1993

Modification of oxide surfaces

Vivian Hui Tang
San Jose State University

Follow this and additional works at: https://scholarworks.sjsu.edu/etd_theses

INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

Order Number 1354166

Modification of oxide surfaces

Tang, Vivian Hui, M.S.

San Jose State University, 1993

U·M·I

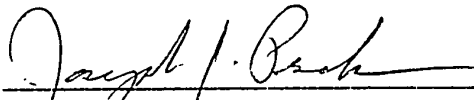300 N. Zeeb Rd.
Ann Arbor, MI 48106

Modification of Oxide Surfaces

A Thesis
Presented to
The Faculty of the Department of Chemistry
San Jose State University

In Partial Fulfillment

of the Requirements for the Degree
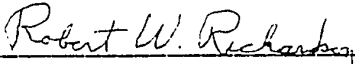
Master of Science

By

Vivian Hui Tang

August, 1993
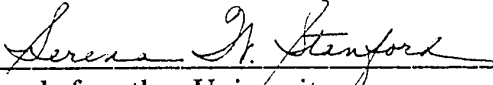
Approved for the Department of Chemistry

Dr. Joseph Pesek

Dr. Sam Perone

Dr. Robert Richardson

Approved for the University

ABSTRACT

Modification of Oxide Surfaces
by Vivian Hui Tang

Alumina, zirconia, titania and thoria were confirmed as potential stationary phases for High Performance Liquid Chromatography through a new study of modification of these oxide surfaces. Hydride-modified alumina (Al_2O_3), zirconia (ZrO), titania (TiO_2) and thoria (ThO_2) were prepared for further synthesis. A silanization procedure was used to create a Si-H monolayer on the surface of these oxides. The supports were then reacted with a terminal olefin (C_8 or C_{18}) compound in the presence of a transition metal catalyst, successfully producing an alkyl-bonded material. Results were tested using the following analytical techniques: Thermoanalytical with TGA and DSC, Solid chemical spectroscopy with FTIR and ^{29}Si, ^{13}C, ^{27}Al CP/MAS FT-NMR and Chromatography with GC. The resulting surface structural measures revealed equivalent results for all supports tested. Therefore, all substrates tested can be successfully used as stationaly phases for HPLC.

ACKNOWLEDGMENTS

LIST OF TABLES

LIST OF FIGURES

viii

CONTENTS

CHAPTER

CHAPTER 1

INTRODUCTION

1.1. BACKGROUND

High Performance Liquid Chromatography (HPLC) is a very powerful separation technique used in the field of chemistry. The technological developments of HPLC have dramatically improved in recent years. It is known that the chemical nature of the support used as the stationary phase in HPLC can strongly affect the efficiency of the separation. Chemical modification of the solid phase has become a well known technique for improving the separation efficiency.

Properly fabricated porous metal oxides have a number of physical characteristics which make them nearly ideal supports for HPLC. They are mechanically stable and can be processed into highly porous microparticulates which have a high proportion of mesopores. In addition, these particles display great resistance to chemical attack.

Historically, silica-based supports have been commonly used as the stationary phase in column packing chromatography. Today, more than 90% of column packings used in normal and reversed-phase liquid chromatography are based on silica (1).

In the late 1960's, bonded phases on a silica gel surface were first fabricated by using an esterification reaction between an alcohol and silanol groups to give Si-O-C linkages(2). The major disadvantage with this phase was its relative susceptibility to hydrolysis. This precluded the use of water in the mobile phase and created the potential for exchange at the surface with alcohols in either the mobile phase or the sample.

In the early 1970's, commercial phases using organosilanes became available (3). This method employs reactions of alkylchlorosilanes with surface silanols to produce Si-O-Si-C linkages. The major advantage of these bonded phases is their greater stability against hydrolysis over a wider pH range. This is the most popular method for the production of commercial chemically bonded stationary phases. The method can be used to prepare both monomeric and polymeric materials. However, they display limited long-term hydrolytic stability when an aggressive mobile phase is used.

In the late 1970's, chlorination of the silica surface followed by reaction with either a Grignard reagent or an organolithium compound was demonstrated. This two step reaction sequence method gives a highly stable Si-C linkage from the chlorinated silica substrate. Because the chlorination reaction scheme results in a different type of bond to the silica surface, chromatographically desirable properties result. Based on the relative bond strengths in silicon chemistry, the Si-C linkage product which results from the chlorination reaction is a more hydrolytically stable bonded phase than that obtained by the corresponding organosiloxane type (Si-O-Si-C linkages) structure. This chlorination reaction method also produces undesirable side-products such as MgClBr or LiCl. These salts can often become entrapped in the silica matrix and produce undesirable and nonuniform retention characteristics in the final product, particularly between different synthetic batches. In order to solve this side-product problem, a clean-up procedure must be used to reduce all the residual salts to a lower level (< 0.2 atom % as detected by Electron Spectroscopy for Chemical Analysis (ESCA)). But, the experimental set-up for the clean-up procedure is quite complicated, and the clean-up procedure results in dissolving the salt. Furthermore, both chlorination and organometallation steps are extremely sensitive to moisture and involve time-consuming procedures, particularly for the chlorination step. Therefore, it becomes necessary to find

another pathway to solve the limitation of the chlorination and organometallation sequence; one way to do this is by producing a hydride intermediate silica support.

Recently, new approaches for producing both covalently-bonded silica based supports and polymeric organic stationary phases have attracted the most attention. The most recent method of silica modification has been done by a previous student in our research group. This silica silanization with TES (triethoxysilane) provides an Si-H monolayer on the silica support as an intermediate. This method has been proved to simplify the reaction procedure, shorten process time and increase Si-H coverage. Also, moisture-free conditions are not required for this method. With dioxane as a solvent and aqueous 0.1 M HCl as a acid catalyst, reaction time is about 40 to 60 minutes. The reaction temperature is about 80°C for a gentle reflux. Results from this method show that TES silanization provides about 80% to 100% Si-H coverage with about 10% to 40% molar excess (4).

Another new bonding reaction which is known as hydrosilation for producing Si-C linkages on silica supports has recently been reported by Sandoval and Pesek (5). In their studies, a hydride intermediate silica support containing Si-H surface groups was first synthesized and then reacted with an olefin in the presence of a suitable catalyst to form an addition product on the silica surface. The bonding reaction is known as hydrosilation which involves the catalytic addition of a terminal double bond to the surface silicon hydride (Si-H) species. This approach provides an extensive coverage of the attached groups. The different types of reactions for producing bonded phases are described in Table I.

For most chemically bonded silicas, stability problems are relatively minimal where the pH is between 2 and 8. In this pH

TABLE I

Types Of Reactions For
Producing Bonded Phases

Reaction Type	Reaction	Surface Linkages	Part #
Esterification (2)	$Si\text{-}OH + ROH \longrightarrow Si\text{-}OR + H_2O$	Si-O-C	1
Organosilane (3)	$Si\text{-}OH + X\text{-}SiR'_2R \longrightarrow Si\text{-}O\text{-}SiR'_2R + HX$	Si-O-Si-C	2
Chlorination followed by reaction of Grignard reagents and organolithium compounds (7)	Toluene (1) $Si\text{-}OH + SOCl_2 \longrightarrow SiCl + SO_2 + HCl$ (a) $Si\text{-}Cl + BrMgR \longrightarrow Si\text{-}R + MgClBr$ o r (b) $Si\text{-}Cl + LiR \longrightarrow Si\text{-}R + LiCl$	Si-C	3
TES Hydrosilanization (4)	Si-OH Si-O-Si-H TES Si-OH ------>Si-O-Si-H Si-OH Si-O-Si-H	Si-H monolayer	4
Hydrosilation (5)	Catalyst $Si\text{-}H + CH_2{=}CH\text{-}R \longrightarrow Si\text{-}CH_2\text{-}CH_2\text{-}R$ (R = C_6 or C_{16})	Si-C	5

range, the amount of soluble silica remains nearly constant and very small. When the pH is below 2, the bonded organic phase can undergo hydrolysis, and at pH above 8 the silica matrix itself begins to dissolve due to the formation of silicate ions and monosilicic acid:

$$SiO_2 + 2H_2O \Longleftrightarrow Si(OH)_4$$

$$Si(OH)_4 + OH^- \Longleftrightarrow [Si(OH)_5]^-$$
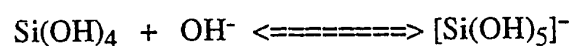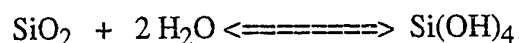
Recently, in order to avoid these pH stability problems, there has been a resurgence of interest in the use of other metal oxide particles as supports for stationary phases for HPLC. These materials have many of the characteristics of an ideal support including the mechanical strength, chemical stability, high surface area and high percentage of mesopores.

Among the many possible oxide materials, aluminum oxide, zirconium oxide, titanium oxide and thorium oxide have great potential for successful use. For example, aluminum oxide (alumina) is insoluble in water, slowly soluble in alkaline solutions with the formation of hydroxides and insoluble in non-polar organic solvents. Pure aluminum oxide (Al_2O_3) is a very stable compound which has a cation with a preference for only a single valence state (Al^{3+}). Therefore, in the absence of impurities, the stoichiometry is fixed. Also, aluminum oxide is one of the hardest materials known and is a very good electrical insulator which retains its high resistitivity up to very high temperatures. Therefore, it has been widely used as an insulating material(8). Zirconium oxide (zirconia) is stable over the pH range from 1 to 14 (6). Titanium oxide (titania) has high acid resistance and is insoluble in water, HCl, HNO_3 or diluted H_2SO_4 (soluble only in hot concentrated H_2SO_4 and HF). Thorium oxide (thoria) has high resistance in both acid and base and is insoluble in water or alkalies (soluble in acid with difficulty) (12).

Such chemical resistance is an advantage when corrosive eluents are used.

Comparing these metal oxide matrices with a silica matrix, it is known that aluminum oxide, zirconium oxide, titanium oxide and thorium oxide have much better chemical and thermal stability than silica and offer greater stability when exposed to high pH (9). For these reasons, if these oxides can be successfully modified on their surface by chemical methods, they would show great potential as stable support materials for HPLC.

Most work including surface modification of other metal oxides for use in HPLC has involved aluminum oxide. Pure aluminum oxide (Al_2O_3) is a very stable compound which has a cation with a preference for only a single valence state (Al^{3+}). Therefore, in the absence of impurities, the stoichiometry is fixed. Also, aluminum oxide is one of the hardest materials known, and is a very good electrical insulator which retains its high resistivity up to very high temperatures. Therefore, it has been widely used as an insulating material (8). The most common method for modification of aluminum oxide involves using organochlorosilanes in a manner similar to those used for silica (10). Several reactions which can be used to modify silica surfaces might be applicable to the modification of alumina (11). For example, using the organosilanization method (listed on Table I, part 2), the chemistry can be described as follows:

$$\equiv Al-OH \ + \ X{-}\underset{R'}{\overset{R'}{Si}}{-}R \ \xrightarrow{\hspace{1cm}} \ \equiv Al-O-\underset{R'}{\overset{R'}{Si}}-R \ + \ HX$$
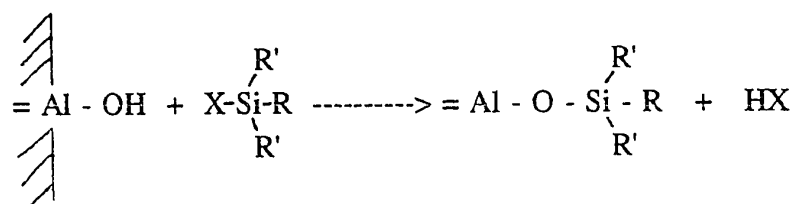
R' is generally a methyl group for typical monomeric and methoxy or ethoxy for polymeric stationary phase. Aluminum oxide (alumina) reacts with triorganochlorsilanes to form a monolayer of organosiloxane-type linkages. However, from the results of a previous study, there still exist significant unreacted Al-OH groups after this reaction. These unreacted Al-OH groups

may strongly interact with the species under separation. This is due to steric hindrance of the triorganosilyl group causing a relatively limited coverage of the organic moieties on the support surface. Also, the Al-O-Si-C linkages have poor hydrolytic stability. This is undesirable since these linkages are hydrolyzed easily under acidic conditions. Therefore, it would be useful to find another chemical pathway to produce a more stable bonded phase on the surface of aluminum oxide with less unreacted Al-OH groups remaining after the reaction.

Until recently, very little work has been done on the surface modification of zirconium oxide, and none on titanium oxide and thorium oxide as a stationary phase for HPLC. So, in this project, we attempt to develop a chemically bonded phase on the surfaces of aluminum oxide, zirconium oxide, titanium oxide and thorium oxide supports for use in HPLC. The surface bonded phases should also offer high chemical and thermal stability.

1.2. GOAL OF THIS WORK

The purpose of this project is to modify the surfaces of four different oxides, alumina, zirconia, titania and thoria, to produce a variety of useful column packings as stationary phases for HPLC. A primary goal of this project is to prepare an Si-H monolayer on the surfaces of the four metal oxides as an intermediate by utilizing the simple method of silanization with TES which has successfully produced an Si-H monolayer on the surface of silica (listed on Table I, part 4). The advantage of this method is its high Si-H coverage and short process time. The chemistry can be described as follows:

On an oxide surface:

```
  /|                        /|          /
 / |                       / |         /
   |                          |        
 M - OH                    M- O - Si - H
  /|            TES         |        \
 / |                        |         O
   |          ----->        |        /
 M - OH                    M- O - Si - H
  /|                        /|        \
 / |                       / |         O
   |                          |        /
 M - OH                    M- O - Si - H
  /|                        /|        \
 / |                       / |         O
   |     ( M can be =Al, -Zr, -Ti or -Th )     /
```
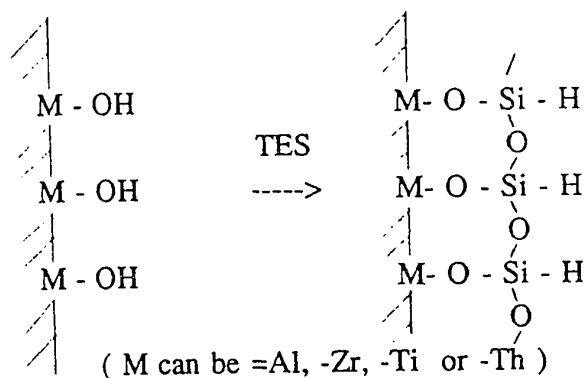
The Si-H monolayer on the surface of these metal oxides is expected to produce a maximum of siloxane linkages and minimum of uncondensed silanols.

A second objective of this project is to fully evaluate the hydride intermediate of these oxides in terms of their spectroscopic, thermal, and chemical properties. The analytical techniques used for this are FTIR (DRIFT mode), FT-NMR (CP-MAS), DSC, and GC.

The third and final goal of this research is to subsequently modify the intermediate phases by reacting the oxide hydride intermediate with an olefin (1-octadecene or 1-octene) to form an addition product on the surface. The method of hydrosilation which can be used for reaching this modification goal is listed in Table I, part 5. The chemistry can be described as follows:

On an oxide surface:

```
  /|         /                              /|          /
 / |        /                              / |         /
   |                                          |        
 M-O-Si-H                                 M-O-Si-CH2-CH2-R
  /|   O            Catalyst                |        \
 / |  /                                     |         O
   |                                        |        /
 M-O-Si-H  +  CH2=CH-R  ----->            M-O-Si-CH2-CH2-R
  /|   O                                   /|        \
 / |  /                                   / |         O
   |                                          |        /
 M-O-Si-H                                 M-O-Si-CH2-CH2-R
   |   O                                   /|        \
   |  /                                   / |         O
                                             |        /
```
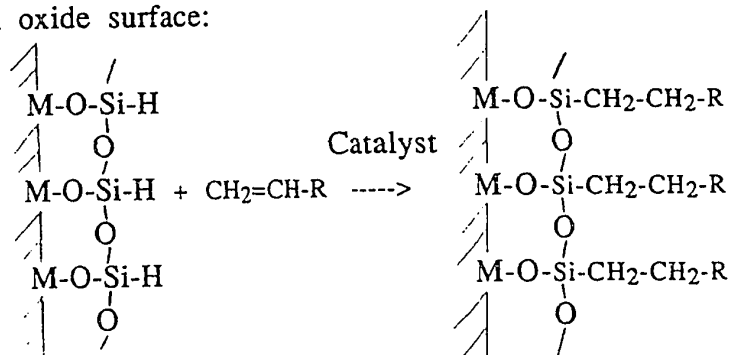
(M is =Al, -Zr, -Ti or -Th, R=C_{16} for alumina and R=C_8 for zirconia, titania and thoria experiments. The catalyst is either dicyclopentyl platinum II or hexachloroplatinic acid.)

The final products of the modification were expected to provide a dense and hydrolytically stable bonded phase on the surface of alumina, zirconia, titania and thoria particles. These final products were also fully characterized by using analytical methods such as FTIR in DRIFT mode and FT-NMR by CP-MAS .

1.3   ANALYTICAL INSTRUMENTATION USED IN THIS WORK

In order to evaluate the hydride-modified material and the final product, several analytical techniques were used to identify the bonded phase on the oxide surfaces. The general discription of these techniques is given as below.

1.3.1   TGA BACKGROUND

In a Thermogravimetric Analysis (TGA) experiment, the mass of a sample is recorded continously as its temperature is increased linearly from ambient to as high as 1200°C. A thermogram (a plot of mass as a function of temperature) provides both qualitative and quantitative information. The data from TGA is presented as the gradual weight loss of the sample in the specific temperature range.

1.3.2   DSC BACKGROUND

In a Differential Scanning Calorimetry (DSC) experiment, the sample and a reference substance are subjected to a continuously increasing temperature (at a constant rate). Heat is added to the sample or to the reference as necessary to maintain the two at identical temperatures. The added heat, which is

recorded, compensates for that lost or gained as a consequence of endothermic or exothermic reactions occurring in the sample (16). Both exothermic and endothermic processes produce the differential peaks in DSC thermograms.

1.3.3   GC BACKGROUND

The advantage of Gas Chromatography (GC) is that mixtures of volatile organic components can be separated into individual components for identification. Separation is achieved in a column located in a temperature controlled oven. Separation occurs when the components of a mixture partition between the stationary phase and an inert carrier gas (mobile phase). The separation profile of the sample components depends on their relative affinities for the stationary and mobile phases. The column temperature programming is used to manipulate retention time for the components, increasing the temperature for highly retained components or decreasing the temperature to gain more retention for low boiling components. The retention time is a characteristic property of the component in the liquid phase at a given temperature. The components eluting from the column are then recorded as a function of time by a detector.

1.3.4   FTIR BACKGROUND

Fourier Transform Infrared (FTIR) Spectroscopy is the study of molecular vibrations. It provides specific information about chemical bonding and molecular structure, most suitably for organic materials. The technique is based on the fact that bonds and groups of bonds vibrate at characteristic frequencies. When the sample is exposed to infrared radiation, a molecule selectively absorbs infrared frequencies that match those of its allowed vibrational modes. Therefore, the infrared absorption spectrum of a material reveals which vibrations, and thus functional groups, are present in its structure. The vibrations

which do not involve a change in dipole moment, as in O_2 and N_2, do not absorb infrared radiation. Thus FTIR spectra can be collected in air.

1.3.5   FT-NMR BACKGROUND

In general, Nuclear Magnetic Resonance Spectroscopy (NMR) is based upon the measurement of absorption of electromagnetic radiation in the radio frequency region of roughly 4 to 600 MHz, which corresponds to a wavelength range of about 75 to 0.5 m. The nuclei of atoms are involved in the absorption process. NMR Spectroscopy is one of the most powerful tools available to the chemist and biochemist for elucidating the structure of both organic and inorganic species (16). Also, it has proved to be useful for the quantitative determination of absorbing species (17, 18, & 19).

The Fourier Transform interferometric method has as a principal advantage that it requires a short time to obtain a large number of interferograms. Therefore, by averaging the interferograms to improve the signal/noise ratio, the use of an FT-NMR spectrometer has greatly increased the sensitivity of NMR measurements (20), particularly for the nuclei whose isotope is in low natural abundance and/or has a relatively small magnetogyric ratio, such as ^{13}C, ^{15}N, ^{19}F, [29]Si and [31]P. There are three distinctly different types of FT-NMR developed, which are called pulsed, stochastic and rapid-scans correlation. The pulse technique is the most common one. In pulse FT-NMR, the sample irradiated periodically with brief, highly intense pulses of radio-frequency(RF) radiation (intense enough to cause saturation for all of the absorbing nuclei), which is followed by a free induction decay signal (a characteristic radio frequency emission signal) stimulated by the irradiation which is recorded as a function of time. Typically, 1 to 10 usec pulses are employed and the observation time between pulses is approximately 1 second.

Generally, NMR spectra of solids are characterized by very broad, uninterpretable peaks due to the fixed orientation. In order to eliminate the line broadening effect, Magic Angle Spinning (MAS) and Cross Polarization (CP) techniques are commonly employed to extract all the chemical shift information hidden under the broad peaks. Under MAS technique, dipolar line broadening effects are eliminated by mechanically spinning the sample in an air-driven rotor with the angle of 54.7° between the rotation axis and the magnetic field direction. In the CP technique, the higher spin density of ^{1}H is transferred to the signals of nuclei of low natural abundance and small magnetogyric ratio (such as ^{13}C and ^{15}N) during the contact time. This results in sensitivity enhancement and the relaxation rate increase.

CHAPTER 2

EXPERIMENTAL

2.1. MATERIALS

All materials used for this research were reagent grade. In most cases, the standards and reagents were used directly from the container without further handling. Following are the materials that were used in this project. Also, the preparation procedures used for some of the materials are described in this section.

1. p-Dioxane[$(CH_2)_4O_2$] (J.T. Baker Chemical Co., Phillipsburg, NJ) was dried by contact with Calcium hydride(CaH_2) (Sigma Chemical Co., St. Louis, MO) for about one week in a glass flask. Then, it was distilled right before use. Section 2.1.1. is a flowchart which depicts the steps of the distilling procedure. The distilling apparatus is shown in Figure 1.

2. Triethoxysilane(TES) (Petrarch Systems Silanes and Silicons, Bristol, PA) was used as the hydrosilane reagent. It was stored in a refrigerator. 0.21 M TES in dry dioxane solution was prepared right before use. The procedure for preparation of the TES solution (0.21 M in dry dioxane) is described in Section 2.1.2. The apparatus for this preparation is given in Figure 2.

3. A 3.1 M hydrochloric acid (HCl) solution, used as a catalyst, was prepared by dilution of concentrated HCl (12 M) (Fisher Scientific, Fair Lawn, NJ). The procedure for preparing this solution is described in Section 2.1.3.

