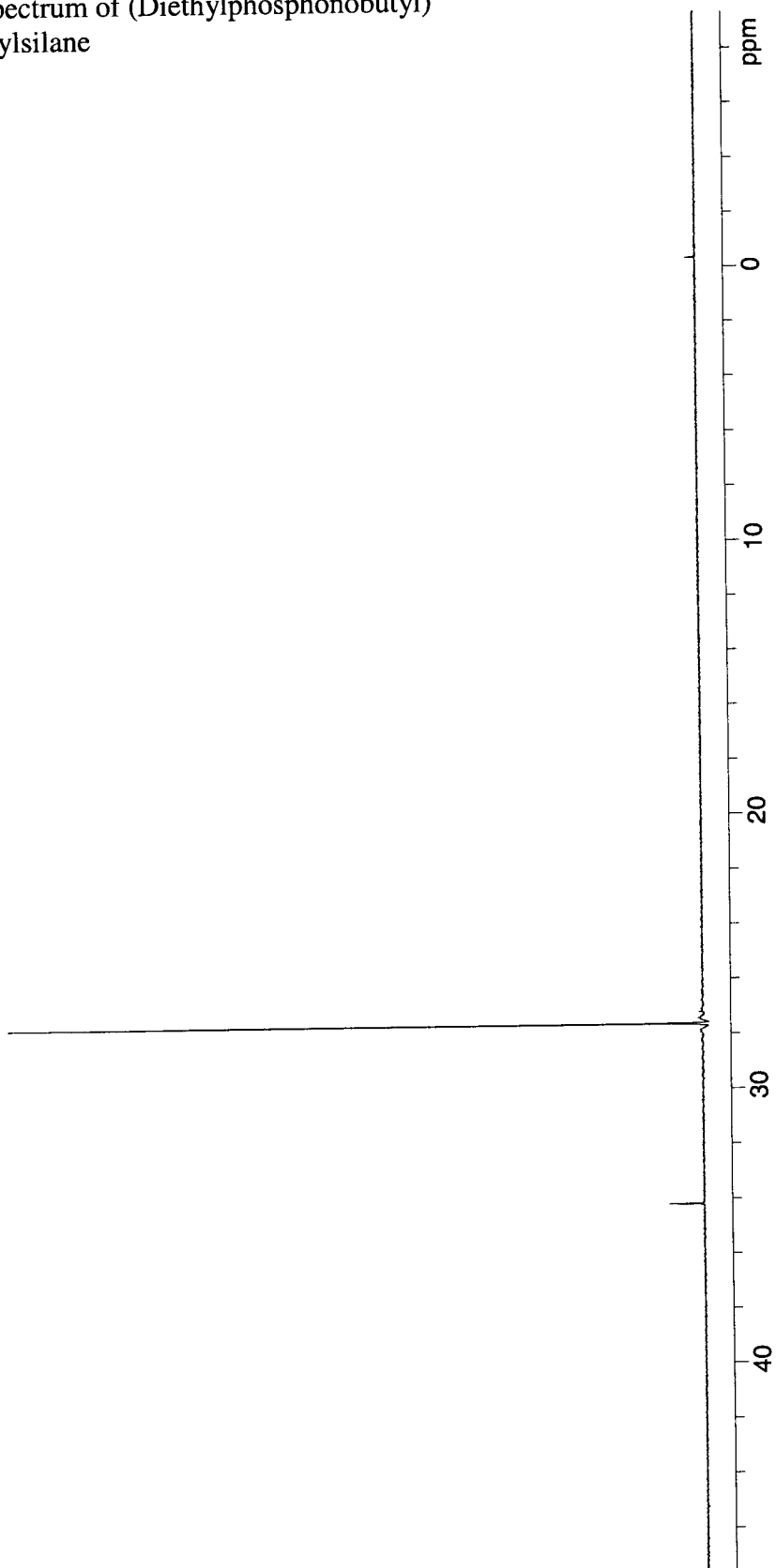
Acquisition Parameter:

Ion Source	APCI	Polarity	Positive
Mode	Std/Normal	Skim 1	26.0 volt
Cap Exit Offset	77.0 Volt	Trap Drive	30.0 Volt
Scan Range	15.00 m/z	Average	10 Spectra
Accum. Time	20000 µs		
MS/Ms			