4. Ethanol 95% (Gold Shield Chemical Co., Hayward, CA) was used as received for the hydrosilane coverage determination by Gas Chomatography.

5. Triphenylsilane 97% [$(C_6H_5)_3SiH$] (Sigma Chemical Co., St. Louis, MO) was used as received. It was used as a standard for the determination of hydrosilane coverage by Gas Chromatography.

6. Potassium bromide (KBr) (Harshaw/Filtrol Partnership, Solon, OH) was ground in a mortar and pestal. It was used as a background baseline material and diluting agent for FT-IR spectra.

7. Tetrahydrofuran (THF) $(OCH_2CH_2CH_2CH_2)$ (J.T. Backer Chemical Co., Phillipsburg, NJ) was used as received for the washing steps in the hydrosilanization procedure.

8. Diethyl ether (anhydrous) [$(CH_3CH_2)_2O$] (Curtin Matheson Scientific, Inc. Houston, Texas) was used as received for the washing steps in the hydrosilanization procedure.

9. Trifluoroacetic acid (TFA) 99% (CF_3CO_2H) (EM Science, Gibbstown, NJ) was prepared to 0.1% v/v aqueous solution containing 20% v/v dioxane.

10. Chloroform $(CHCl_3)$ was used as received as the solvent for preparing the 50 mM dicyclopentadienyl platinum II chloroform solution.

11. Toluene $(C_6H_5CH_3)$ 99% (Aldrich Chemical Co. Inc., Milwaukee WI) and Dichloromethane (CH_2Cl_2) (Mallinckrodt, Inc. Paris, Kentucky) were used as received for the washing steps in the olefin bonding experiment.

12. 1-octadecene $(C_{18}H_{36})$ 97% (Sigma Chemical Co., St. Louis, MO) and 1-octene [$CH_3(CH_2)_5CH=CH_2$] 98% (Aldrich Chemical Company Inc., Milwaukee WI) were used as received for the olefin bonding experiment.

13. Dicyclopentyl platinum II or hexachloroplatinic acid (H_2PtCl_6), the catalysts in the olefin bonding

experiment, was first made by J. Sandoval, and prepared as a 50 mM solution in dry chloroform.

14. Alumina, zirconia, titania and thoria support materials were predried before use. Their major physical properties are shown in Table 2. The steps for the drying treatment of the support materials are given in Section 2.1.4.

15. Deionized water obtained from a milli-Q water purification system (Millipore Corp., Bedford, MA) was filtered before use.

16. Iso-propyl alcohol (IPA) (EM. Science, Gibbstown, New Jersey) was used as received as the solvent for preparing 50 mM Hexachloroplatinic acid IPA solution.

2.1.1. PROCEDURE FOR DISTILLATION OF DIOXANE

The distilling system was installed as shown as in Figure 1. The dioxane was predried by contacting with CaH_2 and placed in a round bottom flask (1). Helium (He) gas was purged from the top (point A, in the absence of a thermometer) through the distilling system for about 2 minutes. The thermometer (2) a s shown in the system of Figure 2 was then inserted. The variable autotransformer connected to the heating mantle (4) was turned on and the dioxane was heated to its boiling point (101°C). The distilling rate was controlled at 1 to 2 drops/second by adjusting the variable autotransformer. The freshly distilled dry dioxane was collected in flask (3). When a small amount of dioxane was still left in the flask, the autotransformer was turned off and the thermometer was removed. Helium gas was allowed to flow through the system for about 1 minute. A serum cap stopper was put on flask (3) immediately and a copper wire was tightened on it. It should be noted that the system was never allowed to be distilled to dryness.

2.1.2. PROCEDURE FOR PREPARATION OF TES SOLUTION

The system was installed as shown in Figure 2 (it should be noted that end A of the long needle is not in the liquid phase). With nitrogen gas flowing through the system from the serum cap stopper (B), 4 ml of TES was transferred to the 100 ml volumetric flask (2) by a 5 ml glass syringe through the stopper (C). End A of the long needle was pushed in the dioxane liquid, then dioxane was transferred from flask (3) to volumetric flask (2) through the long needle. At the time dioxane is added close to the mark on flask (2), end A of the long needle was pulled out from the dioxane liquid phase. When dioxane is added to the mark of the volumetric flask (2), end D of the long needle was pulled out from flask (2), allowing the excess dioxane in the long needle to come out of the system. End D in flask (2) was injected again, and the system was allowed to purge with nitrogen gas for 2 minutes. Then, the nitrogen gas was turned off, and all needles were removed from flasks (2) and (4). In this procedure, it was necessary that TES should be transferred under nitrogen gas at all times.

2.1.3. PROCEDURE FOR PREPARING 3.1 M HCl SOLUTION

25.8 mL of concentrated hydrochloric acid (HCl, 12M) was pipetted in a 100 ml volumetric flask, and deionized HPLC grade, filtered water was added into the flask until up to its mark. This 3.1 M HCl was used as the catalyst in the silanization with TES experiments; it was chosen because silane deposition increases with acid concentration. Secondly, polycondensation of TES which produces polyhydrosiloxane gel (polymeric materials of the type $[HSiO_{3/2}]_n$) speeds up with increasing amounts of acid catalyst.

2.1.4. PREDRYING TREATMENT FOR SUPPORT MATERIALS

Raw support materials were placed in a glass beaker. Then, this beaker was placed in the vacuum oven (VWR Scientific, model 1410) at a temperature of 101°C, under a vacuum of about -50 KPa for at least 12 hours before use. The support materials in this work are alumina, zirconia, titania and thoria.

2.2   INSTRUMENTATION

In this project, several methods for chemical evaluation were used to assess the bonded phases. These methods included thermoanalytical techniques such as TGA and DSC, Spectroscopic techniques such as FTIR and Magic Angle Spinning FT-NMR, and chromatography such as GC.

2.2.1. THERMOANALYTICAL TECHNIQUES

The thermoanalytical techniques used in this study included Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). TGA was used to obtain the silanol concentration on the bare oxide surfaces, and DSC was used to evaluate the hydride-modified oxides in this work.

2.2.1.1   TGA

In this work, TGA experiments were performed under an inert gas such as nitrogen (N_2) or argon (Ar). The TGA data were obtained by using a Perkin-Elmer model TGS-2 thermogravimetric system. The sample size was about 5 to 10 mg. Samples (bare alumina, zirconia, titania and thoria) were

(1) – Round bottom flask
(2) – Thermometer
(3) – Flask
(4) – Heating mantle
(5) – Condensor
(6) – Drying tube
(7) – CaH$_2$

(6)

(2)

A

(5)

)H$_2$O

)H$_2$O

(3)

(4)

(1)

(7)
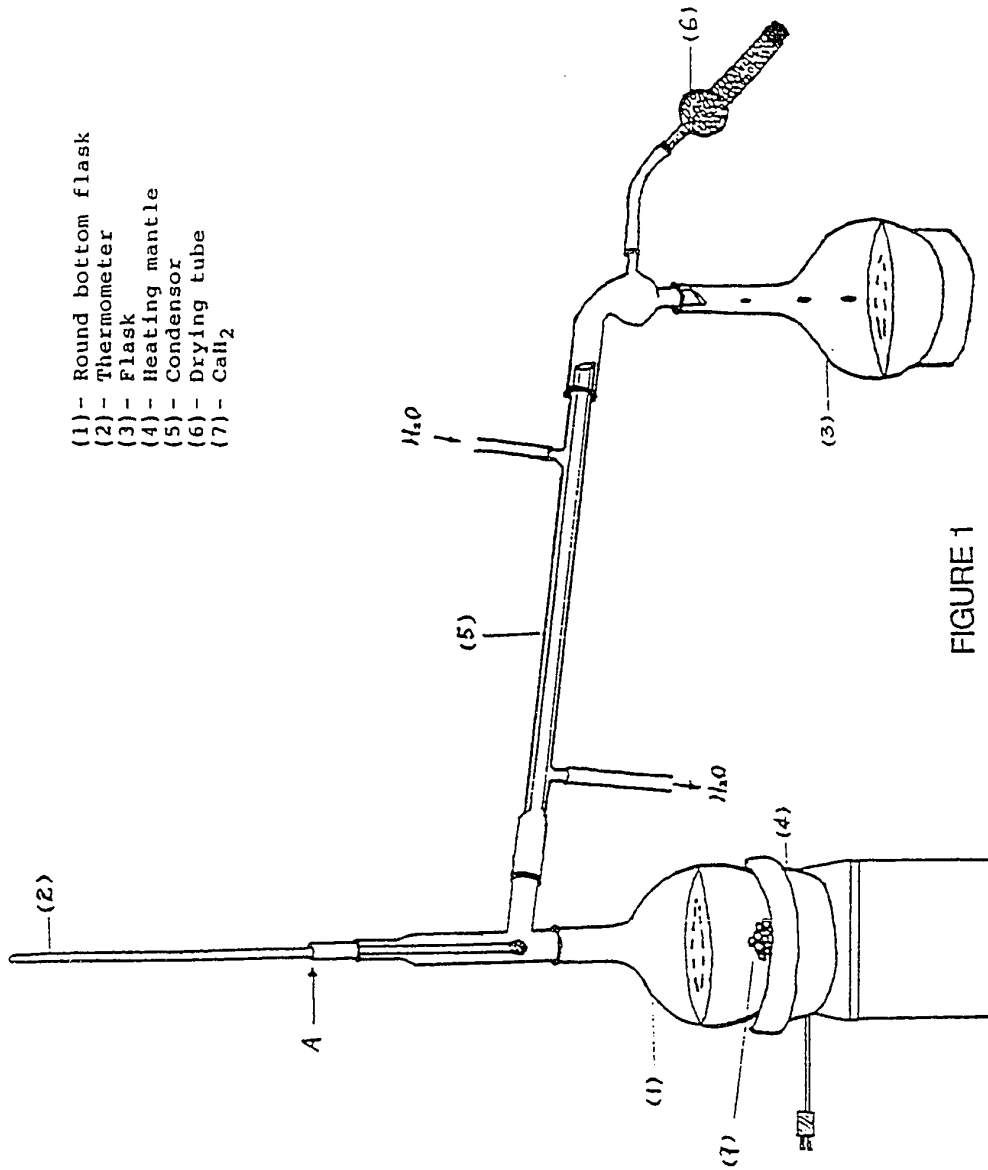
FIGURE 1

APPARATUS OF DISTILLING DRY DIOXANE

FIGURE 2

APPARATUS OF PREPARING TES SOLUTION
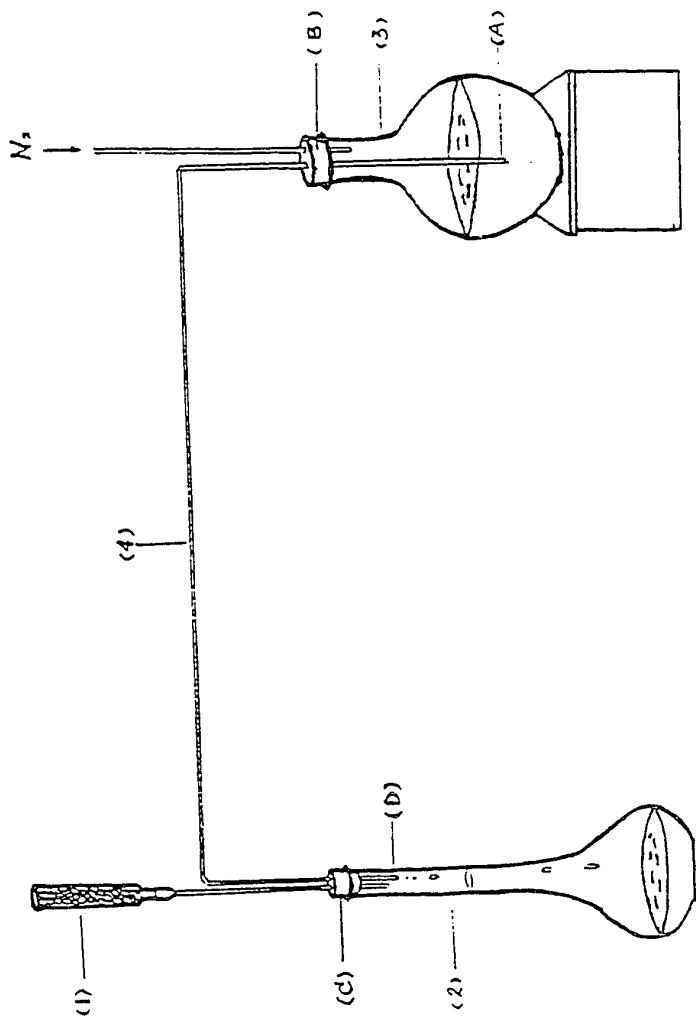
(1) - Syringe filled with dryer
(2) - Volumetric flask
(3) - Flask
(4) - Long needle with sharp ends (A&D)
(B)&(C) - Serium cap stopper

TABLE II

MAJOR PHYSICAL PROPERTIES OF SUPPORT MATERIALS

Name	Particle size Mean Diam.(um)	Pore size Mean Diam(Å)	Spec. surf. Area m^2/g	Manufacturer
U-Al (Al_2O_3)	5	100	50	Bio Tage
R-Al (Al_2O_3)	10	60	33	Bio Rad
ZrO_2-(1)	5 - 10	32.37	13.1	Chevron
ZrO_2-(2)	5 - 10	160[1]	39.7[1]	U of Minnesota
TiO_2	5 - 10	30 - 100	unknown	Fisher Scientific Co.
ThO_2	5 - 10	30 - 100	unknown	Fisher Scientific Co.

[1] This data was obtained using B.E.T. nitrogen adsorption method by graduate student Kaynam Chun in the Department of Materials Enginering at San Jose State University.

loaded into a platinum pan and were heated up to 110°C at the rate of 80°C/min. The temperature was held at 110°C until all the moisture contained in the sample was eliminated as shown by the weight signal indicating no deflection. Then, the temperature was raised from 110°C to 900°C at the rate of 20°C/min. Then, the temperature was held at 900°C until no weight loss signal could be detected.

2.2.1.2   DSC

DSC experiments were performed in air. The thermograms were obtained by using a Perkin-Elmer model DSC-7 instrument system. The sample size of alumina, zirconia, titania and thoria hydrides were about 5 to 10 mg. Samples were loaded into a platinum pan. The temperature was then raised from 200°C to about 700°C at a rate of 20°C/min. The DSC system was calibrated by using Lead (Pb) and Zinc (Zn), two metal calibration standards .

2.2.2. SPECTROSCOPIC TECHNIQUES

2.2.2.1   FTIR SPECTROSCOPY

The FTIR technique was used for qualitative analysis of the alumina, zirconia, titania and thoria supports and the modified samples. The samples were mixed with 50% pure potassium bromide (KBr) powder which was ground in an agate mortar and pre-dried in an oven at 110°C for at least 24 hours. Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectra were obtained by using a Perkin-Elmer model 1800 FTIR Spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector. The mixed sample was filled into the DRIFT accessory cup (3.5-mm diameter, 2-mm depth), and a smooth sample surface was formed by gently pressing a microscope slide

on the cup. In order to get a maximum signal throughput, the height of the sample cup was adjusted by applying an alignment routine in the Perkin-Elmer standard software. FTIR spectra were obtained in the region of 4000 to 450 cm^{-1} with a nominal resolution of 2 cm^{-1}. The number of scans was one hundred, and the pure KBr was run as the background reference Spectrum and displayed to 100% transmittance.

2.2.2.2 FT-NMR SPECTROSCOPY

Nuclear Magnetic Resonance (NMR) Spectroscopy was used for characterization of the modified products such as alumina hydride, zirconia hydride, titania hydride, thoria hydride and their olefin bonded phases. All peaks for carbons, silicons and aluminums in different chemical environments can be discerned with this method. A Bruker MSL 300 NMR Spectrometer, an Aspect 3000 Computer System which was equipped with a Hewlett Packard 7550A Graphics Plotter, and an MAS-DB pneumatic unit were used for the qualitative Magic Angle Spinning analysis of ^{29}Si, ^{27}Al and ^{13}C. For ^{29}Si and ^{13}C, the CP time used in the experiments was 5 ms with an MAS rate of about 5 KHz. The recycle time was 10 s. For ^{27}Al, a recycle time of 5 s and a contact time of 5 ms, required about 2000 scans to obtain the typical spectrum.

2.2.3. GAS CHROMATOGRAPHY

In this work, the gas chromatographic technique was used to determine the Si-H coverage on the surface of alumina hydride. A Varian Aerograph model 204 GC which was equipped with a Houston Instrument Omni Scribe chart recorder and a Spectra-Physics integrator was employed to measure the amount of Hydrogen (H_2) gas evolved from the hydride samples. The gas samples were injected into the instrument by using a 5 ml gas-tight syringe (Precision Sampling Corp., Baton Rouge, LA) which

was equipped with a push button valve. The GC was calibrated against triphenylsilane (Ph_3SiH). A 15 to 20 mg sample of hydride alumina was weighed in a septum-sealed vial. A volume of 2 mL of air was withdrawn from the vial by a 5 mL gas-tight syringe. 1 mL of 1 M KOH solution in ethanol was carefully injected. Then, the reaction vial was placed in a heated aluminum block at 60°C and kept at this temperature for one hour. After this, the vial was removed from the block and cooled down. In order to force the evolved gas into the collection syringe, ethanol was injected by another syringe. The valve of the collection syringe was closed and removed from the vial. Then, the gas was injected into the GC instrument and the hydrogen peak area was determinded by the integrator.

2.3. PROCEDURES

2.3.1. ALUMINA MODIFICATIONS

As seen in Table II, there were two sources of alumina used in this study. One is from Bio-Tage (Unisphere), the other one is from Bio-Rad. In this paper, the alumina from Bio-Tage is denoted by UAl, and the one from Bio-Rad by RAl. Predried UAl and RAl were used as the starting alumina materials for this work.

2.3.1.1. HYDROSILANIZATION WITH TES

In the first step of the modification, aluminum oxide was hydrosilanized by reacting it with TES to form a monolayer of trisiloxane-type linkages on the surface. In order to determine the best molar ratio of TES in the hydrosilanization experiment, the following experiment was adopted.

2.3.1.1.1 VARIABLE MOLAR RATIO (OH GROUP ON ALUMINA : TES) EXPERIMENT

A 1.000 g portion of alumina was transferred into a 25 ml 3-neck, round bottom flask (4) which was equipped with a condensor (2), an addition funnel with equalizing tube (1), a heating mantle (5) and a magnetic stirrer (6). A 1-cm stirring bar (7) was used. The apparatus is as shown in Figure 3. A measured amount (from 8.6 to 9.8 mL for UAl, and 15.0 to 17.8 mL for RAl) of predried dioxane was added and a gentle mechanical stirring system was used to mix the contents in the flask throughout the reaction. 0.5 mL of aqueous 3.1 M hydrochloric acid (HCl) solution was added to the dioxane. The suspension was heated to between 70 to 80°C. From the addition funnel, a measured amount (from 5.2 to 6.4 mL for UAl, and from 12.3 to 15.0 mL for RAl) of 0.21 M TES/dioxane solution was added drop by drop into the suspension. The addition was completed in 10 to 15 minutes and the total liquid volume was 15 mL. Upon completion of the addition of TES solution, monitoring of the reaction time was begun. The suspension was allowed to gently reflux for one hour at a temperature of 80°C. The quantities of materials used in each individual experiment are shown in Table III.

After the one hour reaction time, the heating mantle was removed and the contents were allowed to cool. The products were carefully transferred to a 40 mL centrifuge tube. The washing steps consisted of adding 30 mL each of the following solvents (twice) to the centrifuge tube:

1) THF : H_2O (80 : 20)
2) THF
3) Diethylether

The contents were fully stirred for about 1 mintue and then centrifuged for 5 minutes in order to separate the product.

2.3.1.1.2   LARGER SCALE EXPERIMENTS FOR A RATIO OF TES/OH 1:1.0

In order to synthesize sufficient product for further bonding studies and characterization analysis, the experiment with a 1:1.0 molar ratio was increased 5 times by using 5 g of alumina in the hydrosilanization step. The apparatus set up was the same as shown in Figure 7 but using larger volume glassware. The reaction procedure and washing steps were the same as with 1 gram of alumina, but the volume of solvents was different (see Table IV). The quantities of materials used are listed in Table IV.

2.3.1.2.   OLEFIN BONDING

A measured amount (60 ml) of 1-Octadecene was added to a 150 mL 3-neck round bottom flask (4); 0.4 mL of 50 mM dicyclopentadienyl platinum II solution in dry chlorform as a catalyst was also added to the 3-neck round bottom flask (4). 4.0000 grams of alumina hydride (UAl and RAl) was placed in an addition funnel with an equalizing tube (1) (as shown in Figure 7). The mixture was heated to 70°C and kept at this temperature until the solution became clear (at least one hour). Then, the hydride alumina was slowly added through the addition funnel by using an electric engraver (model V-74). When the addition was completed, the temperature was raised to 85°C and the system was kept at that temperature for 96 hours. After 96 hours reaction time, the final product was carefully transferred to a 100 mL centrifuge tube. The washing steps consisted of adding about 80 mL each of the following solvents to the centrifuge tube:

Solvent	Number of Washing Steps
Toluene	4 times
Dichloromethane	2 times
Diethyl ether	2 times

The mixture was fully stirred using a 1.5 cm magnetic bar for about 1 minute and then centrifuged for 5 minutes in order to separate the product. The final process consisted of the drying steps as follows:

1) exposure to air at room temperature in the hood for about 12 hours.
2) heating in a vacuum oven (VWR Scientific, model 1410) at 110°C and -50 KPa for an additional 12 hours.

2.3.2. ZIRCONIA MODIFICATIONS

Predried zirconia, ZrO_2-(1), manufactured at Chevron, and ZrO_2-(2), supplied by U of Minnesota, as seen in Table II, were used as starting materials. The procedures in this work for zirconia silanization with TES followed by hydrosilation with an olefin are similar to those used for alumina as described in the previous section.

TABLE III

DIFFERENT OH:TES RATIO OF SILANIZATION
ON ALUMINA

Ratio (-OH:TES)	Alumina (g)	Dioxane (mL)	TES Solution (mL)	3.1 M HCl Solution (mL)
(Unisphere)[1]				
1 : 1.1	1.0009	8.6	6.4	0.5
1 : 1.0	1.0009	9.2	5.8	0.5
1 : 0.9	1.0009	9.8	5.2	0.5
(Bio-Rad)[2]				
1 : 1.1	1.0005	15.0	15.0	1.0
1 : 1.0	1.0016	16.5	13.5	1.0
1 : 0.9	1.0025	17.8	12.2	1.0

1 Total volume of liquid was kept constant at 15.5 mL for each experiment of Unisphere alumina.

2 Total volume of liquid was kept constant at 31.0 mL for each experiment of Bio-Rad alumina.

TABLE IV

LARGER SCALE SILANIZATION ON ALUMINA
(WITH MOLAR RATIO OF OH:TES=1:1.0)

Name	Ratio (-OH:TES)	Alumina (g)	Dioxane (mL)	TES Solution (mL)	3.1 M HCl Solution (mL)
[1]Bio-Rad	1 : 1.0	5.00	82.5	67.5	2.5
[2]Unisphare	1 : 1.0	5.00	46.0	29.1	2.5

1 250 mL 3 neck round-bottom flask was used for reaction and 75 mL of each solvent was used in washing steps for Bio-Rad.