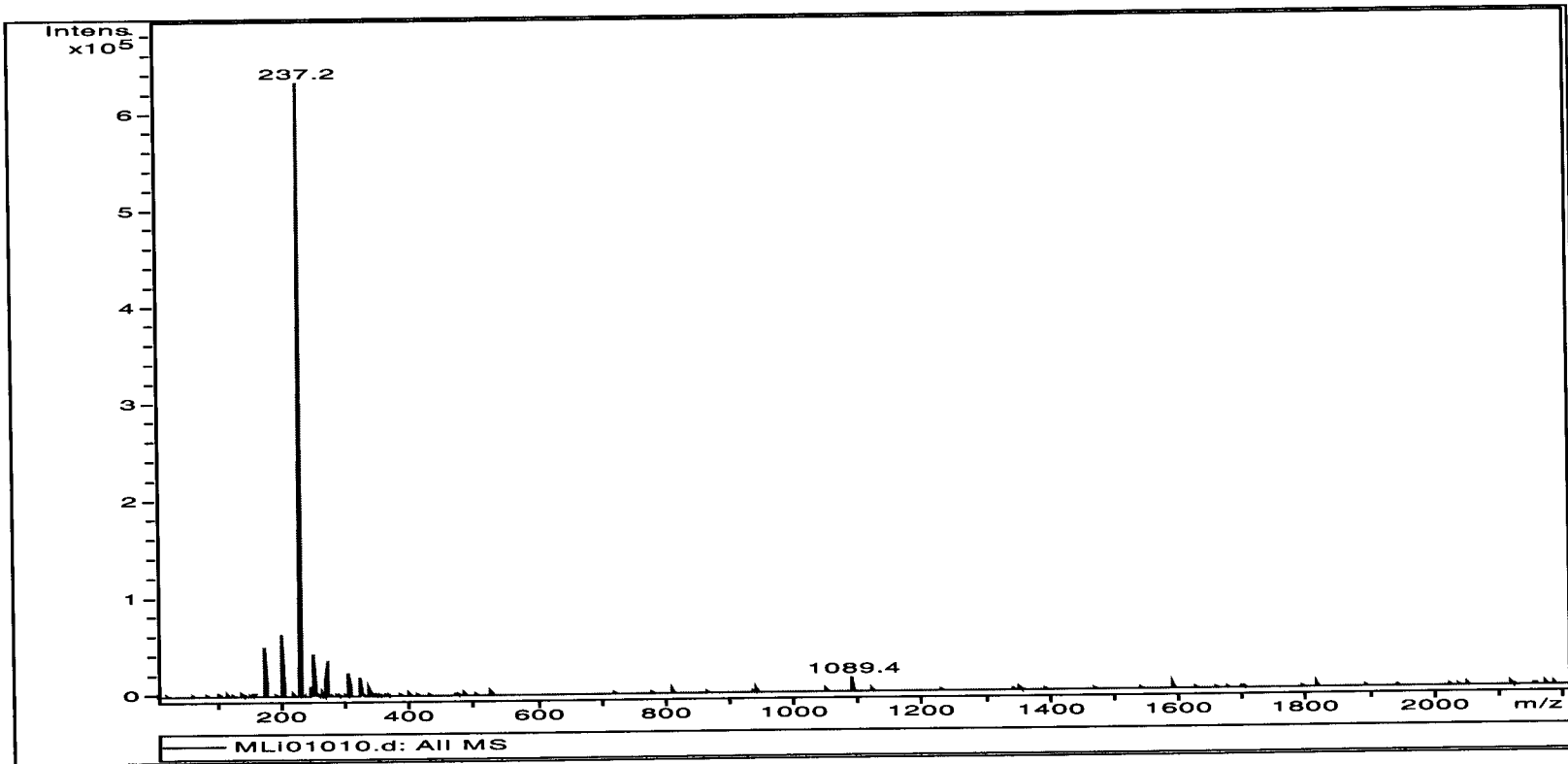
Figure 55   Mass spectrum of (Diethylphosphonobutyl) ethoxymethylsilane

Figure 56 ^{29}Si CP/MAS NMR spectrum of native silica gel
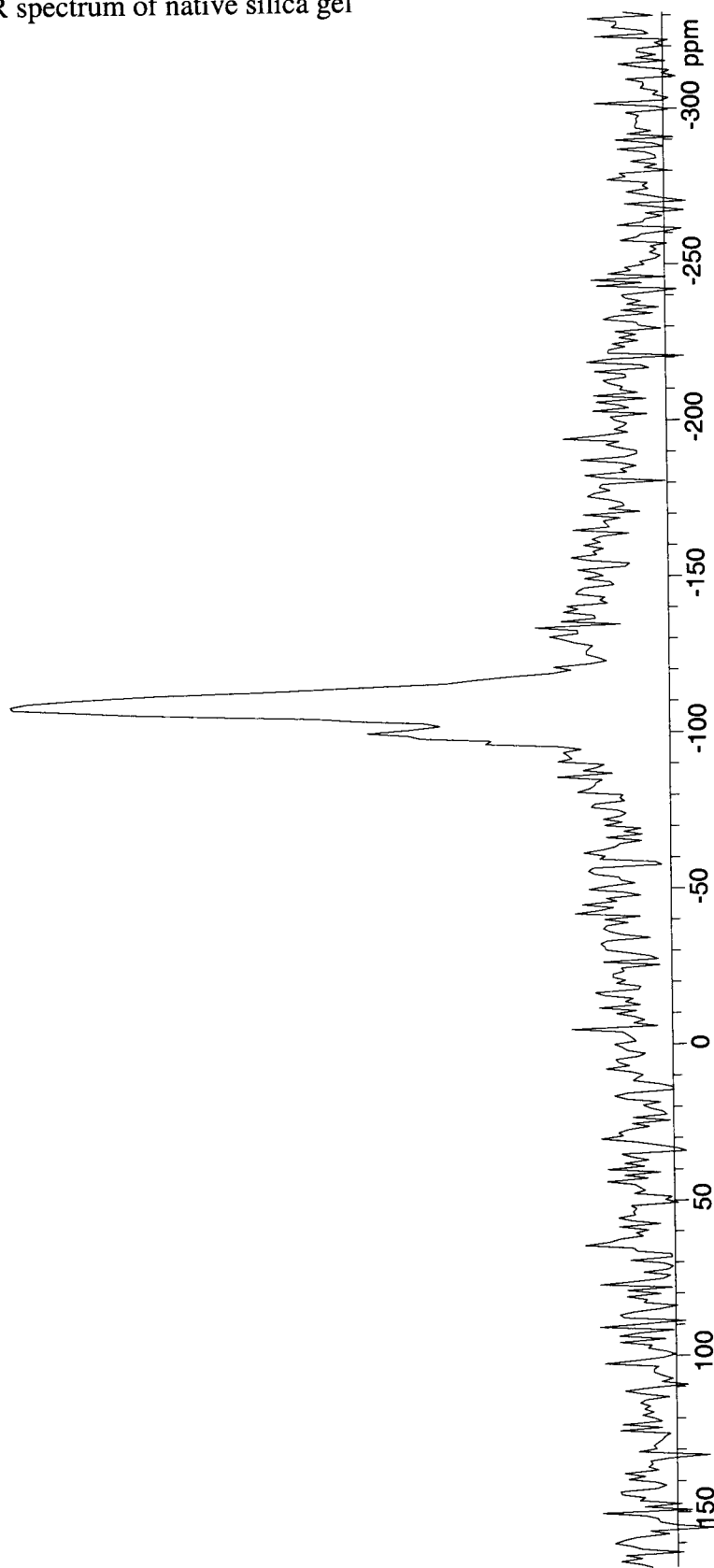
Figure 57 ^{29}Si CP/MAS NMR spectrum of the phosphonate-bonded silica gel, the sample B
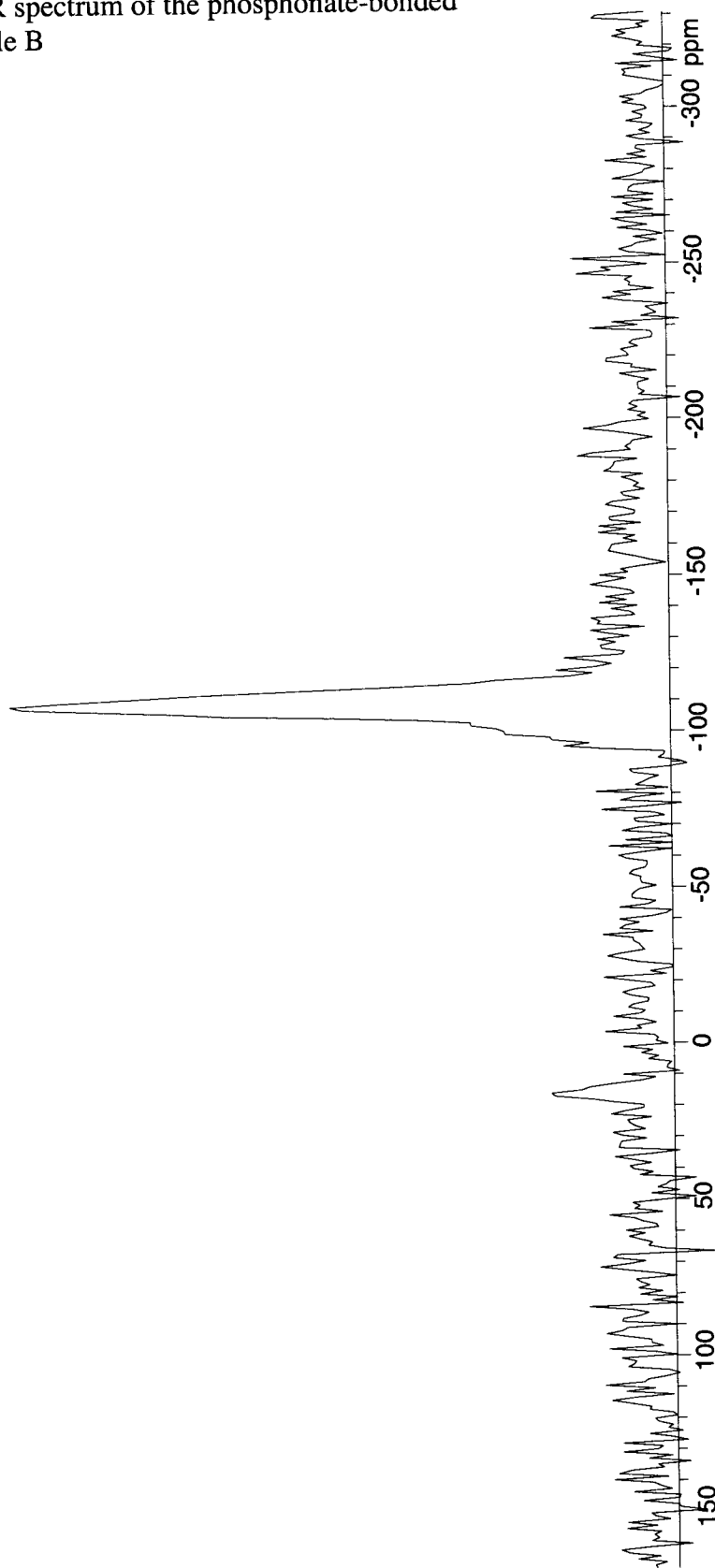
Figure 58 ^{13}C CP/MAS NMR spectrum of the phosphonate-bonded silica gel, the sampe B
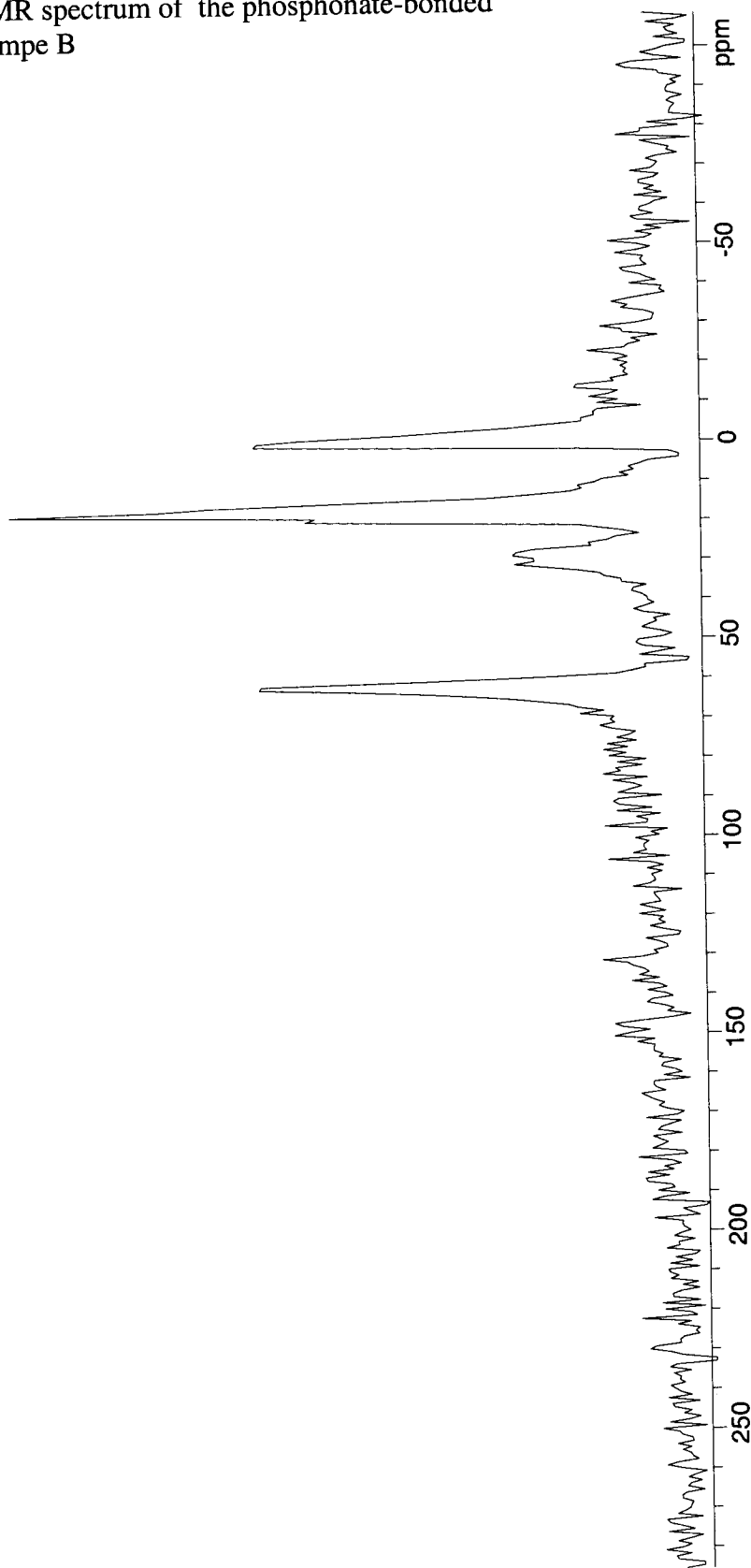
**Figure 59** ^{31}P CP/MAS NMR spectrum of the phosphonate-bonded