2 150 ml 3 neck round-bottom flask was used for reaction and 50 mL of each solvent was used in washing steps for Unisphere.

(1)- Addition funnel with equalizing tube
(2)- Condensor
(3)- Thermometer
(4)- 3-neck round bottom flask
(5)- Heating mantle
(6)- Magnetic stirrer
(7)- Stirring bar
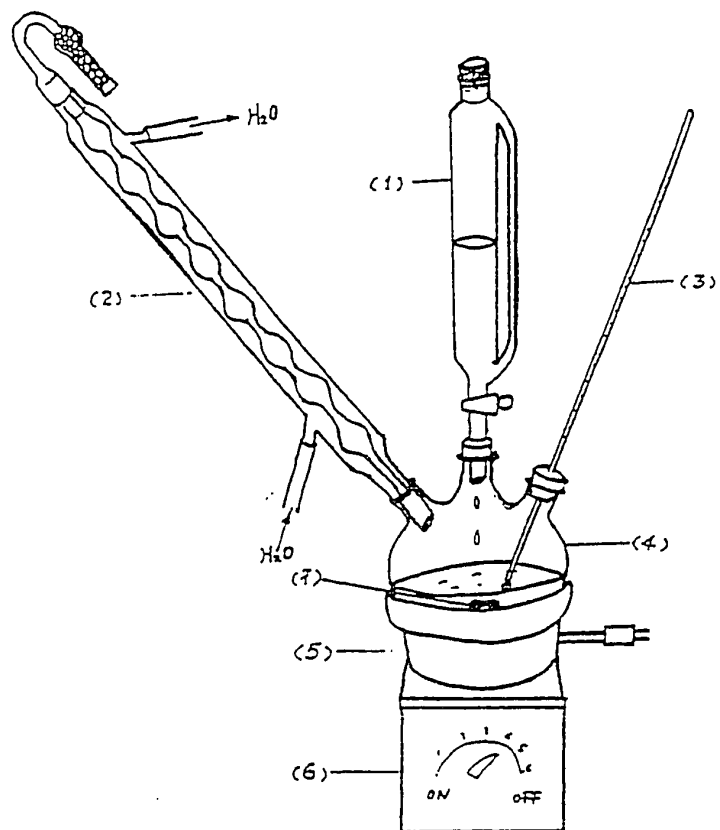
FIGURE 3

APPARATUS FOR SILANIZATION WITH TES
AND OLEFIN BONDING EXPERIMENTS

2.3.2.1. SILANIZATION WITH TES

Silanization with TES to form a monolayer of hydridosiloxane-type linkages on the zirconia surface was the first objective of this section. The silanization experiment with different molar ratios (1:0.8, 1:0.9 and 1:1.0) of TES was done. The procedure was the same as described in section 2.3.1.1.1. The quantities of the various materials used in each experiment are listed on Table V. In the washing steps, a volume of 15 mL of each solvent was used. The apparatus was the same as shown in Figure 3.

2.3.2.2 LARGER SCALE SILANIZATION OF OH:TES=1:1.0 RATIO

In order to synthesize a sufficient amount of hydride-modified zirconia for further bonding studies and characterization analysis, the experiment with an OH:TES=1:1.0 molar ratio (as seen in section 2.3.2.1) was chosen and increased 5 times by using 5 grams of zirconia in the hydrosilanization step. The reaction procedure and washing steps were the same as with the 1 gram-scale experiment, but the volume of solvents was different; a volume of 75 mL of each solvent in the washing steps was used for this large scale experiment. The quantities of materials used are listed in Table V. The apparatus was the same as shown in Figure 3, but larger volume glassware was used.

2.3.2.3 OLEFIN BONDING ON ZIRCONIA HYDRIDE SURFACE

The procedure of olefin bonding on the zirconia hydride (larger scale product) surface was the same as alumina which is described in section 2.3.1.2.

2.3.3. TITANIA MODIFICATIONS

Predried titania (TiO_2) was used as a supporting material (refer to Table II) for this study. In this experiment, titania was first silanized with TES using the previous method. It was then followed by hydrosilation with an olefin (1-octene, C_8) as described below.

2.3.3.1. SILANIZATION WITH TES

Silanization with TES to form a monolayer of hydridosiloxane-type linkages on the titania surface was the first objective of this section. The silanization experiment with various molar ratios (1:1.1, 1:1.0 and 1:0.9) of OH:TES was done. The procedure was the same as described in section 2.3.1.1.1. The quantities of the various materials used in each experiment are listed in Table VI. In the washing steps, a volume of 15 mL of each solvent was used . The apparatus was the same as shown in Figure 3.

2.3.3.2 LARGER SCALE SILANIZATION OF OH:TES=1:1.0 RATIO

For this experiment an OH:TES=1:1.0 molar ratio (as seen in section 2.3.3.1) was chosen. In order to increase the quantity of the titania modification product by a factor of 10, 10 grams of titania were used as a starting material in the hydrosilanization step for synthesizing a sufficient amount of hydride-modified titania for further bonding studies and characterization analysis. The reaction procedure and washing steps were similar to the 1 gram scale experiment, but a volume of 75 mL of each solvent in the washing steps was used for this large scale experiment. The quantities of materials used are listed in Table VI. The

apparatus was the same as shown in Figure 3, but larger volume glassware was used.

2.3.3.3 OLEFIN BONDING ON TITANIA HYDRIDE SURFACE

The procedure of olefin bonding on the titania hydride surface was the same as alumina which is described in section 2.3.1.2. The apparatus was the same as shown in Figure 3.

2.3.4. THORIA MODIFICATIONS

Predried thoria (ThO_2) was used as a support material (refer to Table II). The procedure for silanization of thoria with TES followed by hydrosilation with an olefin (1-octene) is described below.

2.3.4.1. SILANIZATION WITH TES

Silanization with TES to form a monolayer of hydridosiloxane-type linkages on the thoria surface was the first objective of this section. The silanization experiment with various molar ratios of OH:TES (1:0.9, 1:1.0 and 1:1.1) was done. The procedure was the same as the one described in section 2.3.1.1.1. A larger scale experiment for a 1:1.0 molar ratio of OH:TES was also done and is similar to the procedure described in section 2.3.1.1.2. The quantities of the various materials used in each experiment are listed in Table VI. In the washing steps, a volume of 15 mL of each solvent was used. The apparatus was the same as shown in Figure 3.

2.3.4.2 LARGER SCALE SILANIZATION OF OH:TES=1:1.0 RATIO

In order to synthesize a sufficient amount of hydride-modified thoria for further bonding studies and characterization analysis, the experiment with a OH:TES=1:1.0 molar ratio (as seen in section 2.3.4.1) was chosen and increased 10 times by using 10 grams of thoria in the hydrosilanization step. The apparatus was the same as shown in Figure 3, except larger volume glassware was used. The reaction procedure and washing steps were similar to the 1-gram scale experiment, but a volume of 75 mL of each solvent in the washing steps was used for this large scale experiment. The quantities of materials used are listed in Table VI.

2.3.4.3 OLEFIN BONDING ON THORIA HYDRIDE SURFACE

The procedure of olefin bonding on the thoria hydride surface was the same as alumina which is described in section 2.3.1.2. The apparatus was the same as shown in Figure 3.

TABLE V

DIFFERENT OH:TES RATIOS OF SILANIZATION
ON ZIRCONIA

Ratio (-OH:TES)	Zirconia (g)	Dioxane (mL)	TES Solution (mL)	3.1 M HCl Solution (mL)
Zirconia(1) (Chevron) [1]1 : 1.0 1 : 0.9 1 : 0.8	 1.0005 1.0005 1.0003	 10.8 11.3 11.7	 4.2 3.7 3.3	 0.5 0.5 0.5
1 : 0.9	1.0001	11.3	3.7	1.0
Zirconia(2) (U of Mass.) [2]1 : 1.0	 5.0001	LARGER SCALE 49.0	 26.0	 2.5

[1] 25 mL 3 neck round-bottom flask was used for the 1 gram zirconia scale reaction.

[2] 150 mL 3 neck round-bottom flask was used for the 5 gram zirconia scale reaction.

TABLE VI

DIFFERENT OH:TES RATIO OF SILANIZATION
ON TITANIA AND THORIA

Ratio (-OH:TES)	Titania (g)	Dioxane (mL)	TES Solution (mL)	3.1 M HCl Solution (mL)
[1]1 : 1.1	1.0005	12.9	2.1	0.5
1 : 1.0	1.0005	13.1	1.9	0.5
1 : 0.9	1.0003	13.3	1.7	0.5
larger Scale: [2]1 : 1.0	10.0001	131	19	5.0
Ratio (-OH:TES)	Thoria (g)	Dioxane (mL)	TES Solution (mL)	3.1 M HCl Solution (mL)
1 : 1.1	1.0005	11.3	3.7	0.5
1 : 1.0	1.0005	11.7	3.3	0.5
1 : 0.9	1.0003	12.0	3.0	0.5
larger Scale: 1 : 1.0	10.0001	117	33	5.0

1 25 mL 3 neck round-bottom flask was used for the 1 gram titania and thoria scale reaction.

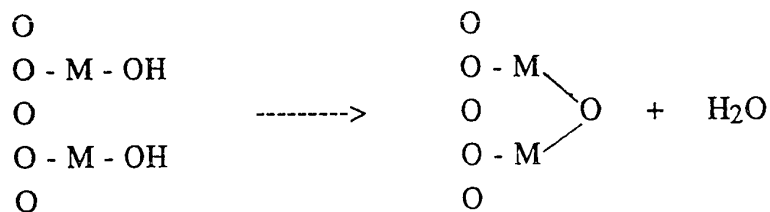2 250 mL 3 neck round-bottom flask was used for the 10 gram titania and thoria scale reaction.

CHAPTER 3

RESULTS AND DISCUSSION

The modified oxide materials which include the silicon hydride-modified supports and the olefin bonded products were evaluated and characterized by several instrumental methods. The results are given and discussed in this chapter.

3.1. TGA DATA

In this work, the purpose of doing the TGA experiments was to obtain quantitative information from this thermal analytical method to detect by gradual weight loss, the number of OH groups on the surface of the oxides. The data from the TGA work are presented as the gradual weight loss of the oxides in the temperature range from 110°C to 900°C. The weight loss occurs because of condensation of two adjacent silanols on the surface of the oxide supports. The chemical process can be easily seen as follow:

```
      O                                    O
      |                                    |
  O - M - OH                           O - M
      |                                    |    \
      O              --------->            O      O   +   H2O
      |                                    |    /
  O - M - OH                           O - M
      |                                    |
      O                                    O
```

(M represents aluminum (Al), zirconium (Zr), titanium (Ti) or thorium (Th) in this case.)
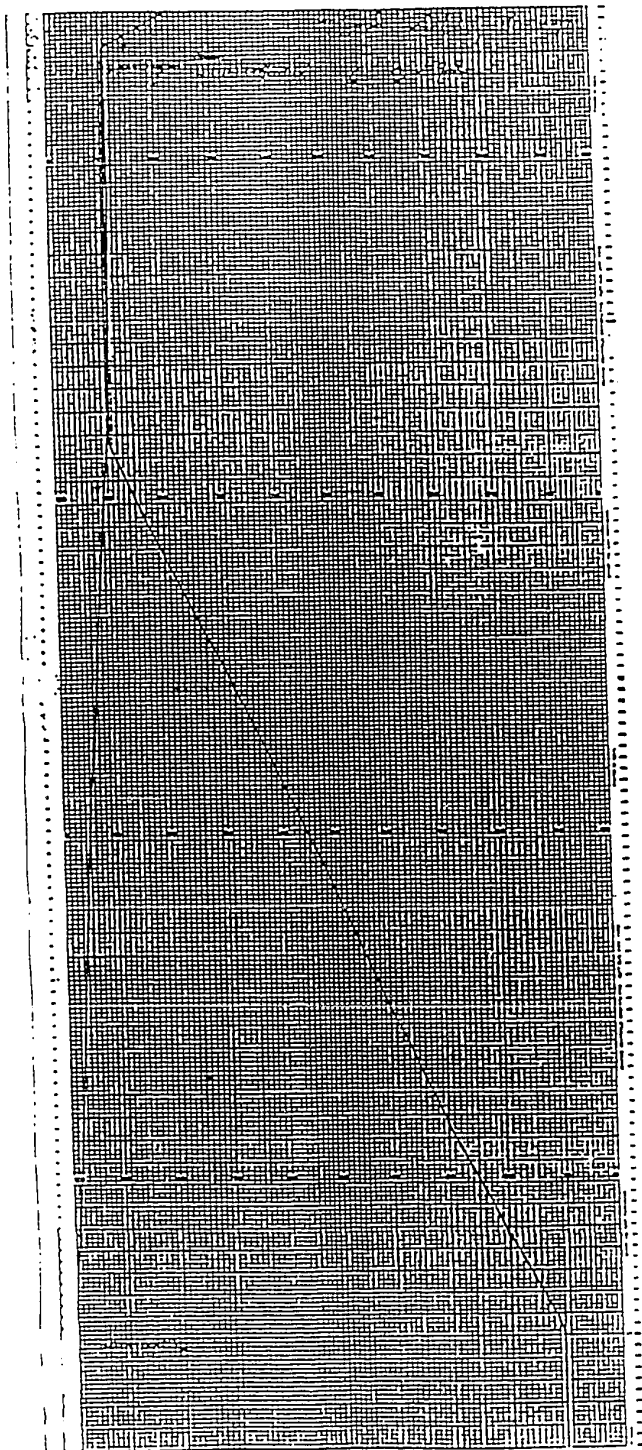
36

Figure 4

TGA THERMOGRAM OF BARE ZIRCONIUM OXIDE

(Temperature range: 110°C to 900°C)

Figure 4 presents a typical TGA thermogram for the temperature range of 110°C to 900°C used in this work. From the TGA data, one can calculate the number of OH groups (mmol/gram) on the surface of the oxides. The equation used to calculate this is :

$$\alpha_{OH} = \frac{\% \text{ weight loss}}{100} \times \frac{10^3}{18.0} \times \frac{2}{1}$$

These calculated values for α_{OH} then were used in the calculation of the variable molar ratios (OH:TES) for the hydrosilanization with TES. Finally, to calculate the amount of TES required (in mL) for the tests, the following equation was used :

$$\text{TES (mL)} = \alpha_{OH} \times \frac{(OH:TES) \text{ ratio}}{1 \text{ m mol OH}} \times \frac{1 \text{ mL TES}}{5.326 \text{ m mol/mL}}$$

Results of the TGA data and calculations of hydroxide content are listed in Table VII.

3.2. DSC DATA

In this work, DSC was used to qualitatively give further insight into the chemical nature of the hydride-modified oxide supports. Because the behavior of poly(hydrosiloxanes) in the presence of oxygen at temperatures above 350°C has been shown to be associated with the oxidative degradation of silane species into silanol groups (5, 14, 15), the DSC experiments were performed in air to provide a source of oxygen. The major process involves an exothermic oxidation of hydrosilane species into silanol groups:

TABLE VII

TGA RESULTS & HYDROXYL CONTENT CALCULATION
(BARE OXIDE SUPPORTS)

Name	% Weight Loss	Hydroxyl Content OH (m mol/gram)
U-Alumina	1.12	1.24
R-Alumina	2.61	2.90
Zirconia-(1)	0.78	0.87
Zirconia-(2)	1.00	1.11
Titania	0.36	0.40
Thoria	0.64	0.71

$$\equiv SiH + 1/2\ O_2 \ \text{-------}> \ \equiv Si\text{-}OH + heat$$
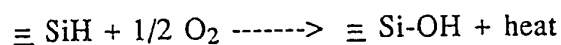
The DSC thermogram shows this thermo-oxidative degradation process by an exothermic peak.

Figure 5 shows DSC thermograms of hydride-modified alumina (UAl) supports at different OH:TES ratios (1:0.9, 1:1.0 and 1:1.1). This figure shows that, for the alumina (UAl) hydride-intermediate, as the TES concentration increases (OH:TES ratio decrease), the DSC oxidation peak tends to be deeper, broader and less symmetric and the peak shifts to lower temperature. Figure 6 shows a DSC thermogram of a hydride-modified alumina (UAl) support in the large scale experiment for OH:TES=1:1.0. This figure shows that the oxidation process dispiays three sharp peaks with the primary peak at 500°C.

Figure 7 shows DSC thermograms of hydride-modified alumina (RAl) supports at different OH:TES ratios (1:0.9, 1:1.0 and 1:1.1). This figure shows that, for the alumina (RAl) hydride-intermediate, as the TES concentration increases, the DSC oxidation peak tends to be deeper, broader and less symmetric. Figure 8 shows a DSC thermogram of a hydride-modified alumina (RAl) support in the large scale experiment for OH:TES=1:1.0. In this figure, a sharp primary peak at 472°C and a wide secondary peak at 410°C are seen.

Figure 9 shows the DSC thermograms of hydride-modified zirconia-(1) supports at different OH:TES ratios (1:0.8, 1:0.9 and 1:1.0) compared with bare zirconia-(1). This figure shows that, for the zirconia (1) hydride-intermediate, as the TES concentration increases, the DSC peak becomes deeper, and a wide secondary peak tends to appear at a lower temperature range. Also the primary peak tends to shift to higher temperatures. Figure 10 shows DSC thermograms of hydride-modified zirconia-(1) supports at the OH:TES=1:0.9 ratio (in 0.5 and 1.0 mL HCl solutions) compared with bare zirconia-(1). This figure shows that increasing the amount of HCl for the same OH:TES ratio (1:0.9) results in a weaker DSC peak. Figure 11 shows the DSC thermograms of hydride-modified zirconia (2) support in the large scale experiment for OH:TES=1:1.0, compared with bare zirconia-(2). This figure shows a wider peak at 485°C than the experiment for the 1 gram-scale experiment.

Figure 12 shows DSC thermograms of hydride-modified titania supports at different OH:TES ratios (1:0.9, 1:1.0 and 1:1.1) compared with the bare support. This figure shows that, for the hydride-modified titania, as the TES concentration increases, the DSC peak becomes deeper, wider and less symmetric. A secondary peak tends to appear at higher temperature. Figure 13 shows DSC thermograms of the hydride-modified titania support in the large scale experiment for OH:TES=1:1.0 compared

with the bare support. In comparison to Figure 12, this figure shows a primary peak at higher temperature, and the secondary peak at lower temperature.

Figure 14 shows DSC thermograms of hydride-modified thoria supports at different OH:TES ratios (1:0.9, 1:1.0 and 1:1.1) compared with the bare support. This figure shows that, for the hydride-modified thoria, as the TES concentration increases, the DSC peak tends to be deeper, less symmetric, and a secondary peak tends to appear at a higher temperature. Figure 15 shows DSC thermograms of a hydride-modified thoria support in the large scale experiment for OH:TES=1:1.0 compared with the bare support. In comparison to Figure 14, this thermogram shows a primary peak at a higher temperature, and a secondary peak at a lower temperature.

Results of the DSC experiments are summarized in Table VIII. In summary, the DSC results show that as the TES concentration increases in the hydrosilanization of alumina, the peak becomes deeper, broader, less symmetric and shifts to lower temperature; for zirconia hydride intermediates, the peak becomes deeper, wider, less symmetric and a secondary peak tends to appear at a lower temperature; for titania hydride intermediates, the peak becomes deeper, broader, and less symmetric; for thoria hydride intermediates, the peak becomes deeper, wider and less symmetric. The peak broadening in the DSC thermograms strongly suggests an increasing contribution of a second component, probably a $(HSiO_{3/2})n$ polymeric material which might have been formed at the relatively high TES concentration used. From the results of previous work by a student in our research group (4), it was comfirmed that a polycondensation of $HSi(OH)_3$ does occur at elevated temperature. Also, it was noticed in that work that there was a stoichiometic excess of TES for the molar ratio OH:TES=1.1. Therefore, multilayer silane condensation could be a strong possibility, especially at elevated temperatures.

TABLE VIII

DSC RESULTS

Samples	Figure #	OH:TES	Exothermic peak (^{o}C)
Alumina-TES (UAl)	5	1:0.9	510
	5	1:1.0	520
	5	1:1.1	500
	6	*V.2 (1:1.0)	500, 520 & 540
Alumina-TES (RAl)	7	1:0.9	475
	7	1:1.0	472
	7	1:1.1	480
	8	*V.2 (1:1.0)	472
Zirconia-TES	9	1:0.8	380
	9	1:0.9	385
	9	1:1.0	390
	11	*V.2 (1:1.0)	385
Titania-TES	12	1:0.9	295
	12	1:1.0	295
	12	1:1.1	295
	13	*V.2 (1:1.0)	275, 440
Thoria-TES	14	1:0.9	320
	14	1:1.0	290, 440
	14	1:1.1	305, 440
	15	*V.2 (1:1.0)	245, 410

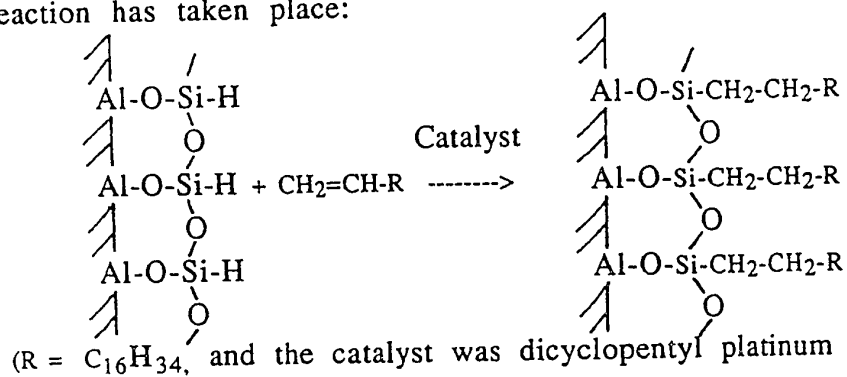*V.2 is large scale experiment.

3.3. FTIR (DRIFT) Data

In these experiments, FTIR spectroscopic analysis was employed to qualitatively identify the Si-H bands in all of the modified products (hydride-modified intermediates and olefin bonded products). The Si-H group has a characteristic strong stretching band in the range of 2300 to 2100 cm^{-1}, along with a relatively weak bending band between 760 and 910 cm^{-1}(13). Therefore, FTIR spectra are able to give structural information about the modified products. In order to identify the change in surface structure of the modified products, the bare oxide supports were also analyzed by FTIR Spectroscopy.