silica gel, the sample B
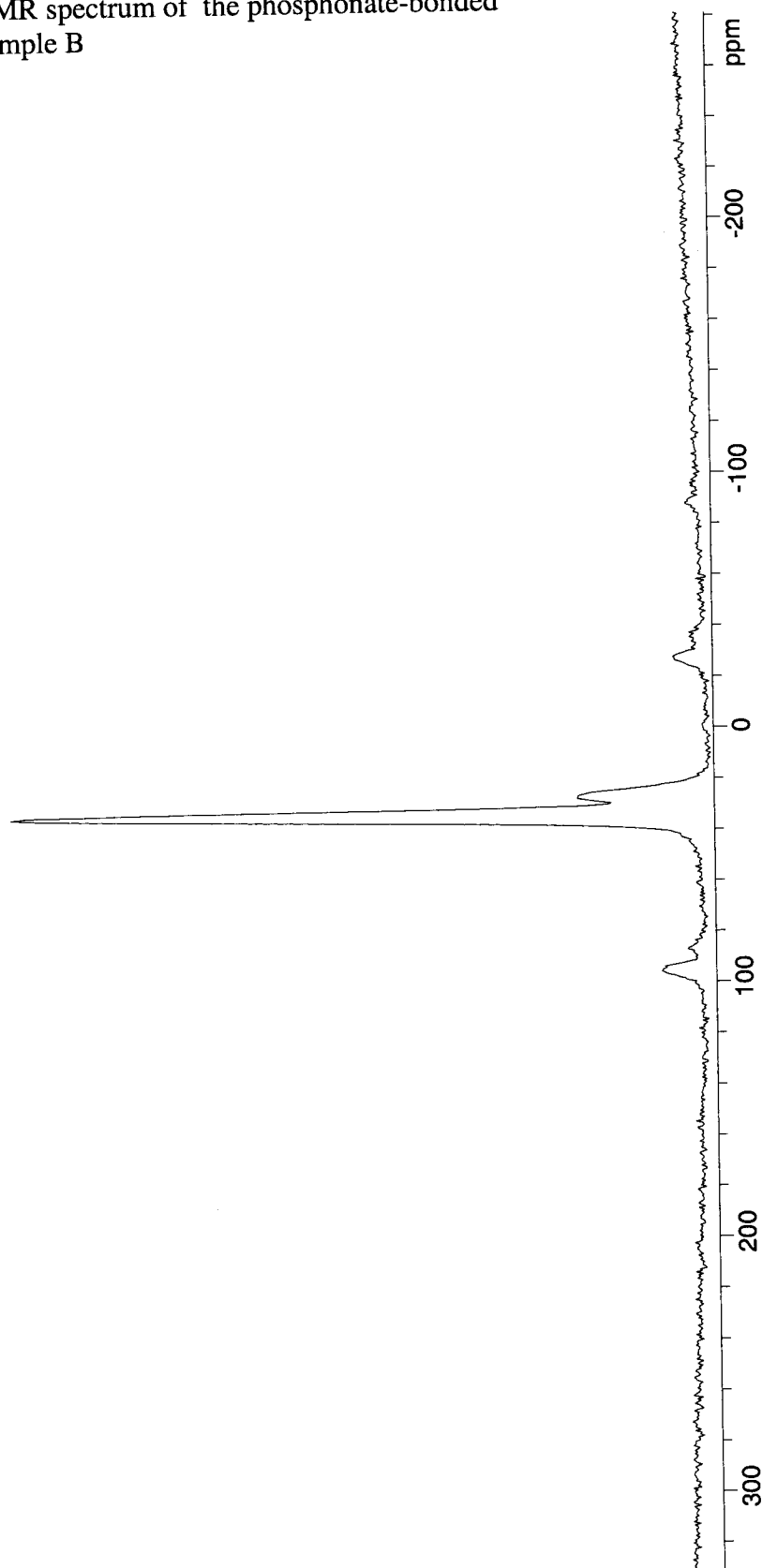
Figure 60 ^{29}Si CP/MAS NMR spectrum of hydride-modified silica gel via direct silylation, the sample C
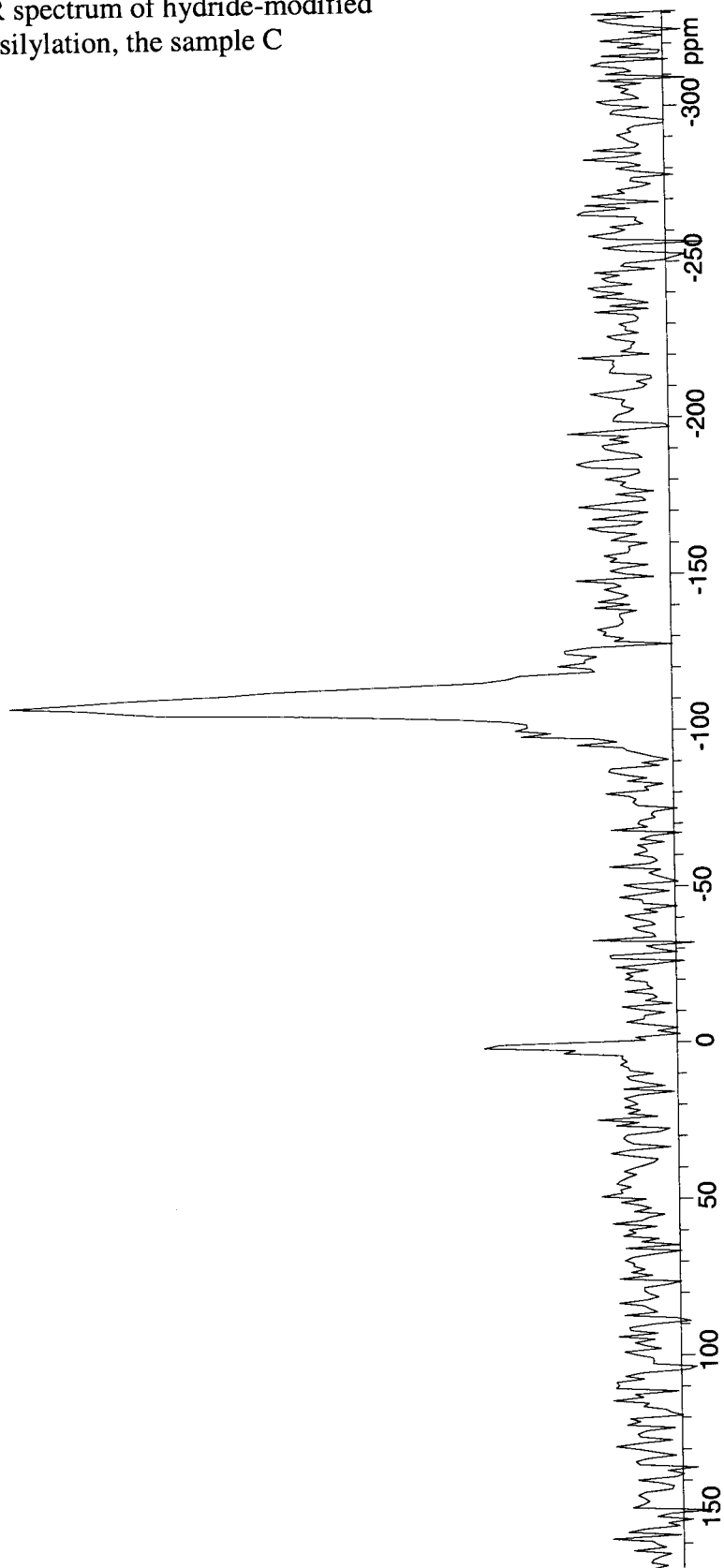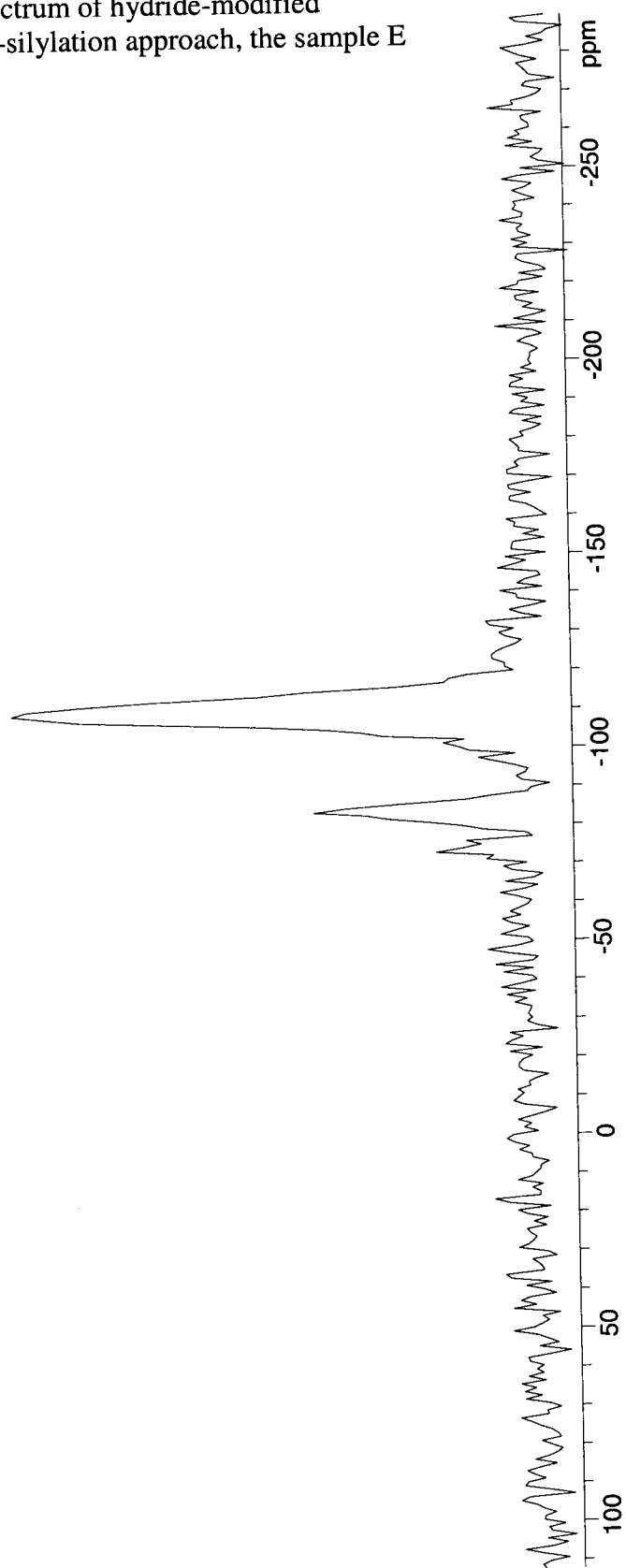
Figure 61 ^{13}C CP/MAS NMR spectrum of hydride-modified silica gel via direct silylation, the sample C
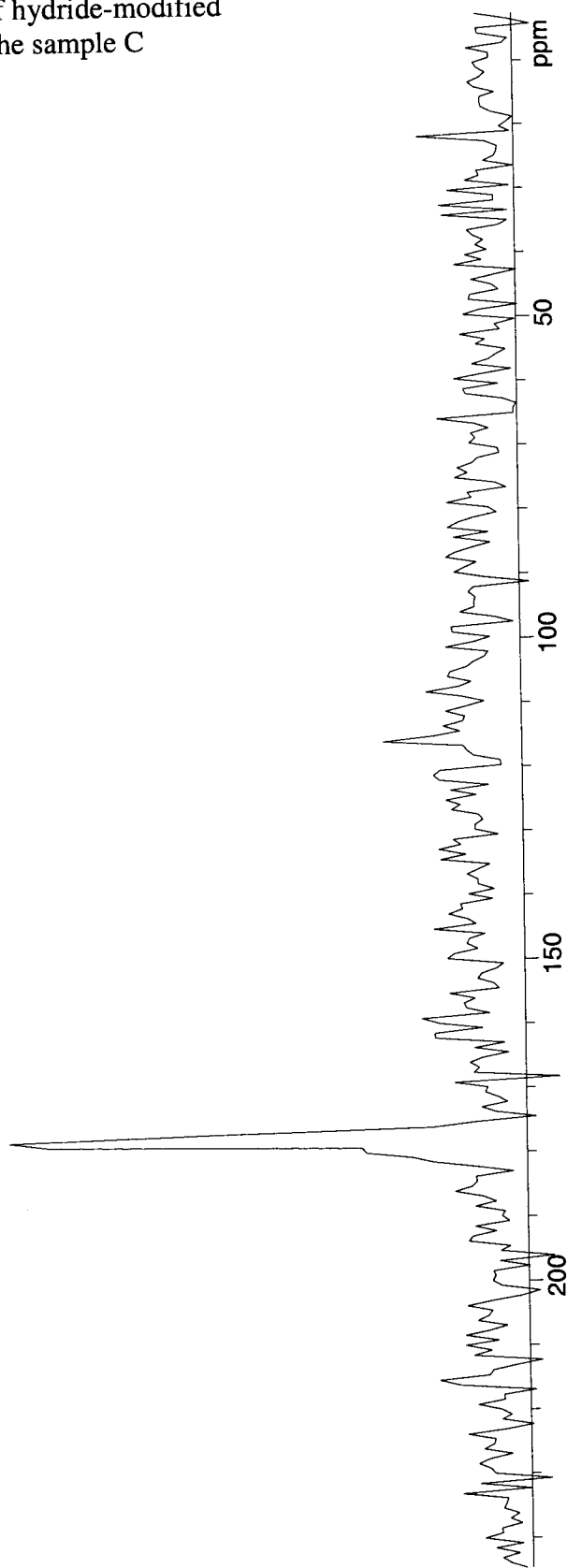
Figure 62 ^{29}Si CP/MAS NMR spectrum of the sample D
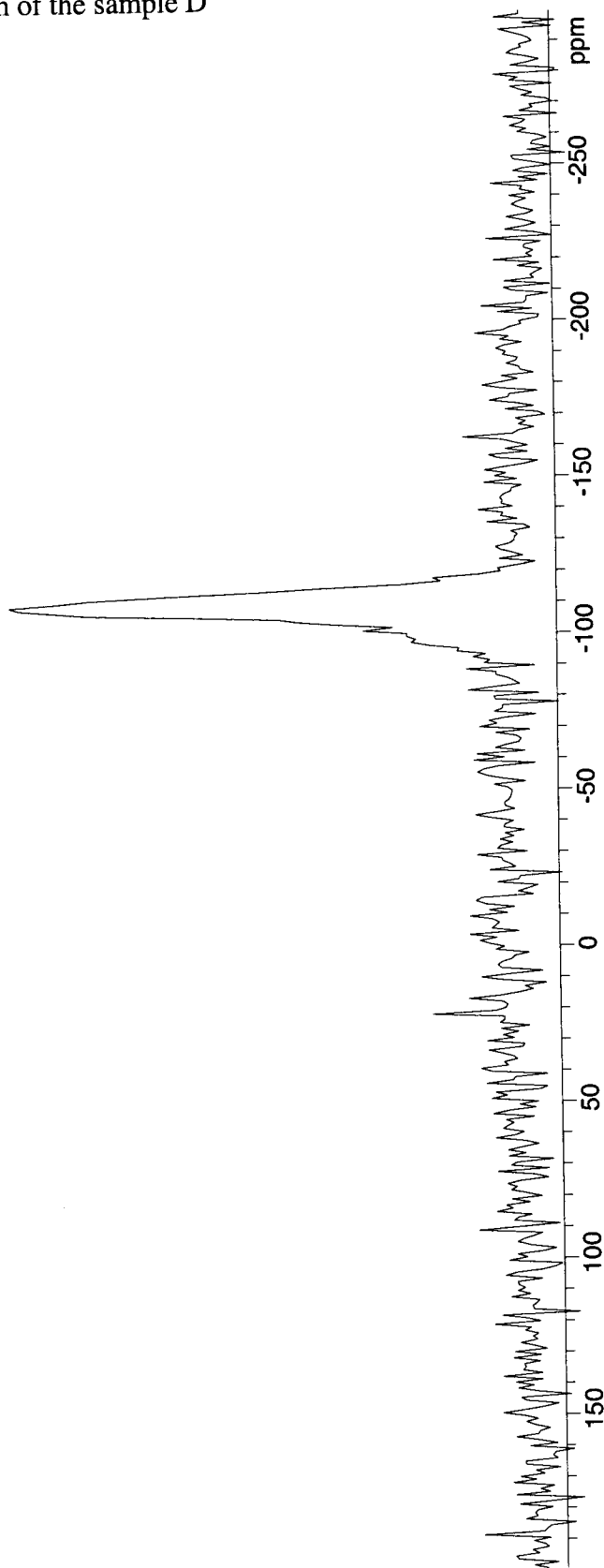