Figures 16 to 19 show results for various modified alumina materials. Figure 16 shows the FTIR spectra of hydride-modified alumina (UAl) products at different OH:TES molar ratios (1:0.9, 1:1.0 and 1:1.1) compared with the bare material. Figure 17 shows the FTIR spectra of hydride-modified alumina (UAl) products in the large scale experiment for OH:TES=1:1.0 and its olefin (C$_{18}$) bonded product compared with the bare material. Figure 18 shows the FTIR spectra of hydride-modified alumina (RAl) products at different OH:TES molar ratios (1:0.9, 1:1.0 and 1:1.1) compared with the bare material. Figure 19 shows the FTIR spectra of hydride-modified alumina (RAl) products in the large scale experiment for OH:TES=1:1.0 and its olefin (C$_{18}$) bonded product compared with the bare material.

In Figures 16 and 18, a strong Si-H stretching band at 2255 or 2248 cm^{-1} was detected by FTIR (Spectra B, C and D) after TES hydrosilanization. This indicates that the silicon-hydride species was sucessfully bonded to the alumina (both UAl and RAl) surfaces. The chemistry can be described as follows:

$$
\begin{array}{ccc}
\text{Al - OH} & & \text{Al- O - Si - H} \\[2pt]
& & \quad\quad\quad\; | \\
& & \quad\quad\quad\; \text{O} \\
\text{Al - OH} & \xrightarrow{\text{TES}} & \text{Al- O - Si - H} \\[2pt]
& & \quad\quad\quad\; | \\
& & \quad\quad\quad\; \text{O} \\
\text{Al - OH} & & \text{Al- O - Si - H} \\
& & \quad\quad\quad\; | \\
& & \quad\quad\quad\; \text{O}
\end{array}
$$
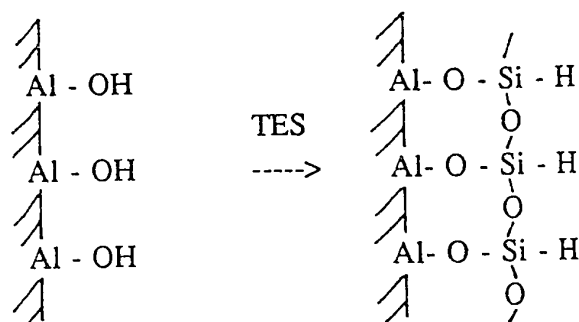
A layer of Si-H which was produced on the alumina surfaces was verified by FTIR Spectroscopy. From Figures 17 and 19, additional C-H stretching bands are seen in the range of 2800 to 3000 cm^{-1} detected by FTIR Spectroscopy after the olefin (C$_{18}$) bonding experiment on the alumina-hydride intermediate surface (Spectrum C). This result indicates that the following reaction has taken place:
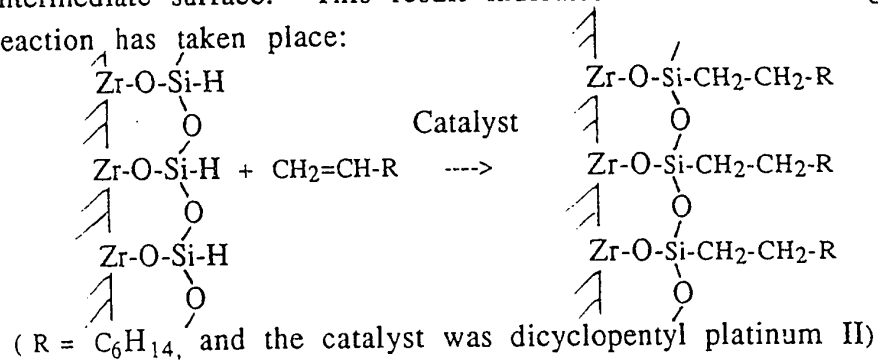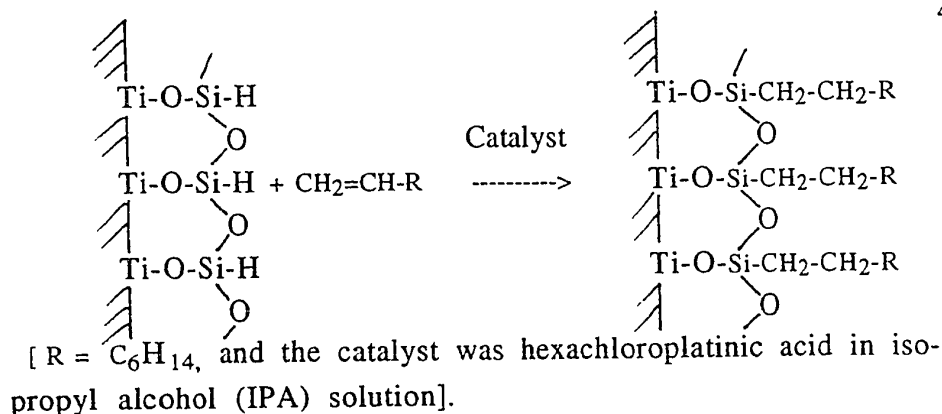
$$
\begin{array}{ccc}
\text{Al-O-Si-H} & & \text{Al-O-Si-CH}_2\text{-CH}_2\text{-R} \\[2pt]
\quad\quad | & & \quad\quad\quad\quad\quad | \\
\quad\quad \text{O} & \text{Catalyst} & \quad\quad\quad\quad\quad \text{O} \\
\text{Al-O-Si-H} + \text{CH}_2\text{=CH-R} & \xrightarrow{\quad\quad} & \text{Al-O-Si-CH}_2\text{-CH}_2\text{-R} \\[2pt]
\quad\quad | & & \quad\quad\quad\quad\quad | \\
\quad\quad \text{O} & & \quad\quad\quad\quad\quad \text{O} \\
\text{Al-O-Si-H} & & \text{Al-O-Si-CH}_2\text{-CH}_2\text{-R} \\
\quad\quad | & & \quad\quad\quad\quad\quad | \\
\quad\quad \text{O} & & \quad\quad\quad\quad\quad \text{O}
\end{array}
$$

(R = C$_{16}$H$_{34}$, and the catalyst was dicyclopentyl platinum II)

Figures 20 to 24 show results for the zirconia modification products in this study. Figure 20 shows the FTIR spectra of the hydride-modified zirconia-(1) products at different OH:TES molar ratios (1:0.8, 1:0.9 and 1:1.0) compared with the bare support material. Figure 21 shows the FTIR spectra of the hydride-modified zirconia-(1) products (OH:TES=1:0.9) using different volumes (0.5 mL and 1.0 mL) of 3.1 M HCl in the silanization step compared with the bare support material. Figure 22 shows the FTIR spectra of the hydride-modified zirconia-(1) products in the large scale experiment for OH:TES=1:1.0 and its olefin (C$_8$) bonded product compared with the bare material. Figure 23 shows the FTIR spectra of the hydride-modified zirconia-(1) products (OH:TES=1:1.0 molar ratio) after acid treatment at pH=1.95 for varying time periods (48 hrs, 96 hrs and 144 hrs)

compared with the support material before the acid treatment. Figure 24 shows the FTIR spectra of the hydride-modified zirconia-(1) products (OH:TES=1:1.0 molar ratio) after basic treatment at pH=10.12 for varying time periods (48 hrs, 96 hrs and 144 hrs).

From Figures 20 and 21, a strong Si-H stretching band at 2255 cm $^{-1}$ was detected by FTIR (spectra B, C and D in Figure 20, spectra B and C in Figure 21) after hydrosilanization with TES. This indicates that the silicon-hydride species was sucessfully bonded to zirconia surfaces and was verified by FTIR Spectroscopy. The chemistry can be described as follows:

$$
\begin{array}{ccc}
Zr-OH & & Zr-O-Si-H \\
& & \overset{|}{O} \\
Zr-OH & \xrightarrow{\;TES\;} & Zr-O-Si-H \\
& & \overset{|}{O} \\
Zr-OH & & Zr-O-Si-H \\
& & \overset{|}{O}
\end{array}
$$
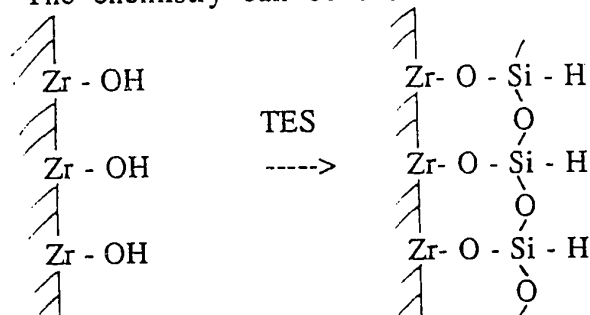
Figure 21 provides information on the effects of varying amounts of HCl for silicon hydride bonded to the oxide surfaces: more HCl results in less silicon hydride species on the oxide surfaces. This effect was possibly due to silane decomposition compet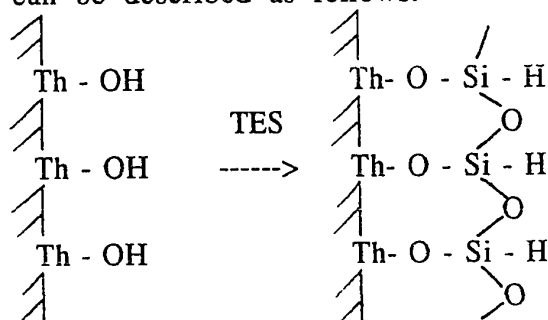ing with the hydrosilanization. In Figure 22, there were additional C-H stretching bands in the range of 2800 to 3000 cm^{-1} detected by FTIR Spectroscopy (Spectrum C) after the olefin (C_8) bonding experiment on the zirconia hydride intermediate surface. This result indicates that the following reaction has taken place:

$$
\begin{array}{ccccc}
Zr-O-Si-H & & & & Zr-O-Si-CH_2-CH_2-R \\
\overset{|}{O} & & Catalyst & & \overset{|}{O} \\
Zr-O-Si-H & + & CH_2=CH-R & \longrightarrow & Zr-O-Si-CH_2-CH_2-R \\
\overset{|}{O} & & & & \overset{|}{O} \\
Zr-O-Si-H & & & & Zr-O-Si-CH_2-CH_2-R \\
\overset{|}{O} & & & & \overset{|}{O}
\end{array}
$$

(R = C_6H_{14}, and the catalyst was dicyclopentyl platinum II)

Figure 23 indicates that the zirconia intermediates showed surface silicon hydride species after acid treatment. By comparing the spectra A, B, C and D, the peak height of the Si-H stretching band at 2255 cm^{-1} degraded very little as the time period increased. Therefore, this indicates that the zirconia hydride intermediate was quite stable at low pH (pH<2). Figure 24 shows that the Si-H stretching band at 2255 cm^{-1} disappeared after basic treatment. This result means that the zirconia hydride intermediates were unstable at high pH (pH>10).

Figure 25 and 26 show results for titania modification products in this study. Figure 25 shows the FTIR spectra of hydride-modified titania products at different OH:TES molar ratios (1:0.9, 1:1.0 and 1:1.1) compared with the bare support material. Figure 26 shows the FTIR spectra of hydride-modified titania products in the large scale experiment for OH:TES=1:1.0 and its olefin (C$_8$) bonded product compared with the bare material.

In Figure 25, a weak Si-H stretching band at 2255 cm^{-1} was detected by FTIR (spectra B, C and D) after hydrosilanization with TES. This indicates that small amounts of silicon-hydride species per gram were bonded to the titania surface and were verified by FTIR Spectroscopy. The chemistry can be described as follows:

Ti - OH
Ti - OH   TES   Ti- O - Si - H
Ti - OH   ----->   Ti- O - Si - H
                            Ti- O - Si - H
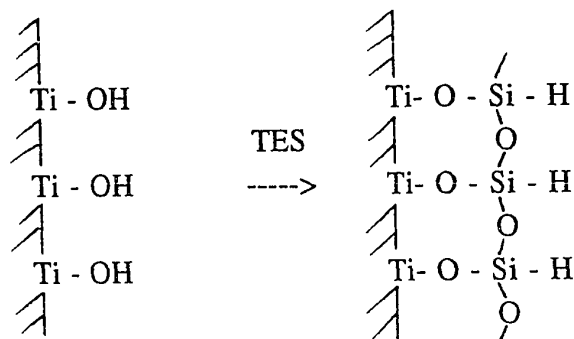
In figure 26, additional C-H stretching bands in the range of 2800 to 3000 cm^{-1} are detected by FTIR Spectroscopy after the olefin (C$_8$) bonding experiment on the titania hydride intermediate surface (Spectrum A). This result can be accounted for by the following reaction:

```
  ⅃               /                      ⅃              /
  ⅃   Ti-O-Si-H                          ⅃   Ti-O-Si-CH2-CH2-R
  ⅃        \                             ⅃        \
  ⅃         )O          Catalyst         ⅃         )O
  ⅃        /                             ⅃        /
  ⅃   Ti-O-Si-H  + CH2=CH-R  --------->  ⅃   Ti-O-Si-CH2-CH2-R
  ⅃        \                             ⅃        \
  ⅃         )O                           ⅃         )O
  ⅃        /                             ⅃        /
  ⅃   Ti-O-Si-H                          ⅃   Ti-O-Si-CH2-CH2-R
  ⅃        \                             ⅃        \
  ⅃         O                            ⅃         )O
  ⅃        /                             ⅃        /
```

[R = C_6H_{14}, and the catalyst was hexachloroplatinic acid in iso-propyl alcohol (IPA) solution].

Figures 27 to 28 show results for the thoria modification products in this study. Figure 27 shows the FTIR spectra of hydride-modified thoria products at different OH:TES molar ratios (1:0.9, 1:1.0 and 1:1.1) compared with the bare support material. Figure 28 shows the FTIR spectra of hydride-modified thoria products in the large scale experiment for OH:TES=1:1.0 and its olefin (C_8) bonded product compared with the bare material.

From Figure 27, an Si-H stretching band at 2255 cm $^{-1}$ was detected by FTIR (spectra B, C and D) after silanization with TES. This indicates that the silicon-hydride species was sucessfully bonded to the thoria surfaces and verified by FTIR Spectroscopy. The chemistry can be described as follows:

```
  ⅃                        ⅃            /
  ⅃  Th - OH               ⅃   Th- O - Si - H
  ⅃                        ⅃            \
  ⅃              TES       ⅃             )O
  ⅃  Th - OH    ----->     ⅃   Th- O - Si - H   /
  ⅃                        ⅃            \
  ⅃                        ⅃             )O
  ⅃  Th - OH               ⅃   Th- O - Si - H
  ⅃                        ⅃            \
  ⅃                        ⅃             )O
```

In Figure 28, additional C-H stretching bands in the range of 2800 to 3000 cm^{-1} were detected by FTIR Spectroscopy after the olefin (C_8) bonding experiment on the thoria hydride intermediate surface (Spectrum A). This result indicates that the following reaction has taken place:

```
  /|              /                    /|              /
 /_|    /        /                    /_|    /        /
  Th-O-Si-H                            Th-O-Si-CH2-CH2-R
  /|      \                            /|      \
 /_|       O         Catalyst         /_|       O
  Th-O-Si-H + CH2=CH-R   -------->     Th-O-Si-CH2-CH2-R
  /|      \                            /|      \
 /_|       O                          /_|       O
  Th-O-Si-H                            Th-O-Si-CH2-CH2-R
  /|      \                            /|      \
 /_|       O                          /_|       O
```

(R = C_6H_{14}, and the catalyst was hexachloroplatinic acid in IPA solution)
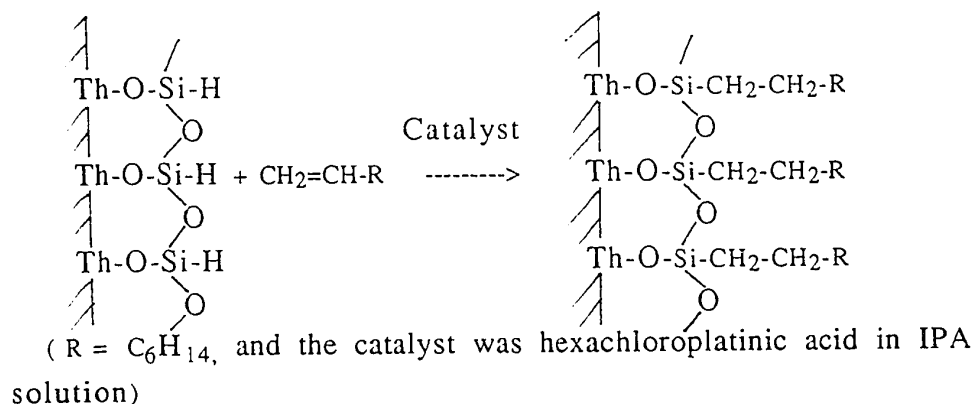
The results of the FTIR experiments are summarized in Table IX. From the FTIR results, a sharp Si-H stretching band was detected in the range of 2248 to 2255 cm^{-1} for all hydride-modified oxides which had undergone silanization with TES. However, the Si-H stretching band for the hydride-modified titania was weaker than the other hydride-modified oxides. This could be due to a low surface area for titania. Also, the intensity of the Si-H stretching band increased as the TES concentration increased in the silanization. These results indicate that the silanization occurred successfully on the surface of all the oxide supports (Al_2O_3, ZrO, TiO_2 and ThO_2). Additional C-H stretching bands in the range of 2800 to 3000 cm^{-1} corresponded to a considerable decline of the Si-H stretching band in the range of 2248 to 2255 cm^{-1} for all of the olefin bonded products (both C_8 and C_{18} terminal olefins). This result indicates that the olefin (both C_8 and C_{18} terminal olefins) was successfully bonded on the surface of all hydride-modified materials.

Table IX
FTIR RESULTS

Samples	Figure #	OH:TES	Si-H Stretching band (cm-1)	C-H Stretching band (cm-1)
Alumina-TES (UAl)	16	1:0.9	2255	
	16	1:1.0	2255	
	16	1:1.1	2255	
	17	*V.2 (1:1.0)	2255	
	17	C$_{18}$ (1:1.0)	2255	2800-3000
Alumina-TES (RAI)	18	1:0.9	2248	
	18	1:1.0	2248	
	18	1:1.1	2248	
	19	*V.2 (1:1.0)	2248	
	19	C$_{18}$ (1:1.0)	2255	2800-3000
Zirconia-TES	20	1:0.8	2255	
	20	1:0.9	2255	
	20	1:1.0	2255	
	22	*V.2 (1:1.0)	2255	
	22	C$_8$ (1:1.0)	2255	2800-3000
Titania-TES	25	1:0.9	2255	
	25	1:1.0	2255	
	25	1:1.1	2255	
	26	*V.2 (1:1.0)	2255	
	26	C$_8$ (1:1.0)	2255	2800-3000
Thornia-TES	27	1:0.9	2255	
	27	1:1.0	2255	
	27	1:1.1	2255	
	28	*V.2 (1:1.0)	2255	
	28	C$_8$ (1:1.0)	2255	2800-3000

*V.2 is larger scale.

3.4   CP-MAS FT-NMR DATA

In these experiments, CP/MAS/NMR Spectroscopic analyses were used to obtain qualitative environmental information about the ^{29}Si, ^{13}C and ^{27}Al nuclei for the hydride-modified and C_{18} (or C_8) bonded products and to confirm FTIR results. For hydride-modified products, if a major peak appears at about -85 ppm in the ^{29}Si CP/MAS/NMR spectrum; this means a $HSi^*(OSi\equiv)_3$ hydride species is chemically bounded on the oxide surfaces. ^{29}Si CP/MAS/NMR gives a better indication of the nature of the hydride-modified material than FTIR. For C_{18} or C_8 bonded products, if a major peak appears at about 30 ppm and two other minor peaks at about 12 ppm and 23 ppm in the ^{13}C CP/MAS/NMR spectrum, this confirms an alkyl ligand was chemically bonded on the hydride-modified site of the C_{18} or C_8 bonded products. In addition, for alumina products, ^{27}Al CP/MAS/NMR spectra were also used to confirm the chemical bonding on the hydride-modified and C_{18} bonded products by comparing the peak shape and the line width of the major peak (O_h) in the range 1 to 60 ppm.

Figures 29 to 55 are the CP/MAS/NMR spectra for the modified products in this study. The results of ^{29}Si CP/MAS/NMR are summarized in Table X. The results of ^{13}C CP/MAS/NMR are summarized in Table XI. The result of ^{27}Al CP/MAS/NMR are summarized in Table XII. These results support the FTIR (DRIFT) spectra which shows the formation of an additional surface species when the oxides were reacted with TES and were followed with an olefin bonding reaction.

The ^{29}Si CP/MAS/NMR was done for the alumina (UAl and RAl), zirconia, titania (OH:TES=1:1.1 only) and thoria (OH:TES=1:1.1 only) modified products. Figures 29 to 33, 38 to 42, 47 to 52, 54 and 55 show these spectra. From Table X and the $^{29}Si/CP/MAS/NMR$ spectra, the modified products [except titania (OH:TES=1:1.1)] show a major peak near -85 ppm; this

indicates a H-Si*(OSi≡)$_3$ hydride species. These data support the FTIR (DRIFT) spectra (sharp Si-H streching peak near 2255 cm-1) which show the formation of an additional surface species when the oxide is reacted with TES. Additional minor peaks were also seen. The peak which is near -75 ppm indicates a H-Si*(OH)(OSi≡)$_2$ group. The peak near -101 ppm indicates the HOSi*(OSi≡)$_3$ surface silanols. The peak near -110 ppm indicates a Si*(OSi≡)$_4$ framework. These additional weak peaks were not expected. They indicate that a small amount of siloxane polymerization has occurred. These resonances are not part of any expected monolayer or multilayer structure since each silicon atom must have a hydride attached to it. These weak peaks must be due to either impurities in the starting reagent or some subsequent decomposition of the hydride-modified surface. The olefin bonded products also showed a peak near -66 ppm which is indicative of the Si*C≡ species. This means that C$_{18}$ or C$_8$ has been successfully bonded to the hydride intermediate (instead of existing merely as a coating or contaminant).