Figure 63 ^{13}C CP/MAS NMR spectrum of the sample D
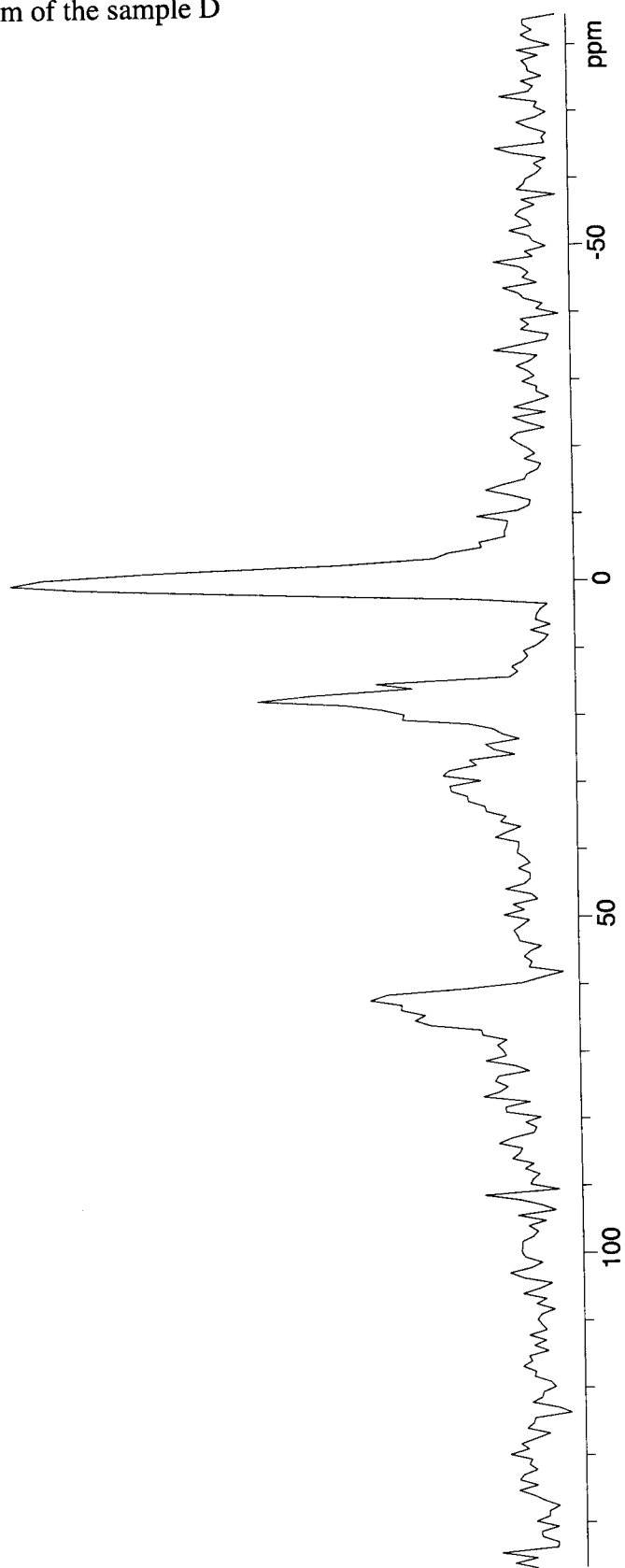
Figure 64 ^{31}P CP/MAS NMR spectrum of the sample D
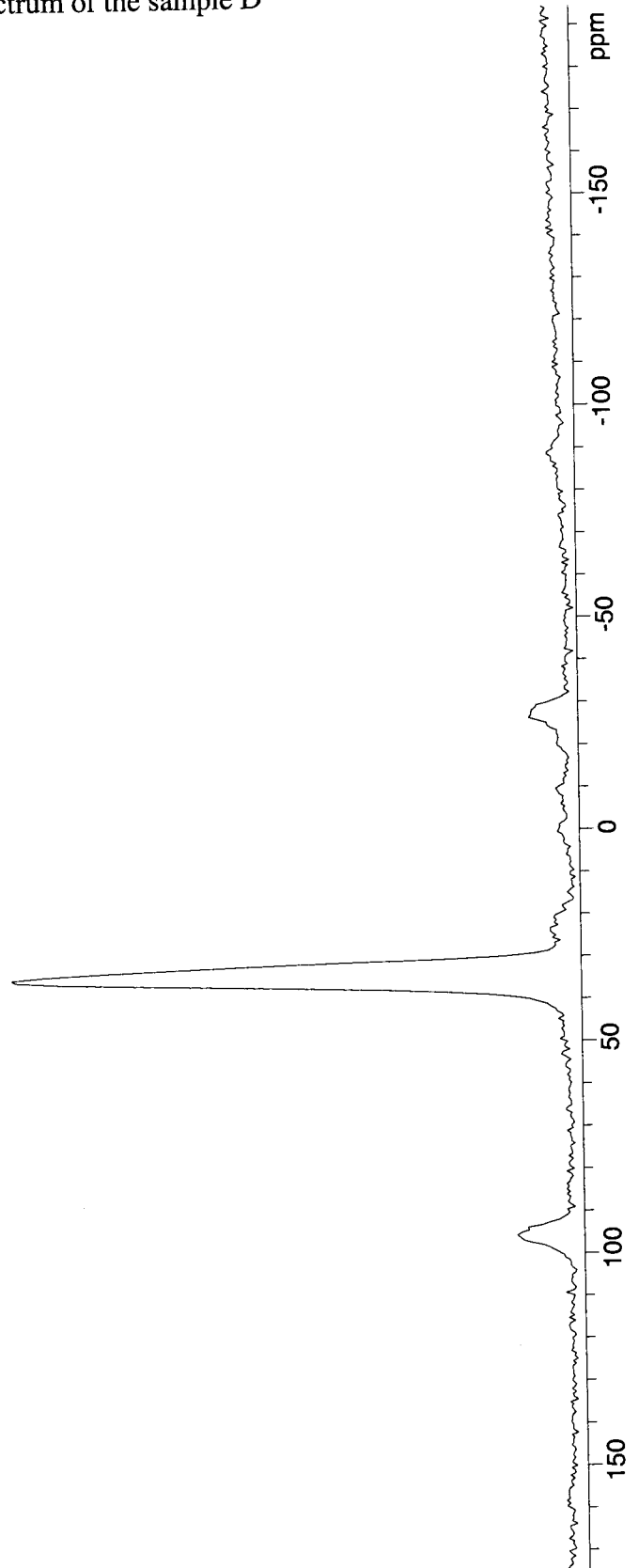
Figure 65 ^{29}Si CP/MAS NMR spectrum of hydride-modified silica gel via hydrolysis-silylation approach, the sample E

Figure 66 ^{13}C CP/MAS NMR spectrum of hydride-modified silica gel via hydrolysis-silylation approach, the sample E
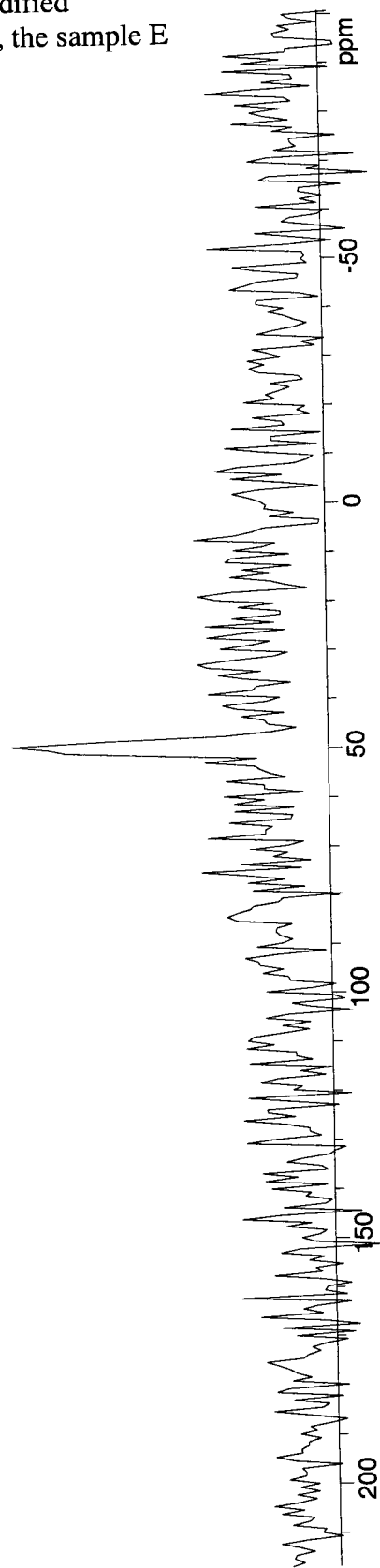
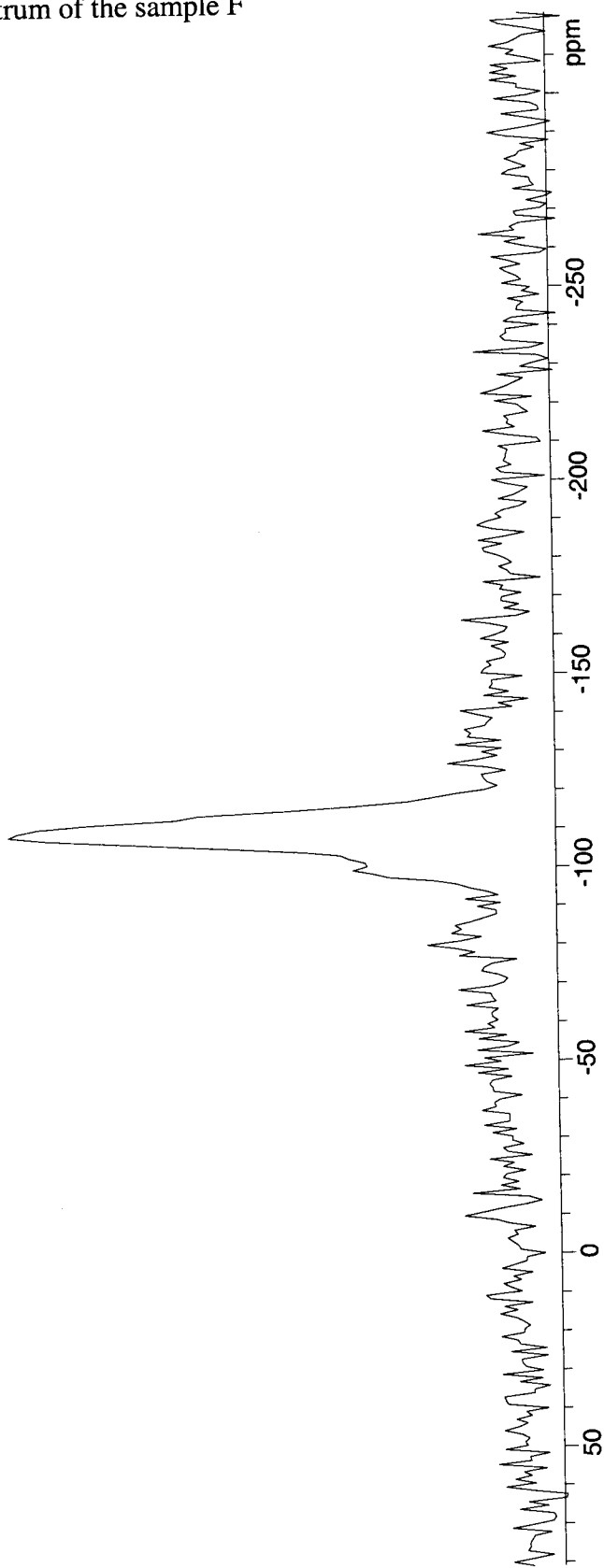**Figure 67** ^{29}Si CP/MAS NMR spectrum of the sample F