^{13}C CP/MAS/NMR was only done for the alumina (UAl and RAl) and zirconia olefin bonded phases of the following structure:

≡Si-CH$_2$-CH$_2$-CH$_2$-(CH$_2$)n-CH$_2$-CH$_2$-CH$_3$

C position:	1	2	3	4-15	16	17	18	(n=12)
				or 4-5	6	7	8	(n=2)
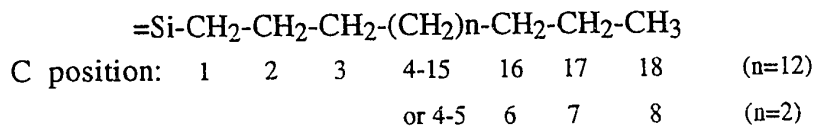
Figures 34, 43 and 53 shows these spectra; these data are summarized in Table XI. The peaks are assigned as follows: 12 ppm to C$_1$ and C$_{18}$, 23 ppm to C$_2$ and C$_{17}$ (or C$_7$), 30 ppm to C$_4$ through C$_{15}$ (or C$_5$), and 32 ppm to C$_3$ and C$_{16}$ (or C$_6$). These ^{13}C CP/MAS/NMR data support the FTIR spectra (peaks in the range of 2800 to 3000 cm-1) which show the formation of additional surface species when the hydride intermediates are reacted with olefin (C$_8$ and C$_{18}$).

TABLE X
29Si CP/MAS/NMR RESULTS

Sample	Figure#	OH:TES	29 Si Chemical Shift (ppm)				
Alumina-TES (UAl)	29	1:0.9		-86			
Alumina-TES (UAl)	30	1:1.0		-86			
Alumina-TES (UAl)	31	1:1.1		-86			
Alumina-TES (UAl)	32	*V.2 (1:1.0)		-83,	-99,		
Alumina-TES (UAl)	33	C18 (1:1.0)	-64,	-83,	-99		
Alumina-TES (RAl)	38	1:0.9	-76,	-86			
Alumina-TES (RAl)	39	1:1.0		-85			
Alumina-TES (RAl)	40	1:1.1	-76,	-85			
Alumina-TES (RAl)	41	*V.2 (1:1.0)	-74,	-83,	-99,	-109	
Alumina-TES (RAl)	42	C18 (1:1.0)	-68,	-85,	-100		
Zirconia-TES	47	1:0.8		-86,	-100,	-110	
Zirconia-TES	48	1:0.9		-84,	-101,	-110	
Zirconia-TES	50	1:1.0		-85,	-101,	-110	
Zirconia-TES	51	*V.2 (1:1.0)	-74,	-84,	-99,	-109	
Zirconia-TES	52	C8 (1:1.0)	-55,	-66,	-83,	-99,	-107
Titania-TES	54	1:1.1	No Peak was detected				
Thoria-TES	55	1:1.1		-82			

* V.2 is larger scale.

TABLE XI

^{13}C CP/MAS/NMR RESULTS

Sample	Figure#	OH:TES	13 C Chemical Shift (ppm)
Alumina-TES (UAl) C18	34	1:1.0	30, 23, 12
Alumina-TES (RAl) C18	43	1:1.0	25, 18, 9
Zirconia-TES C8	53	1:1.0	32, 29, 22, 12

TABLE XII

^{27}Al CP/MAS/NMR RESULTS

Sample	Figure#	27 Al Chemical Shift (ppm)
Native UAl	35	1
UAl-TES (1:1.1)	36	60, 1,
C18 Bonded UAl	37	55.5, 0.9,
Native RAl	44	1
RAl-TES (1:1.1)	45	52.4, 0.9
C18 Bonded RAl	46	52.4, 0.9,

27Al CP/MAS/NMR spectra were used to provide additional evidence to characterize the surface of the modified aluminas. Figures 35 to 37 and 44 to 46 are the 27Al CP/MAS/NMR spectra of the native, hydride-modified and C_{18} bonded aluminas (UAl and RAl). The data from these spectra are shown in Table XII.

Before these spectra can be explained, it is necessary to make reference to previous experimental results on hydride-modified alumina(22). A typical spectrum is shown below:
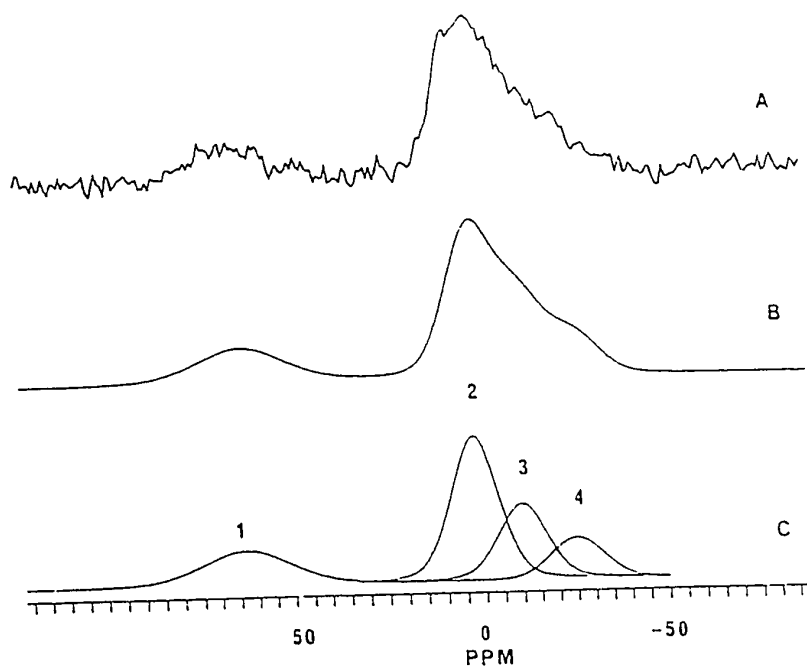
FIGURE 5a. 27Al CP-MAS-NMR spectra of product from the reaction of hydride alumina with 1-octadecene: (A) experimental spectrum, (B) simulated spectrum and (C) simulated spectrum with individual components.

The O_h portion of the ^{27}Al CP/MAS/NMR spectrum can be simulated with three individual components (peaks 2, 3 and 4). These three peaks may possibly represent three different Al^{3+} environments, or may represent an increased distortion of octahedral symmetry by modification that results in enhanced quadrupolar effects because of a non-symmetric electric field gradient. In addition, the appearance of peak 4, which is not seen in the spectrum for the native alumina, can be considered as the formation of a new species (hydride or C_{18} bonded) or as an increased distortion of the O_h symmetry during the modification process.

A comparison of the ^{27}Al CP/MAS/NMR spectra shows a change in peak shape for both alumina samples when comparing the native condition to the hydride-modified and C_{18} bonded products. Specifically, there is less symmetry or greater tailing to the peak shape of the spectra of the reacted products. Also, a peak appears at about -60 ppm in both the reacted products, and is more enhanced in the C_{18} bonded product. These results agree with those previously reported and referenced above(22). Also these ^{27}Al CP/MAS/NMR results give additional evidence to support the FTIR data and the ^{29}Si and ^{13}C CP/MAS/NMR results.

3.5. GC Data

In these experiments, a gas chromatographic technique was employed to quantitatively determine the Si-H coverage (mM/gram). Only silanized alumina (UAl) was measured by this method. It should be pointed out that this GC method is only a "bulk" method: it measures the total silane content independent of the actual chemical structure of the surface species. The results of Si-H coverages are listed on Table XIII. These results showed that the surface silane content increased as the OH:TES molar ratio increased. A comparison of OH to Si-H concentration in Tables VII and XIII reveals that the Si-H concentration is

about 50% of the original OH concentration. This means that with the OH:TES ratio used in this experiment, only about half of the available Al-OH bonds have reacted with TES. This implies that a higher TES ratio should increase the amount of reacted OH. This is, in fact, observed as shown in Table XIII.

TABLE XIII

GC RESULTS FOR ALUMINA (UAl) HYDROSILANIZED PRODUCTS

Samples	SiH coverages (mM/gram)
UAl (OH:TES=1:0.9)	0.534
UAl (OH:TES=1:1.0)	0.586
UAl (OH:TES=1:1.1)	0.686

CHAPTER 4

CONCLUSIONS

As mentioned in the introduction section of Chapter 1, the main goal of this research project was to modify the surface of four oxides (alumina, zirconia, titania and thoria) for potential use as column packings in HPLC. The first goal was to successfully produce an intermediate bearing a surface silicon hydride species for each oxide material by silanization with TES, and to characterize and evaluate these products by analytical techniques such as DSC, FTIR as well as ^{29}Si and ^{27}Al CP/MAS/NMR. The final goal was to subsequently modify the surface of each oxide hydride-intermediate by a surface hydrosilation with a terminal olefin (C_8 or C_{18}), also to characterize or evaluate these final products by analytical methods such as FTIR, ^{13}C and ^{27}Al CP/MAS/NMR. This project can be considered successful based upon the results of twenty-one hydride-intermediate samples and five olefin bonded samples.

A summary of the results from this study is as follows:

1. For alumina modification:

   a: The modified alumina bearing a silicon hydride species on the surface was successfully produced by the method of surface silanization with TES. This conclusion is supported by the results obtained from the instrumental analysis by DSC, FTIR and ^{29}Si and ^{27}Al CP/MAS/NMR.

b: An additional modification of the hydride-
intermediate alumina was successfully done by surface
hydrosilation with a terminal olefin (C_{18}). This
conclusion was supported by the results of FTIR and [13]C
and ^{27}Al CP/MAS/NMR instrumental analysis.

2. For zirconia modification:

a: The modified zirconia bearing a silicon hydride
species on the surface was successfully produced
by the method of surface silanization with TES.
This conclusion is supported by the results obtained
from instrumental analysis by DSC, FTIR and [29]Si
CP/MAS/NMR. From the results of FTIR analysis, it can
be concluded that the amount of HCl used in the
surface silanization with TES could affect the
silicon hydride bonded to the oxide surface.
Also, it was found that the hydride intermediate of
zirconia was fairly stable at lower pH (less than 2) and
was unstable at higher pH (greater than 10).

b: An additional modification of the hydride-
intermediate zirconia was successfully done by a
surface hydrosilation with a terminal olefin (C_8). This
conclusion is supported by the results of FTIR and [13]C
CP/MAS/NMR.

3. For titania modification:

a: The modified titania bearing a silicon hydride
species on the surface was successfully produced by
the method of surface silanization with TES. However,
the results obtained from DSC, FTIR and [29]Si
CP/MAS/NMR indicates that the amount of TES bonded
was not as great as the same modification for alumina,
zirconia and thoria. This may be because titania
particles have lower available surface area.

b: An additional modification of the hydride-intermediate titania was successfully done by a surface hydrosilation with a terminal olefin (C_8). This conclusion is supported by the analytical results of FTIR Spectroscopy.

4. For thoria modification:

a: The modified thoria bearing a silicon hydride species on the surface was successfully produced by the method of surface silanization with TES. The quantity bonded was not as great as the same modification for alumina and zirconia, but greater than the modification for titania. This conclusion is supported by the results obtained from instrumental analysis by DSC, FTIR and ^{29}Si CP/MAS/NMR data. The intensity of the peaks was not as strong as the same modification for alumina and zirconia, but stronger than titania. Like titania, thoria particles have lower available surface area.

b: An additional modification of the hydride-intermediate thoria was successfully done by a surface hydrosilation with a terminal olefin (C_8). This conclusion is supported by the results of FTIR and ^{29}Si CP/MAS/NMR analysis of the final products.

In conclusion, from the data presented in this study, the hydride-intermediates for each oxide, which were expected to create a Si-H monolayer on the oxide surface with a maximum of siloxane linkages and minimum of uncondensed silanols, were produced. However, a small amount of polymeric material $(HSiO_{3/2})_n$ possibly accompanied the products (from the results of DSC data). All of these products were verified by DSC and FTIR analyses, and some of them were also charaterized by ^{29}Si CP/MAS/NMR data. The method of hydrosilation of terminal olefins on the surface of the hydride-intermediate was

successfully applied to the modification for each oxide used in this study. All of these final products were charaterized by FTIR, and some of them were verified by the ^{13}C CP/MAS/NMR technique.

There are several additional suggested investigations which could be done in the future. First, there is a need for further developing the surface silanization method in order to produce more Si-H species on the surface of titania, and reducing the possibility of producing a polymeric material by this method, especially for OH:TES=1:1.0. Second, additional investigations are needed on the hydrolytic stablility at low pH and high pH of the hydride-modified alumina, titania and thoria. Also, the thermal stability of the hydride-modified oxides should be studied. Finally, additional research for evaluation of the olefin bonded phases on alumina, zirconia, titania and thoria is needed by packing these materials as stationary phases in an HPLC column. It is hoped that the data from this study will be useful for the further development of the alternate support materials in HPLC.

61
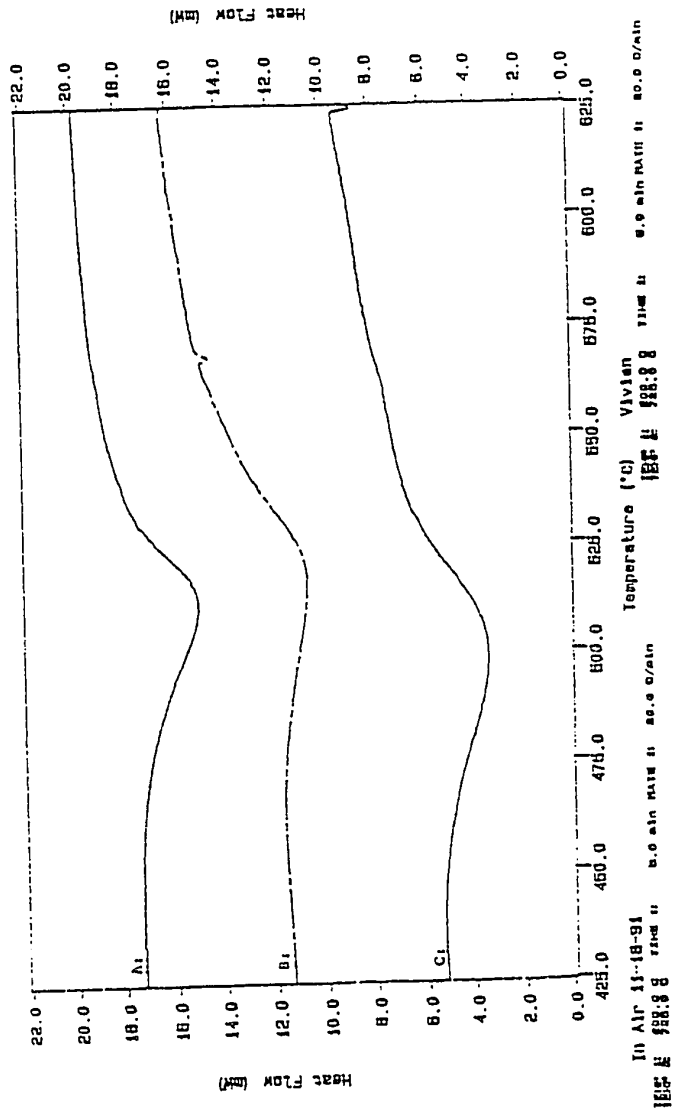
FIGURE 5

DSC THERMOGRAM FOR HYDRIDE-MODIFIED ALUMINA(UA1)

(Different OH:TES Ratios)

DSC THERMOGRAM FOR HYDRIDE-MODIFIED ALUMINA (UAl)

(Larger scale with OH:TES=1:1.0 ratio)

63
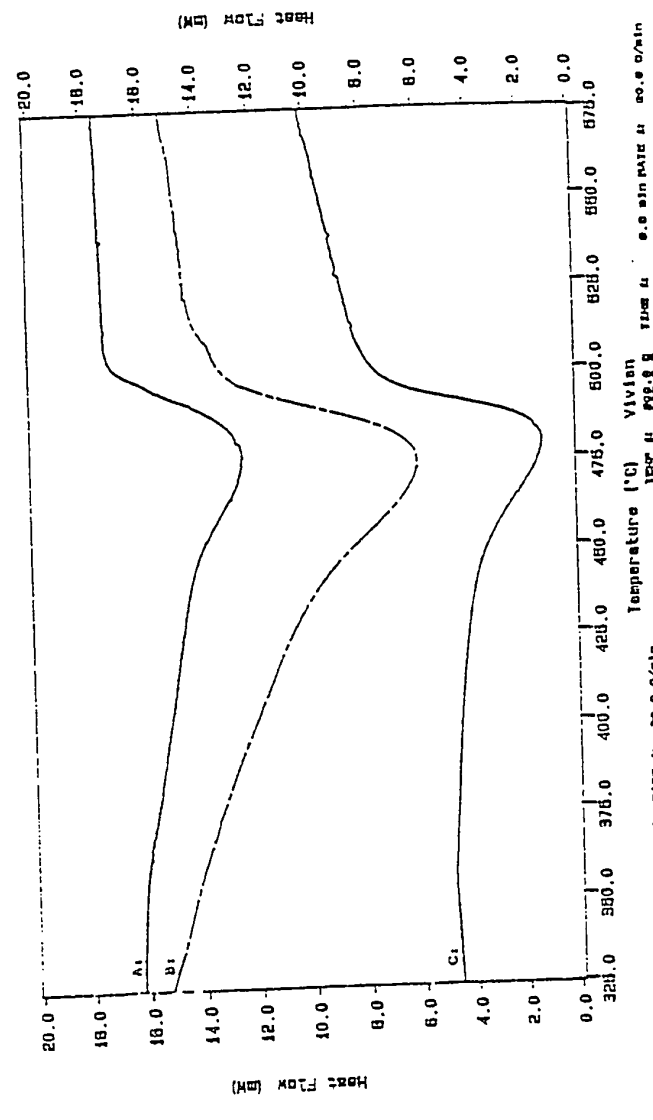
FIGURE 7

DSC THERMOGRAM FOR HYDRIDE-MODIFIED ALUMINA (RA1)

(Different OH:TES Ratios)

DSC THERMOGRAM FOR HYDRIDE-MODIFIED ALUMINA (RA1)

(Larger scale with OH:TES=1:1.0 ratio)

65

FIGURE 9

DSC THERMOGRAM FOR HYDRIDE-MODIFIED ZIRCONIA-(1)

(Different OH:TES Ratios Comparison w/ Bare)
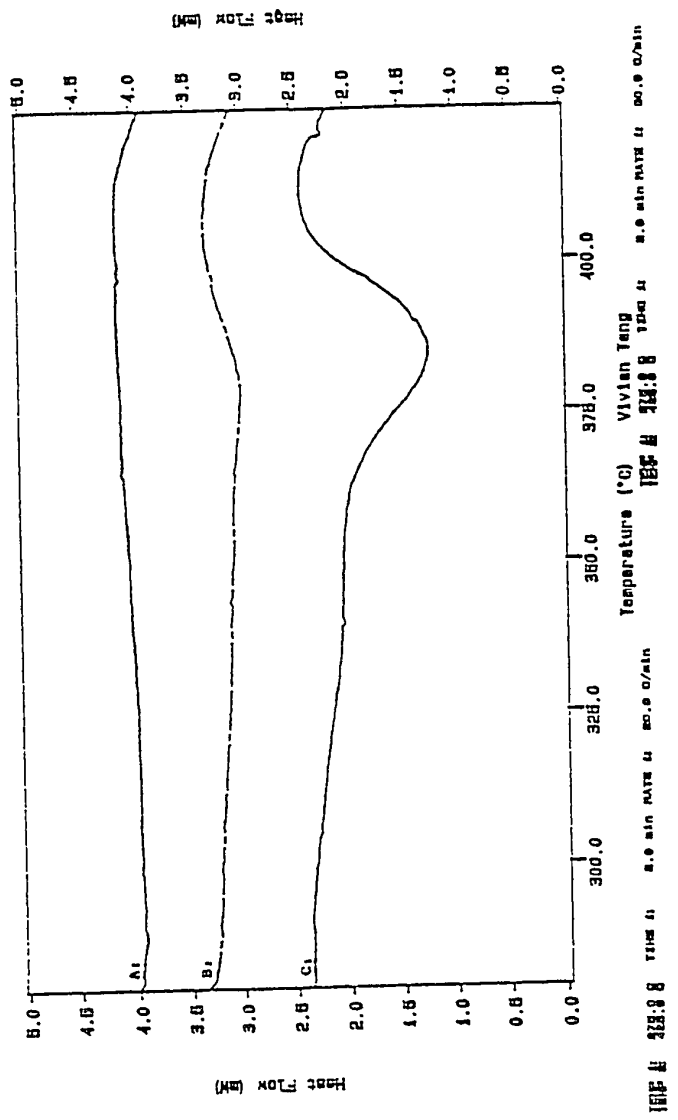
DSC THERMOGRAM OF HYDRIDE-MODIFIED ZIRCONIA-(1)

OH:TES Ratio=1:0.9
(Comparison of Reaction in 0.5 & 1.0 mL HCl)
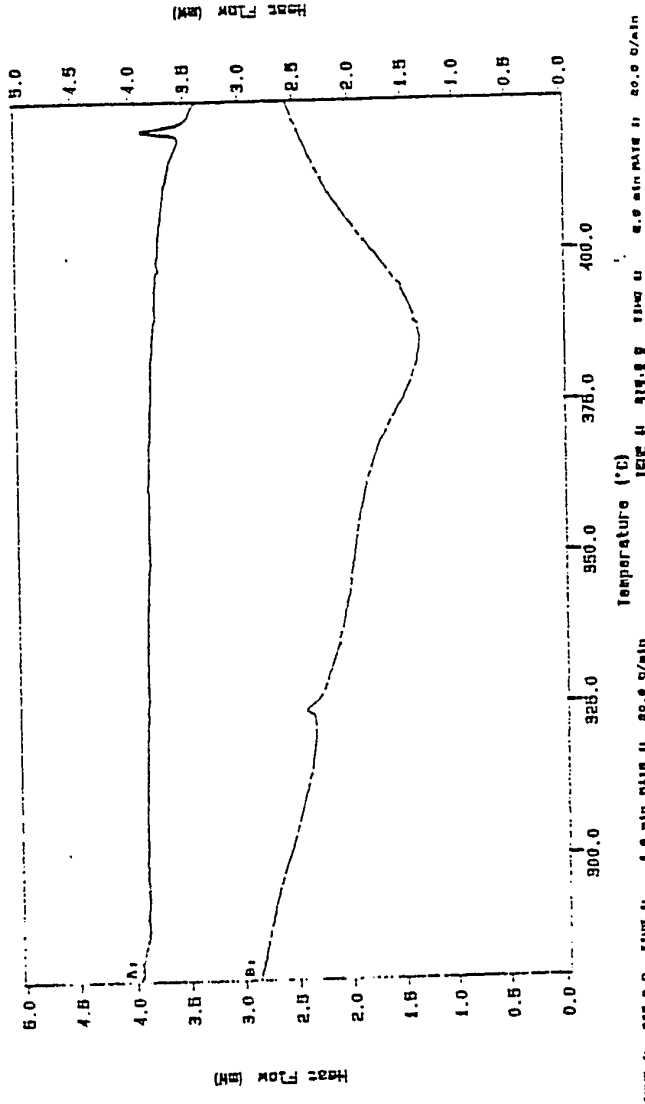
FIGURE 11

DSC THERMOGRAM OF HYDRIDE-MODIFIED ZIRCONIA-(2)

(Larger Scale for OH:TES=1:1.0 Ratio
& Comparison with Bare $ZrO_2-(2)$)
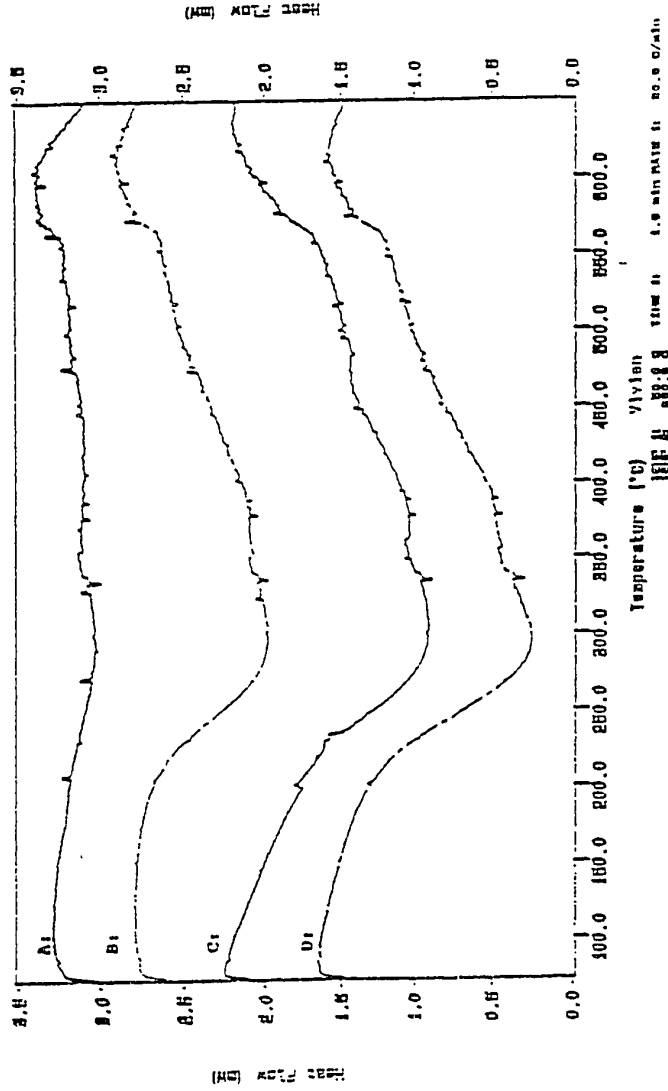
FIGURE 12

DSC THERMOGRAM OF HYDRIDE-MODIFIED TITANIA

(Comparison of Different OH:TES Ratio & Bare)
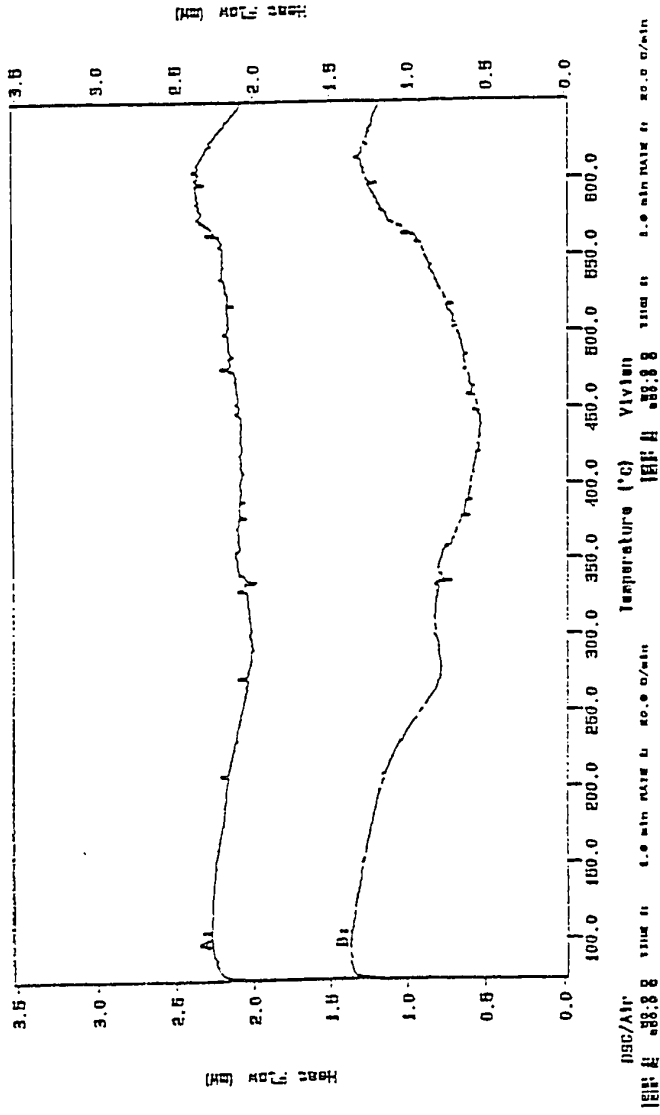
FIGURE 13

DSC THERMOGRAM OF HYDRIDE-MODIFIED TITANIA

(Larger Scale for OH:TES=1:1.0 &
Comparison with Bare TiO_2)
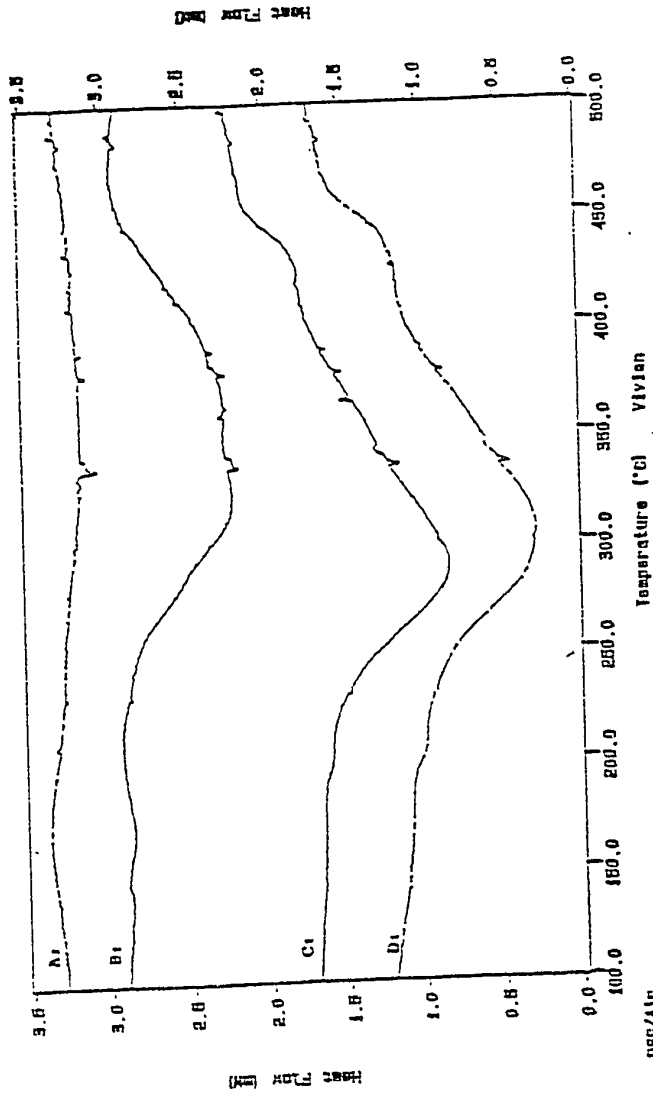
FIGURE 14

DSC THERMOGRAM OF HYDRIDE-MODIFIED THORIA

(Comparison of Different OH:TES Ratio & Bare)
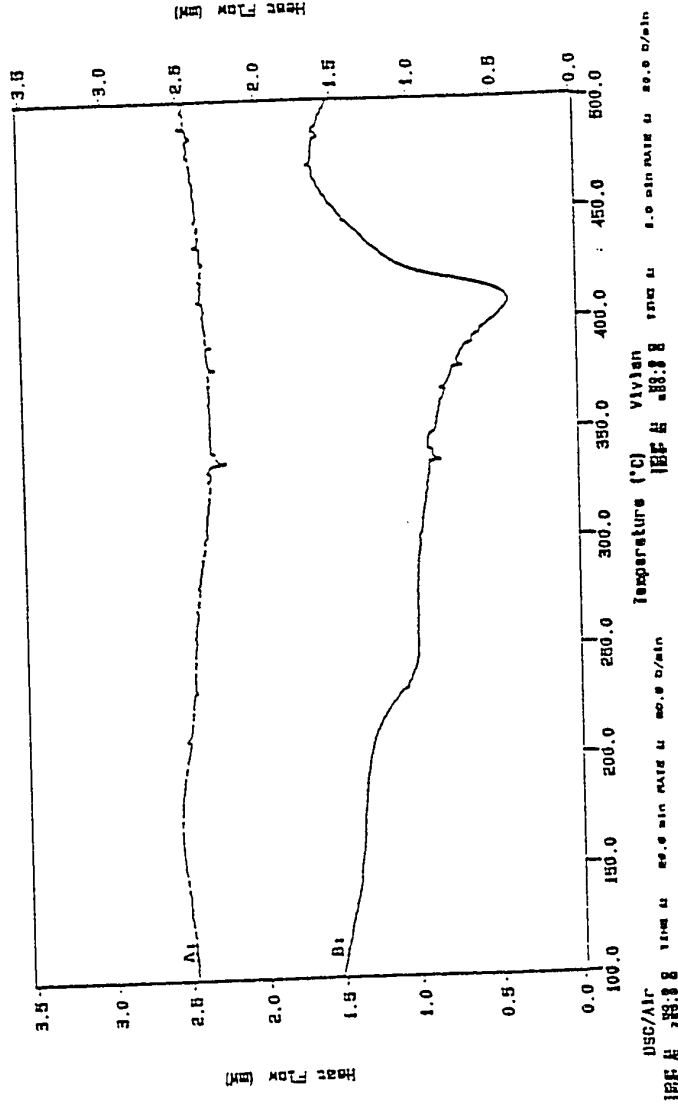
DSC THERMOGRAM OF HYDRIDE-MODIFIED THORIA

(Larger Scale for OH:TES=1:1.0 &
Comparison with Bare ThO_2)

Comparison of U-Al (Bare, TES 1:0.9, 1:1.0 and 1:1.1)

A: Bare UAl
B: UAl-TES (1:0.9)
C: UAl-TES (1:1.0)
D: UAl-TES (1:1.1)
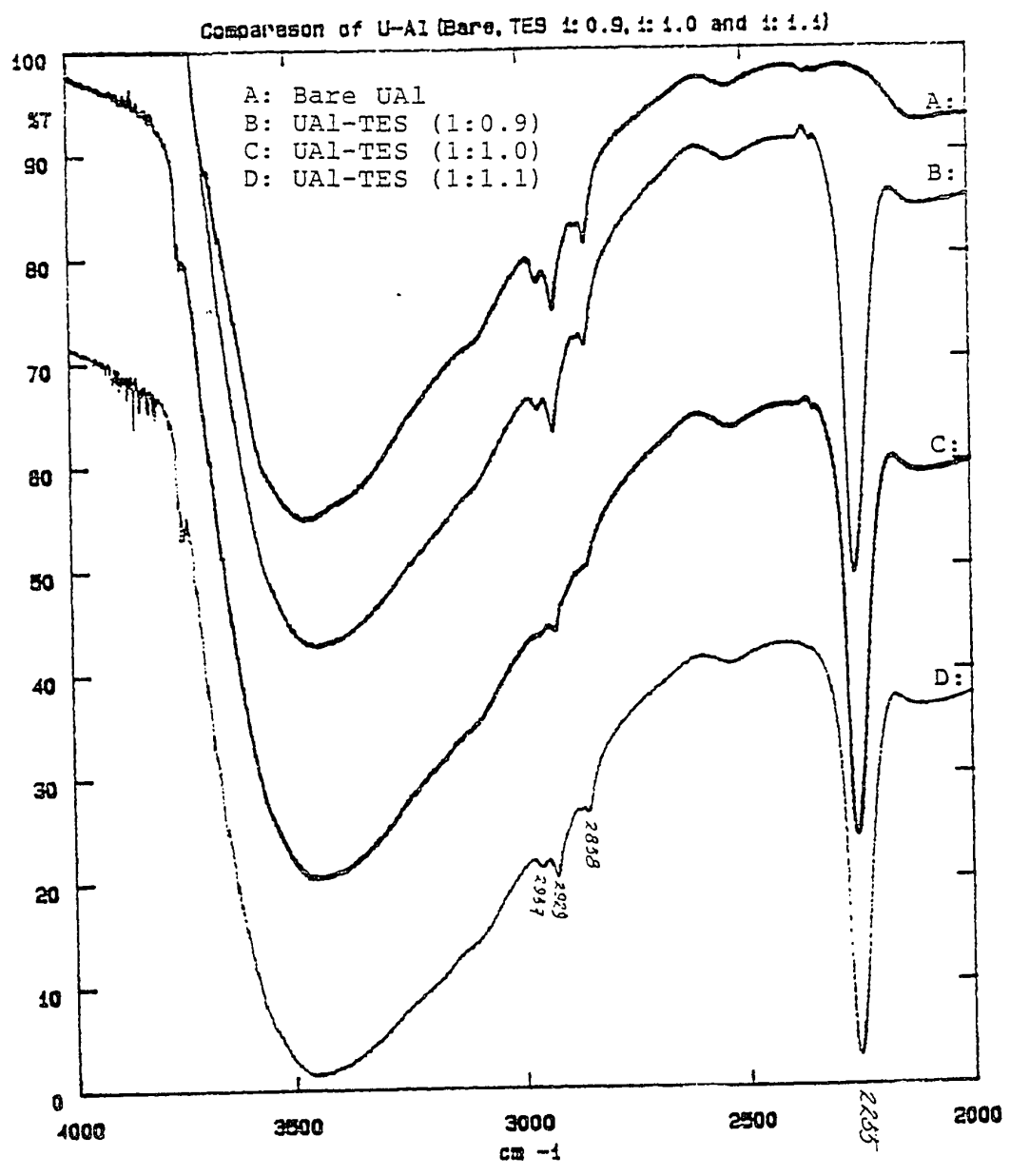
SCANS: 100
RESOLUTION: 2.00

FIGURE 16

FTIR SPECTRA OF HYDRIDE-MODIFIED ALUMINA(UAl)

(Different OH:TES Ratios & Bare)
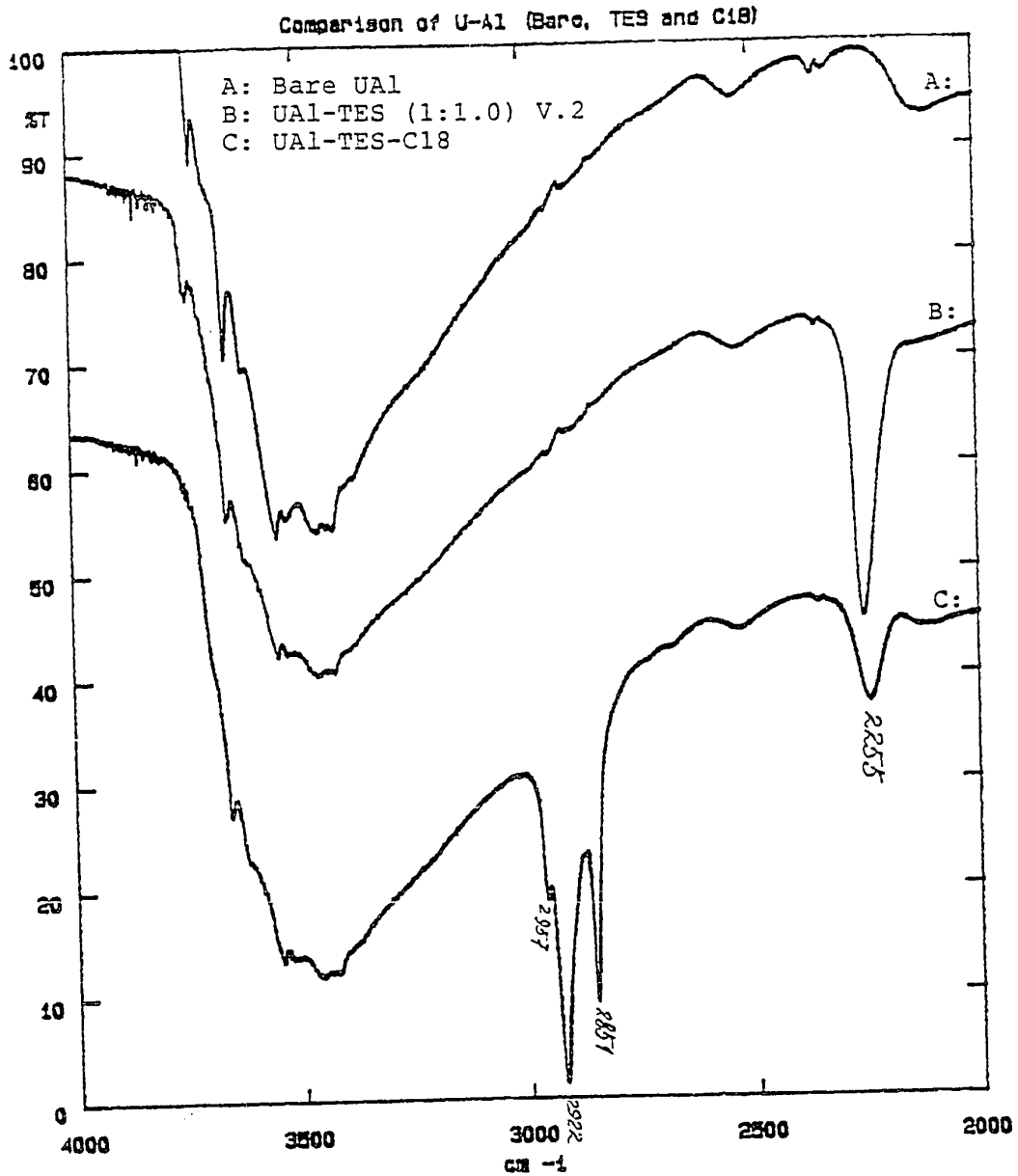
FIGURE 17

FTIR SPECTRA OF MODIFIED ALUMINA (UA1)

(Larger Scale of OH:TES=1:1.0, Olefin Bonded & Bare)

R Al-TES Comparison of Bare, 1:0.9, 1:1.0, and 1:1.1.

A: Bare RAl
B: RAl-TES (1:0.9)
C: RAl-TES (1:1.0)
D: RAl-TES (1:1.1)
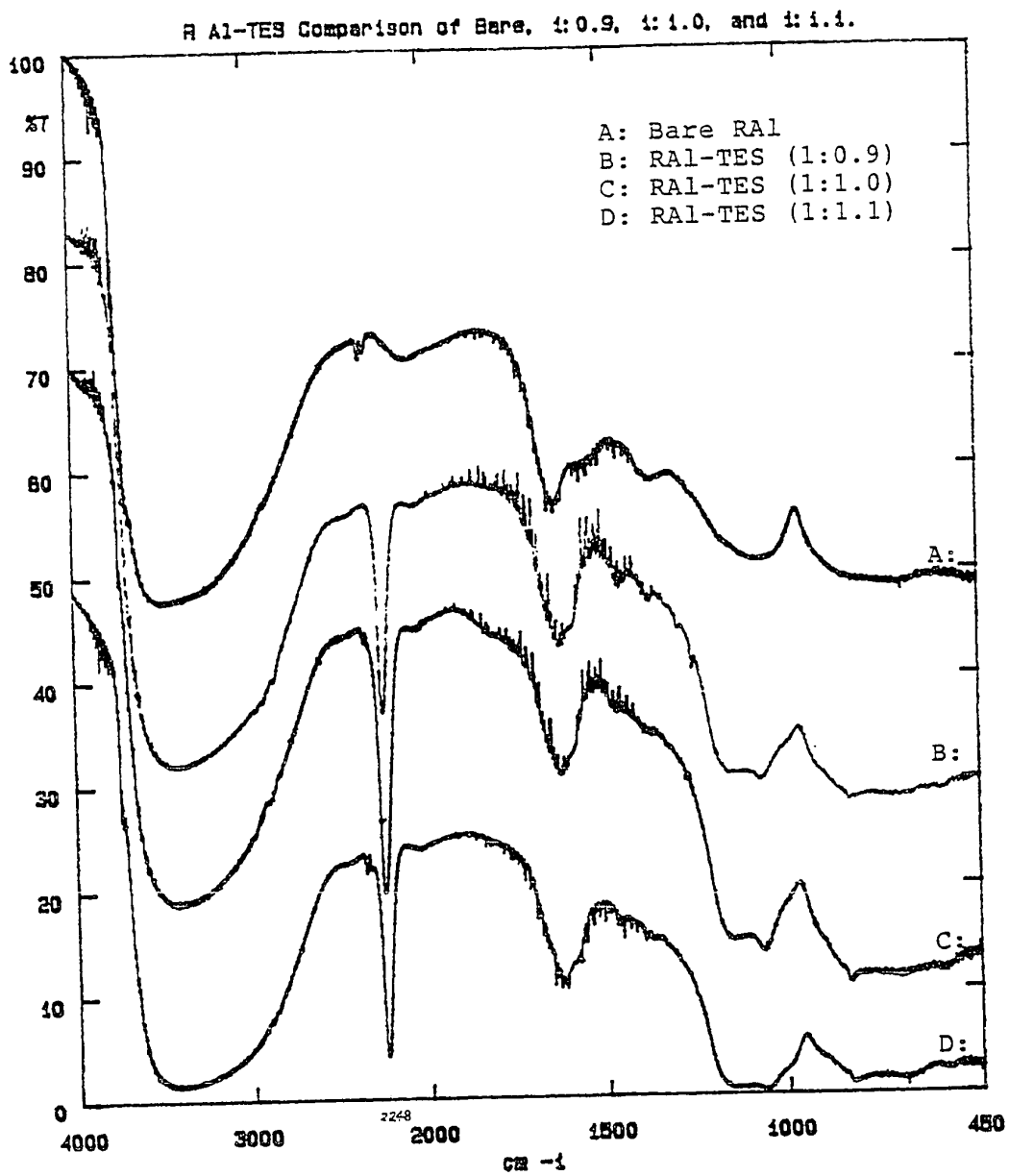
SCANS: 100
RESOLUTION: 2.00

FIGURE 18

FTIR SPECTRA OF HYDRIDE-MODIFIED ALUMINA(RAl)