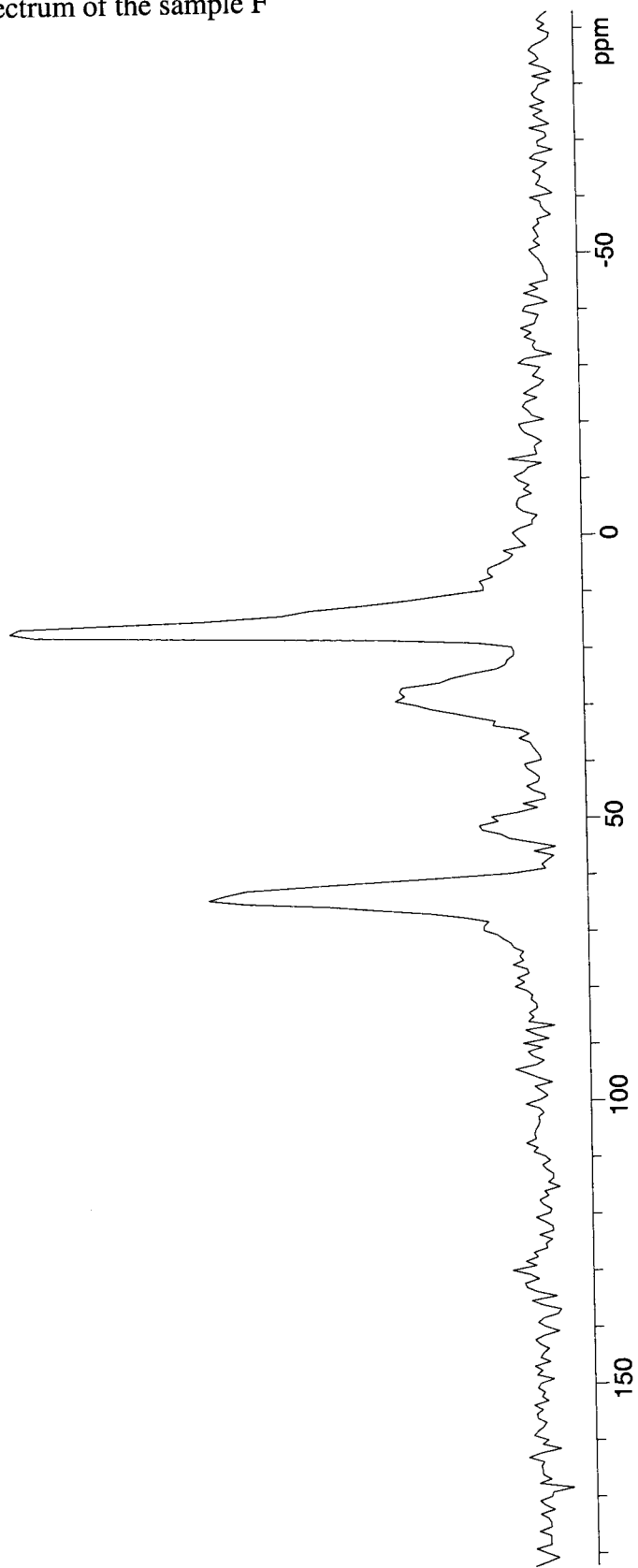**Figure 68** ^{13}C CP/MAS NMR spectrum of the sample F
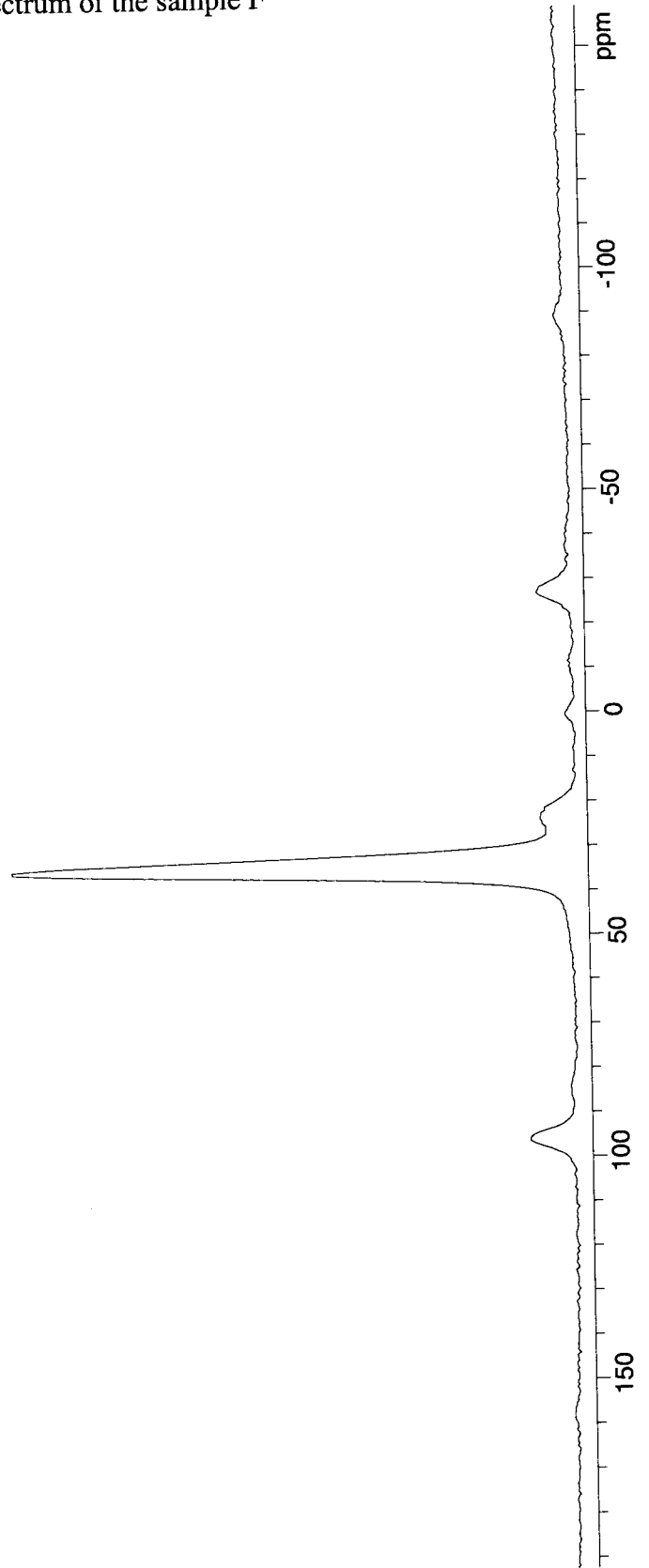
Figure 69 ^{31}P CP/MAS NMR spectrum of the sample F

Figure 70 ^{31}P CP/MAS NMR spectrum of the sample G