(Different OH:TES Ratios & Bare)
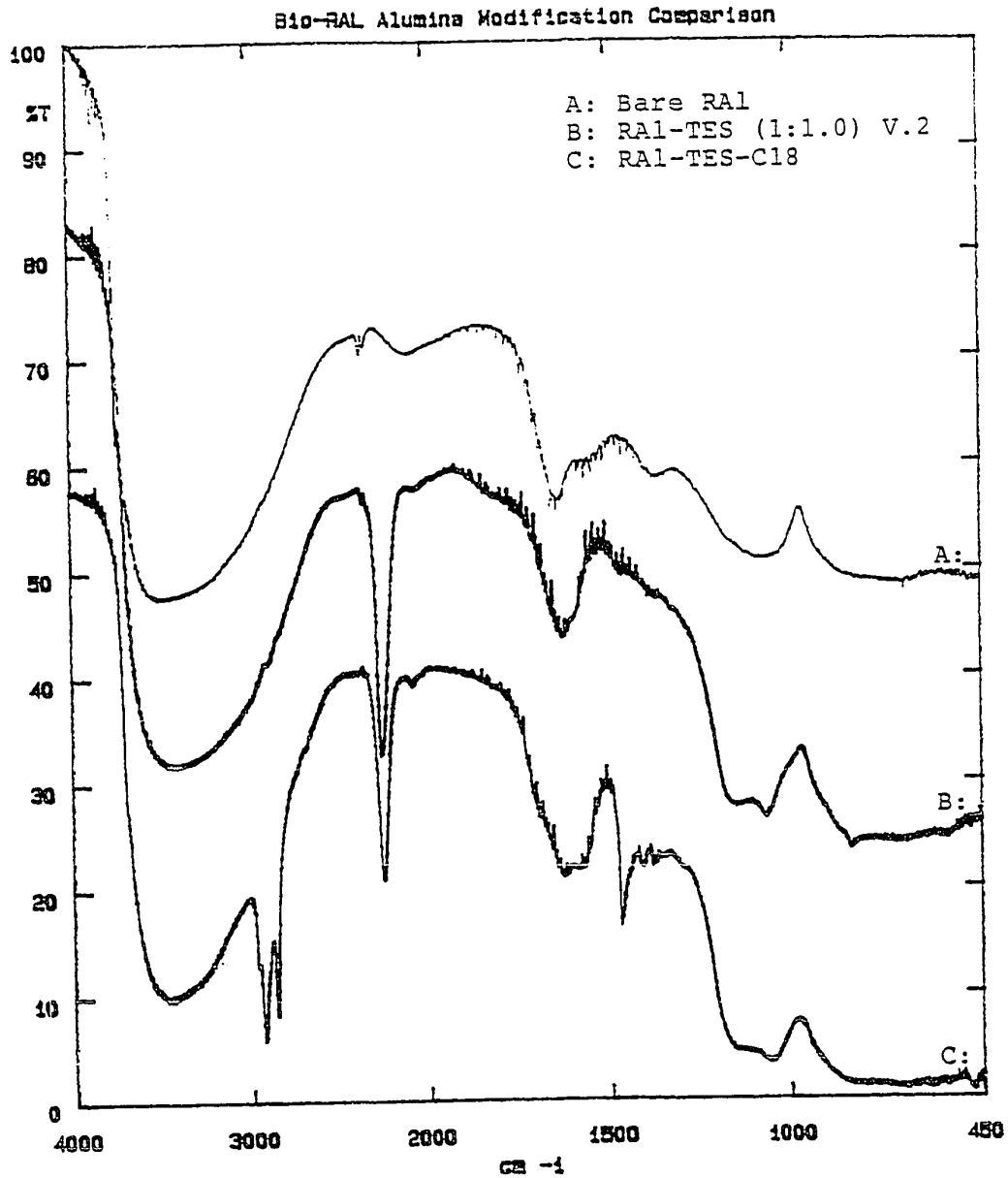
FIGURE 19

FTIR SPECTRA OF MODIFIED ALUMINA (RA1)

(Larger Scale of OH:TES=1:1.0, Olefin Bonded & Bare)

Comparison ZrO2-TES with different OH:TES Ratios

(In 0.5 mL HCl)
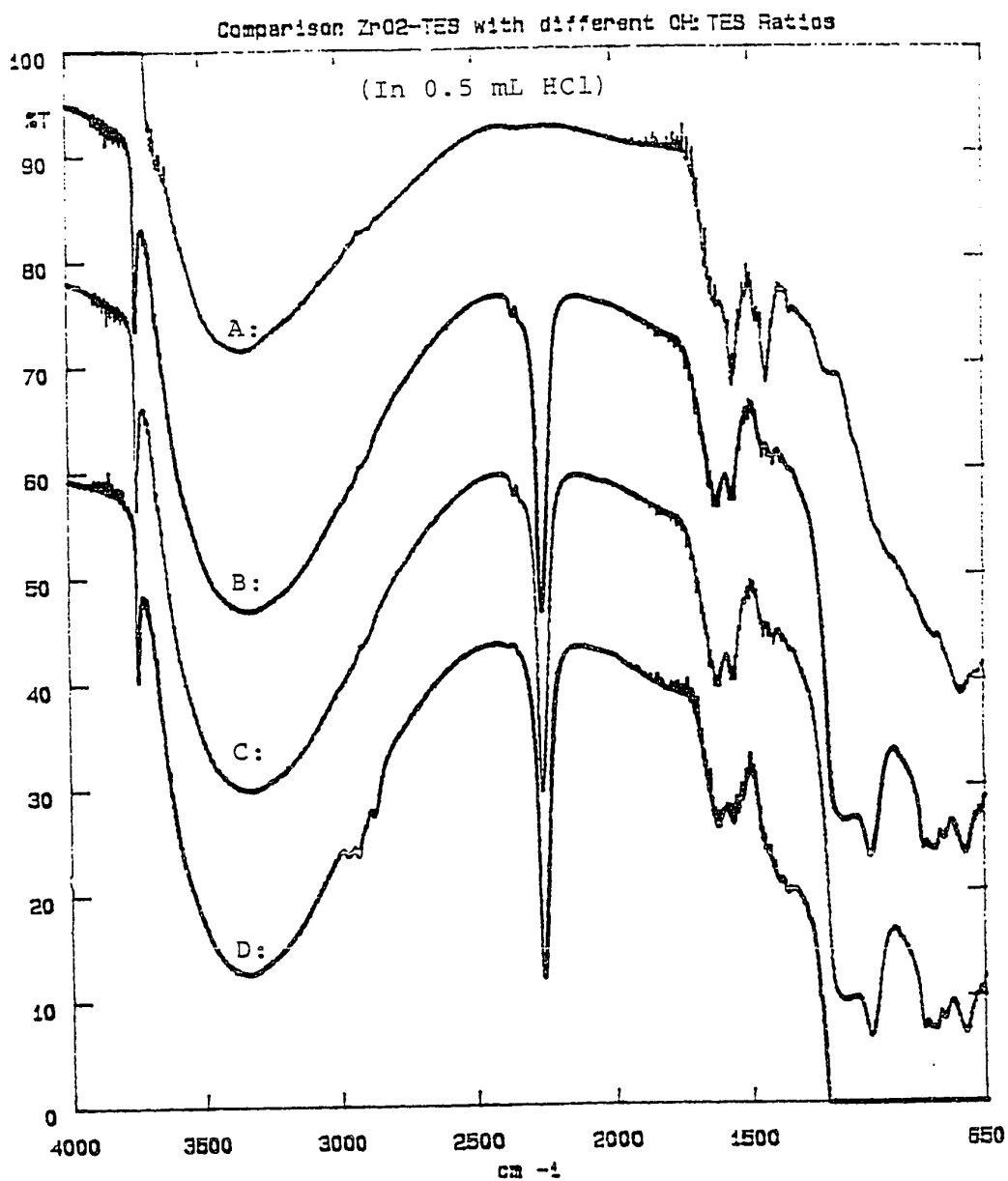
A: Bare Zirconia-(1)
B: ZrO2-TES (1:0.8)
C: ZrO2-TES (1:0.9)
D: ZrO2-TES (1:1.0)

FIGURE 20

FTIR SPECTRA OF HYDRIDE-MODIFIED ZIRCONIA-(1)

(Different OH:TES Ratios & Bare)

Comparison of Z102 (1:0.9) with Different HCl Volume

A: ZrO$_2$-Bare

B: ZrO$_2$-TES(1:0.9)(1.0 mL HCl)

C: ZrO$_2$-TES(1:0.9)(0.5 mL HCl)
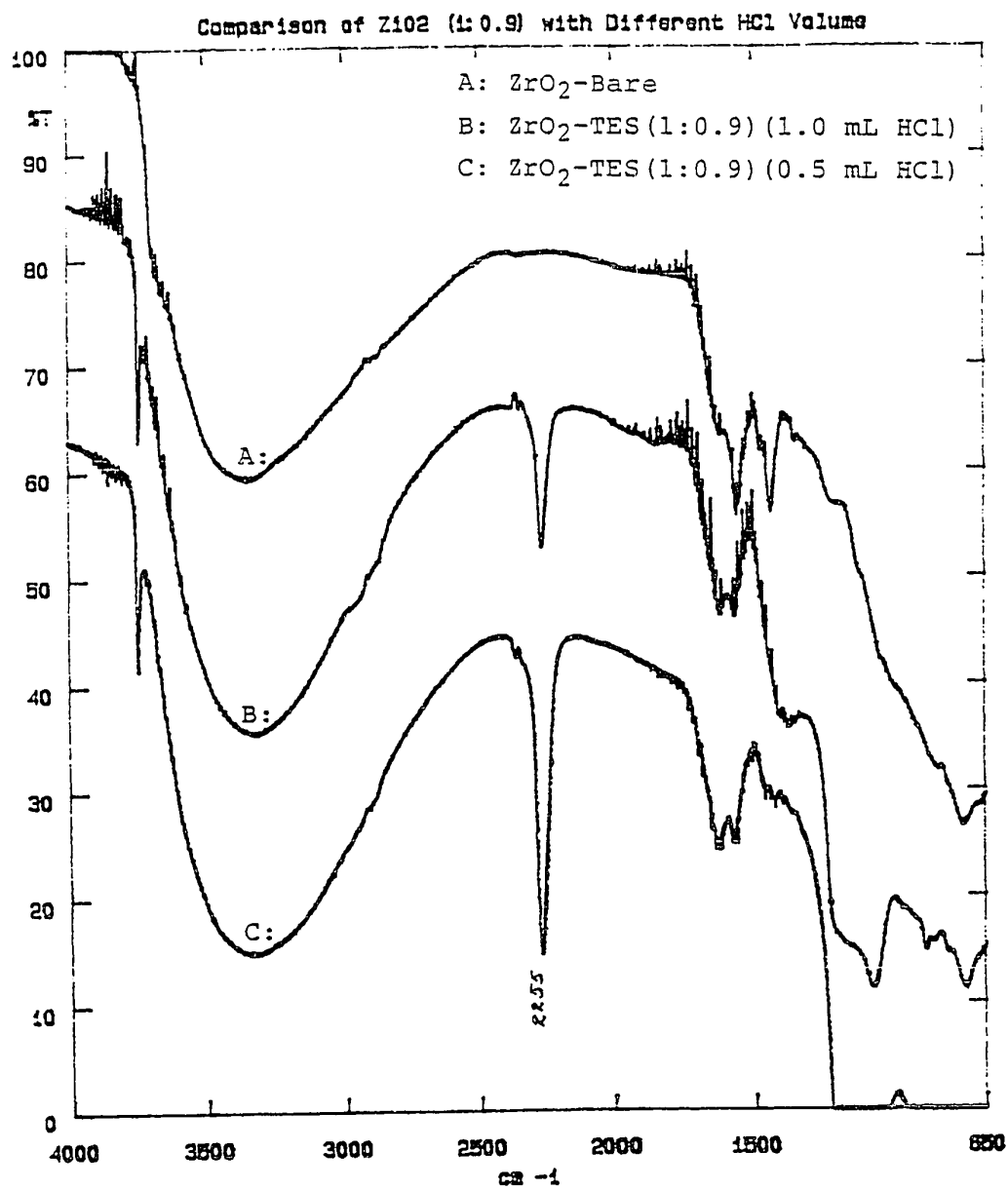
SCANS: 100
RESOLUTION: 2.00

FIGURE 21

FTIR SPECTRA OF HYDRIDE-MODIFIED ZIRCONIA-(1)

(OH:TES=1:0.9 in Different Volume of HCl)
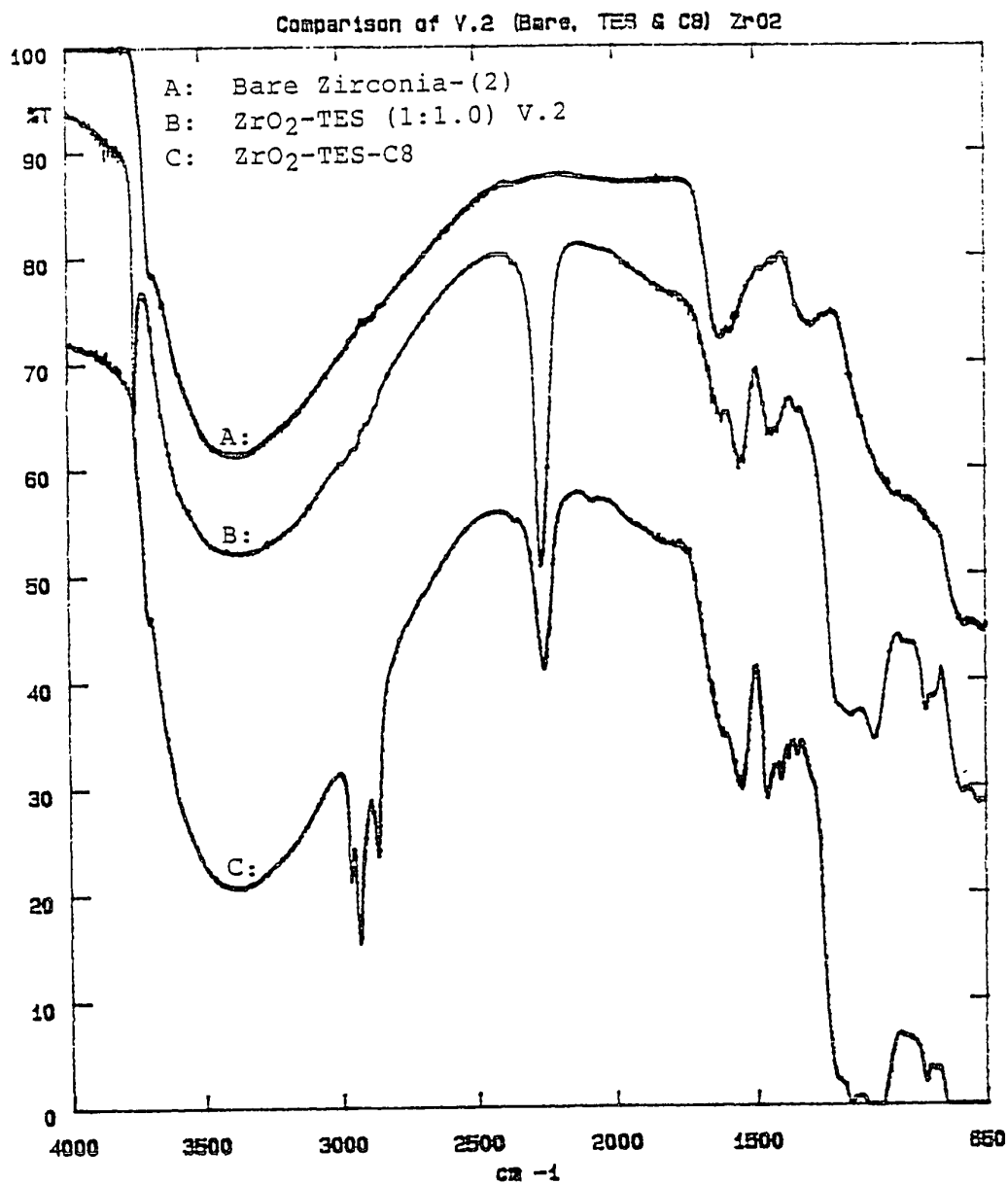
FIGURE 22

FTIR SPECTRA OF MODIFIED ZIRCONIA-(2)
(Larger Scale of OH:TES=1:1.0, Olefin Bonded & Bare)
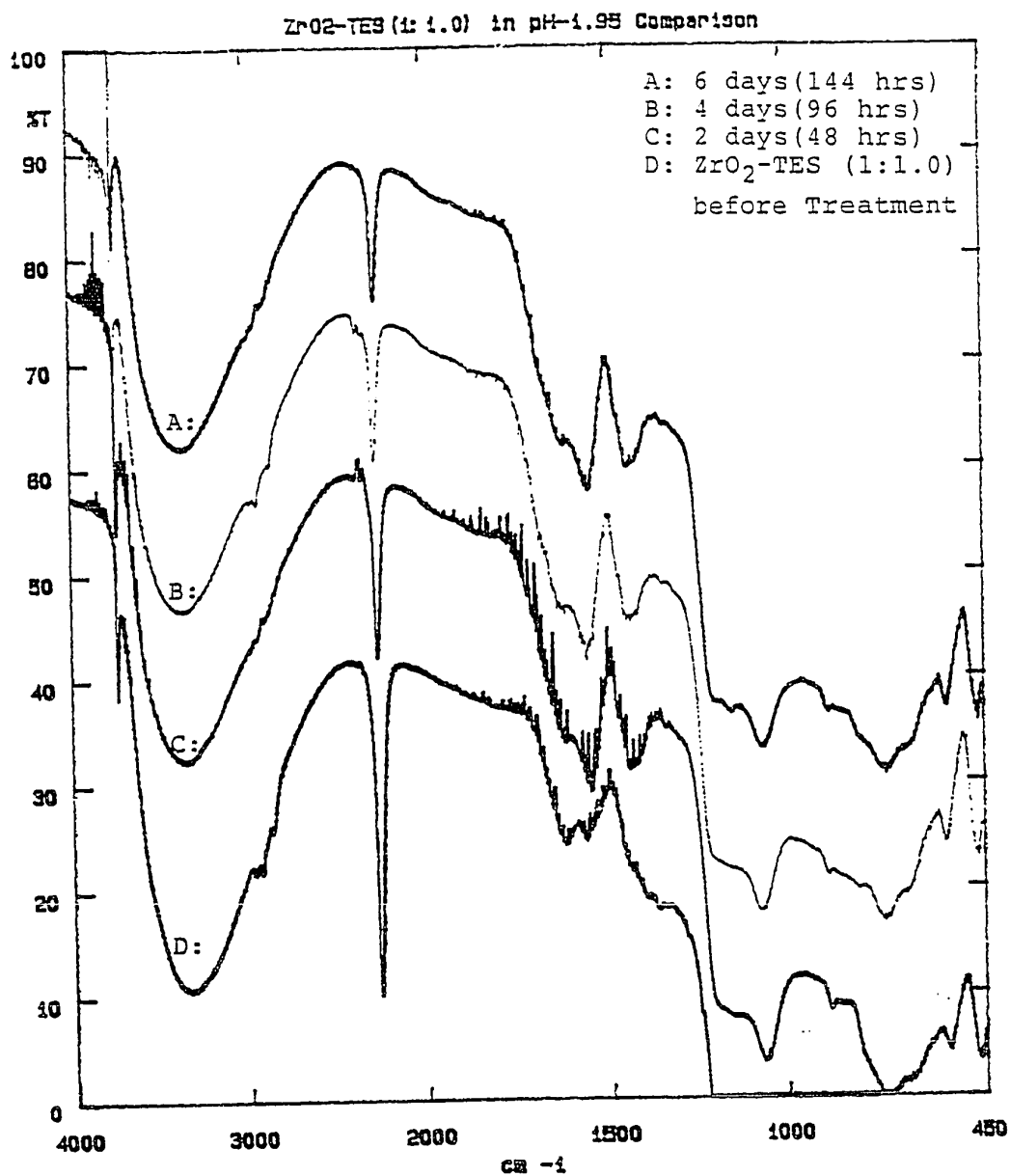
FIGURE 23

FTIR SPECTRA OF ACID TREATMENT FOR HYDRIDE-MODIFIED ZIRCONIA

(ZrO$_2$-TES (1:1.0) in pH=1.95 for Different Time)
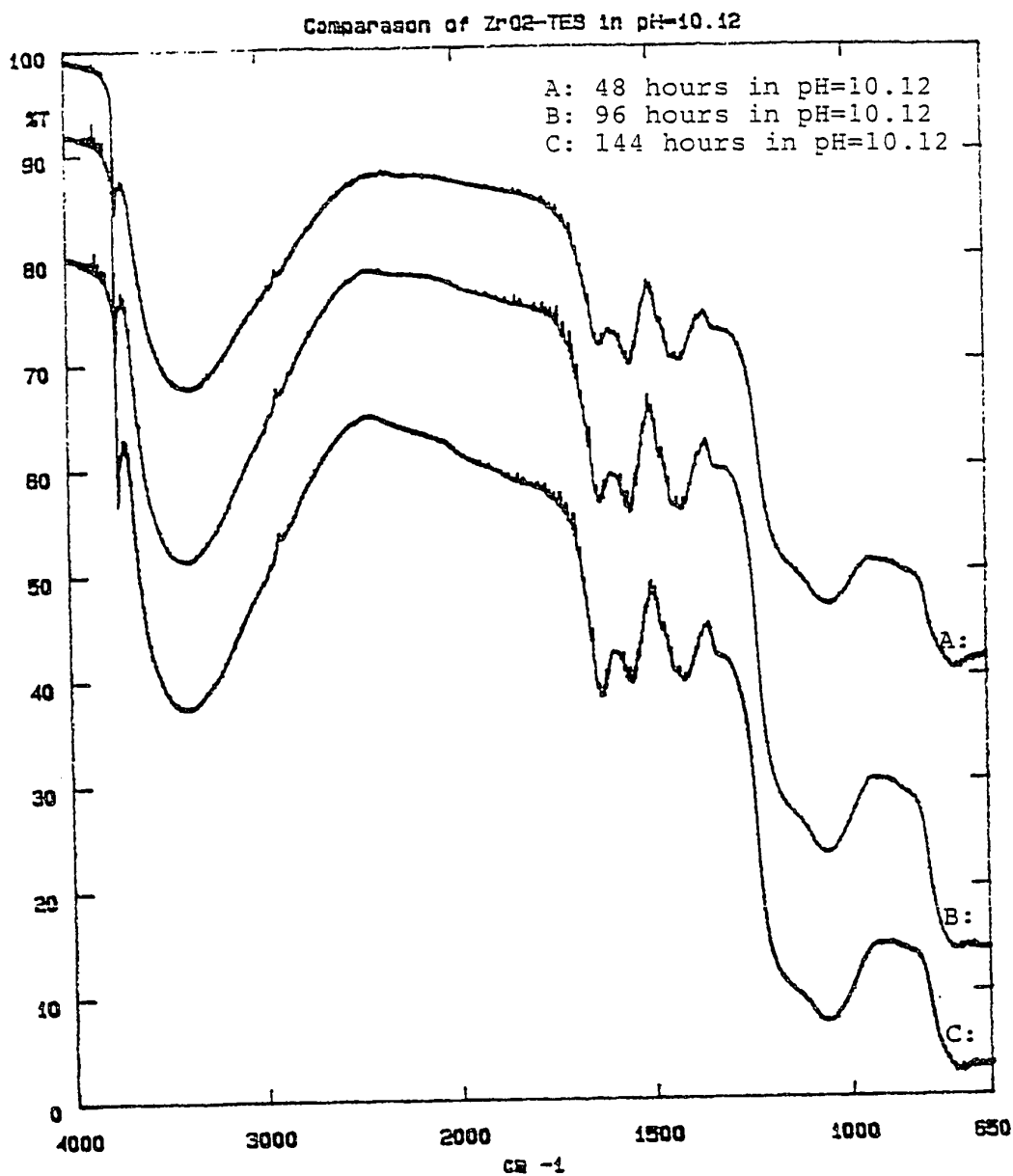
FIGURE 24

FTIR SPECTRA OF BASIC TREATMENT FOR HYDRIDE-MODIFIED ZIRCONIA
ZrO_2 (OH:TES=1:1.0) in pH=10.12 for Different Time)
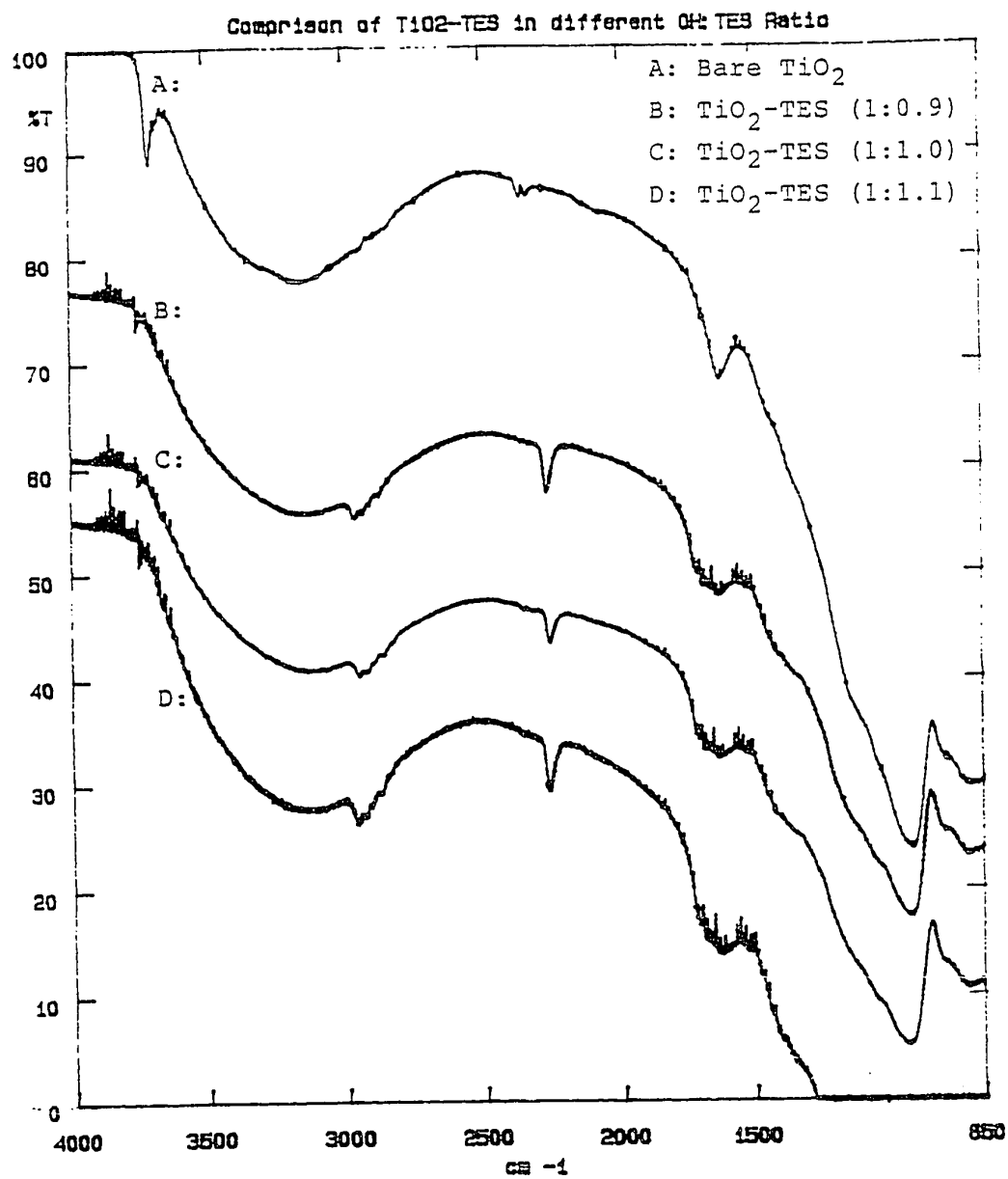
FIGURE 25

FTIR SPECTRA OF HYDRIDE-MODIFIED TITANIA
(Different OH:TES Ratios & Bare)

Comparison of TiO2-TES (V.2) & Olefin bonding

A: TiO_2-C_8

B: TiO_2-TES (V.2)

C: TiO_2-Bare
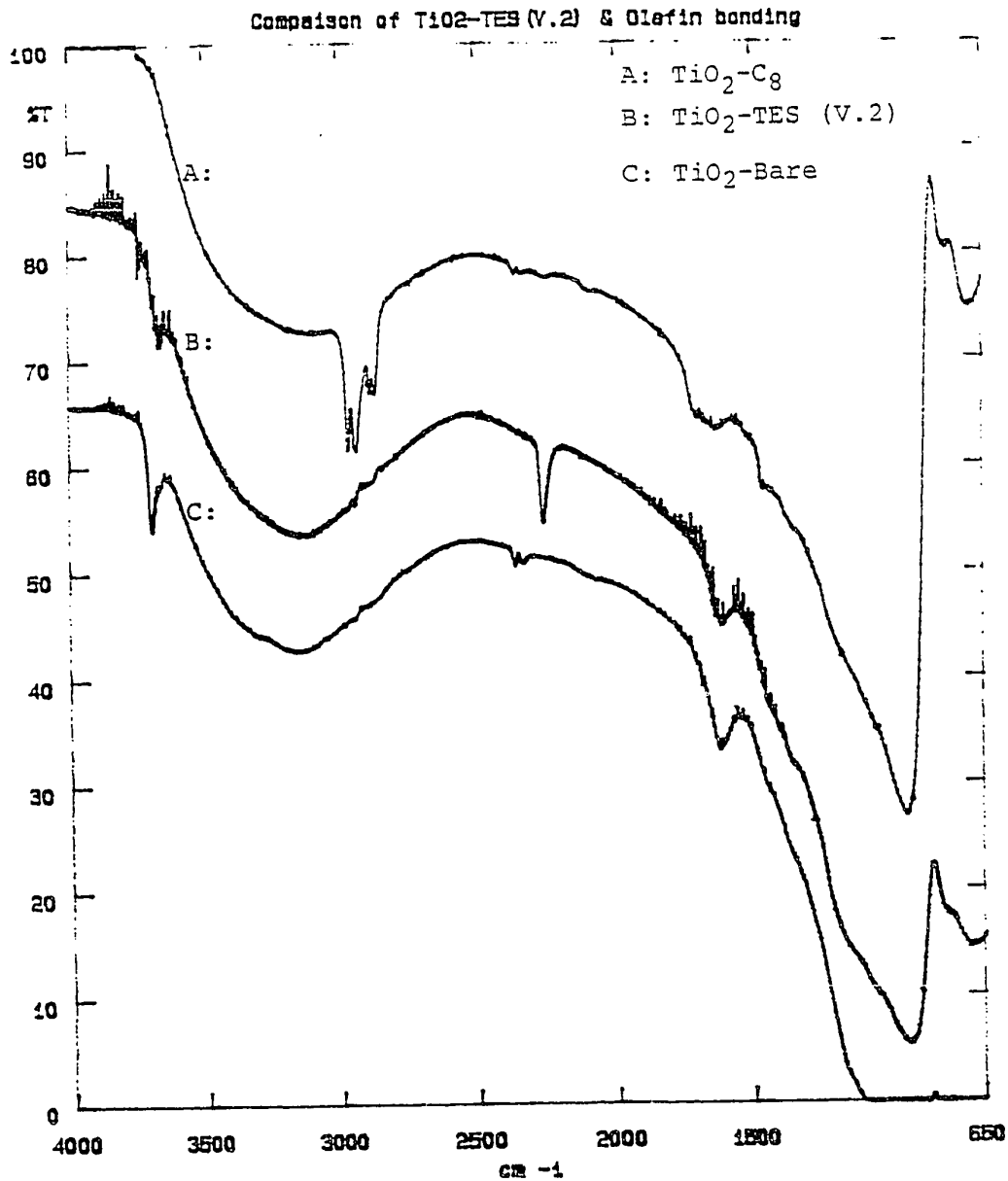
SCANS: 100

RESOLUTION: 2.00

FIGURE 26

FTIR SPECTRA OF MODIFIED TITANIA

(Larger Scale of OH:TES=1:1.0, Olefin Bonded & Bare)
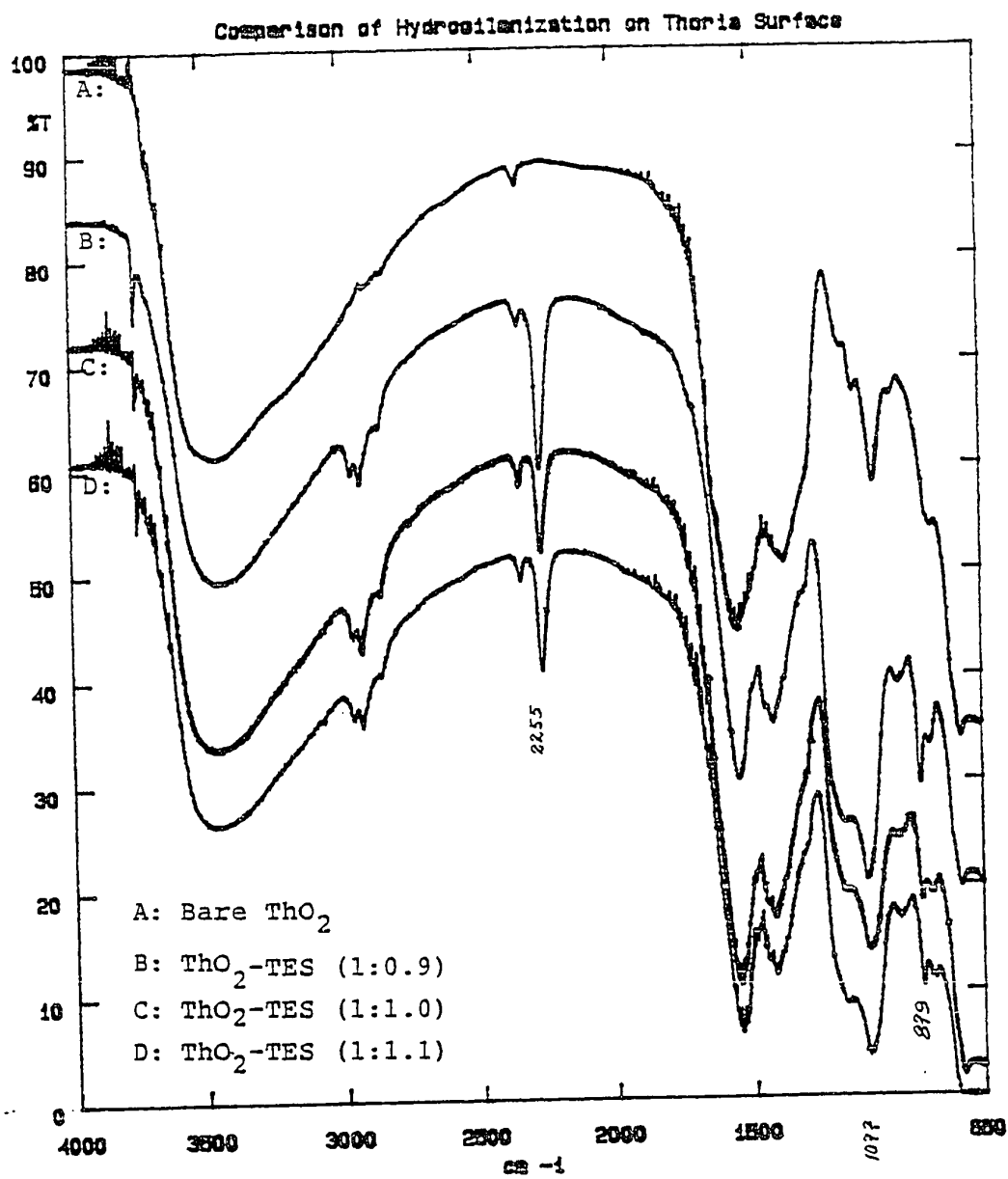
FIGURE 27

FTIT SPECTRA OF HYDRIDE-MODIFIED THORIA

(Different OH:TES Ratios & Bare)

Comarison of ThO2-TES & olefin bonding

A: Bare ThO$_2$

B: ThO$_2$-TES (1:1.0) V.2

C: ThO$_2$-TES-C8
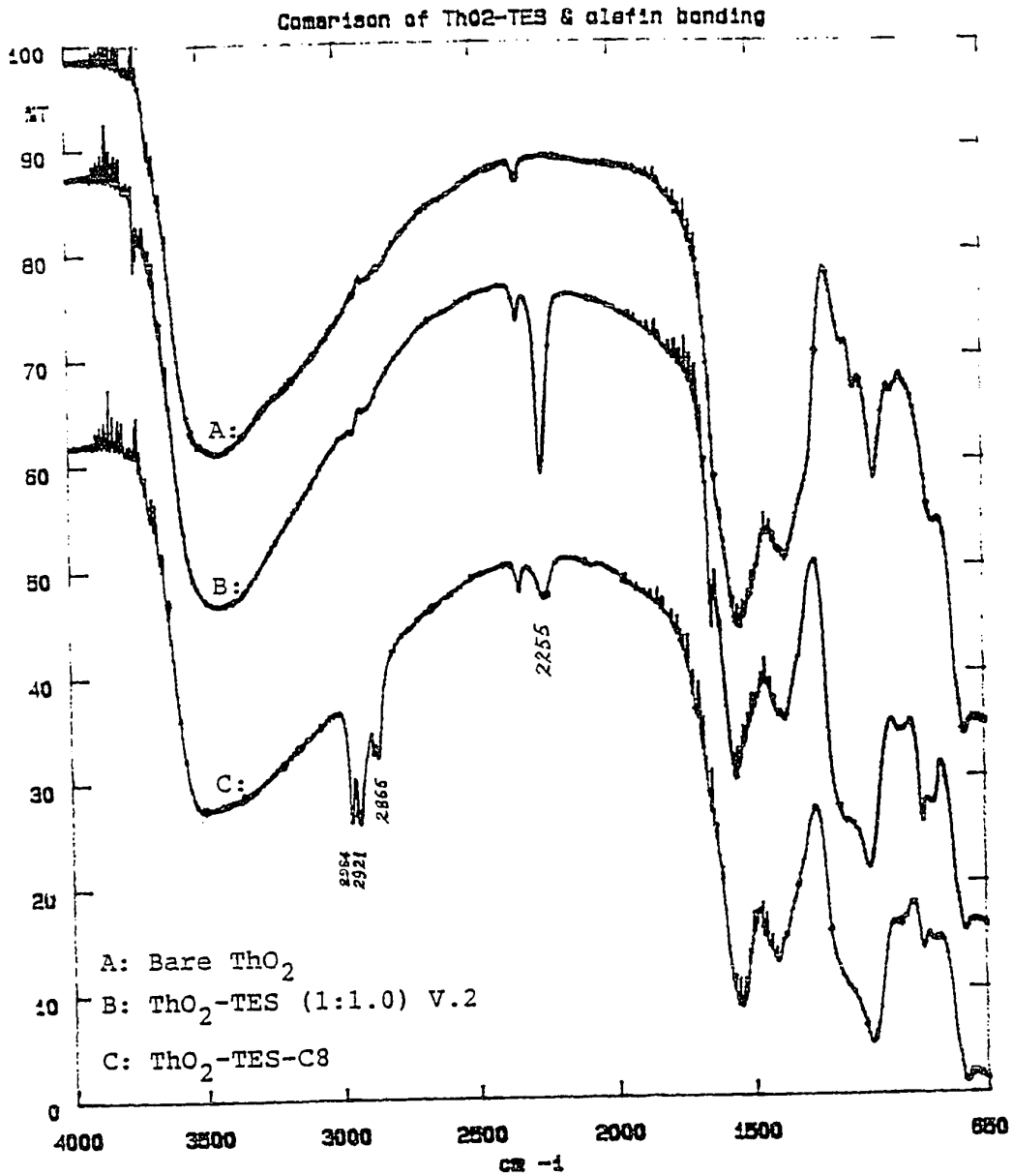
SCANS: 100

RESOLUTION: 2.00

FIGURE 28

FTIT SPECTRA OF MODIFIED THORIA

(Larger Scale of OH:TES=1:1.0, Olefin Bonded & Bare)
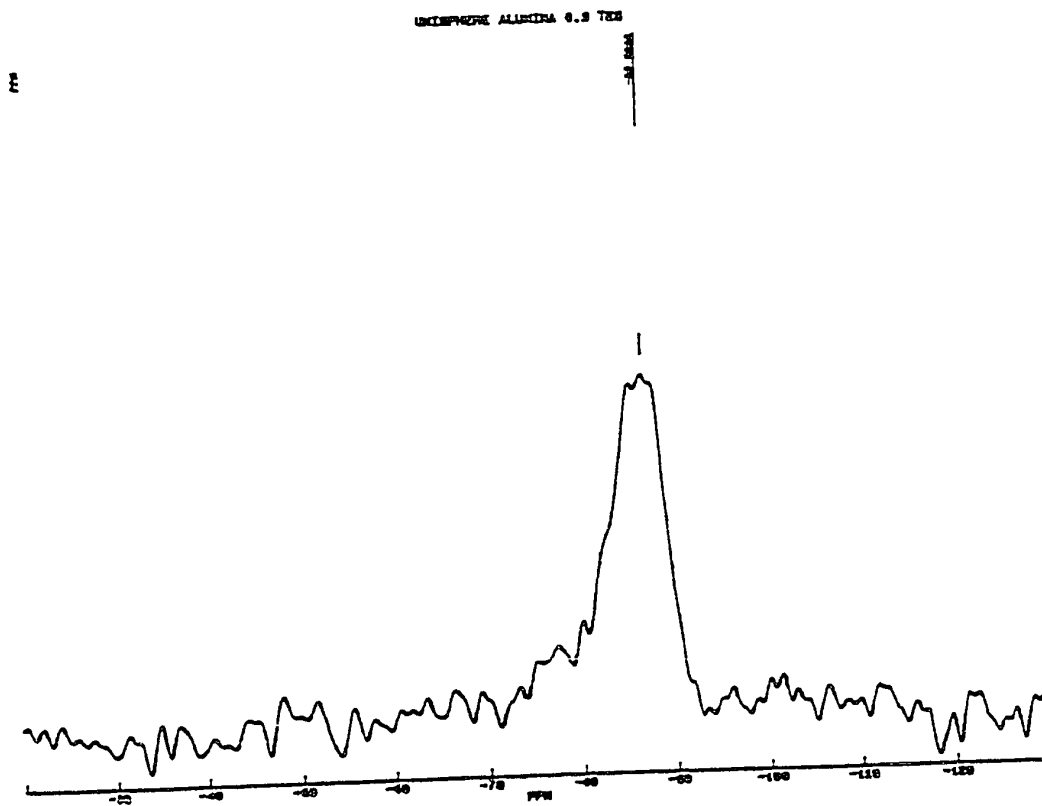
FIGURE 29

^{29}Si CP-MAS NMR Spectrum of Hydride Intermediate
Alumina (UA1) (OH:TES=1:0.9)
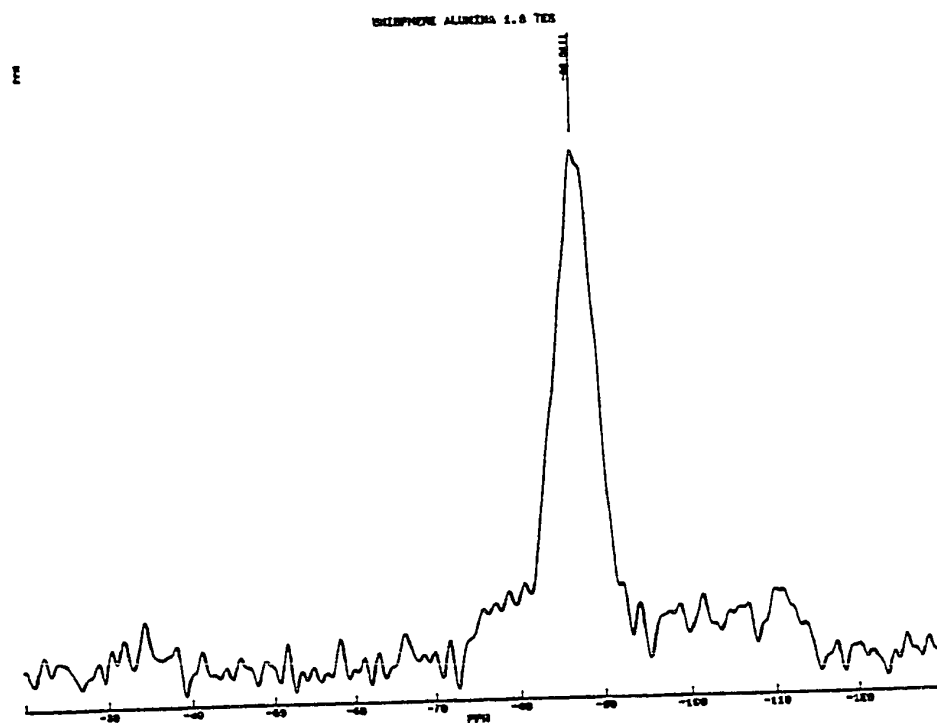
FIGURE 30

^{29}Si CP-MAS NMR Spectrum of Hydride Intermediate

Alumina (UAl) (OH:TES=1:1.0)
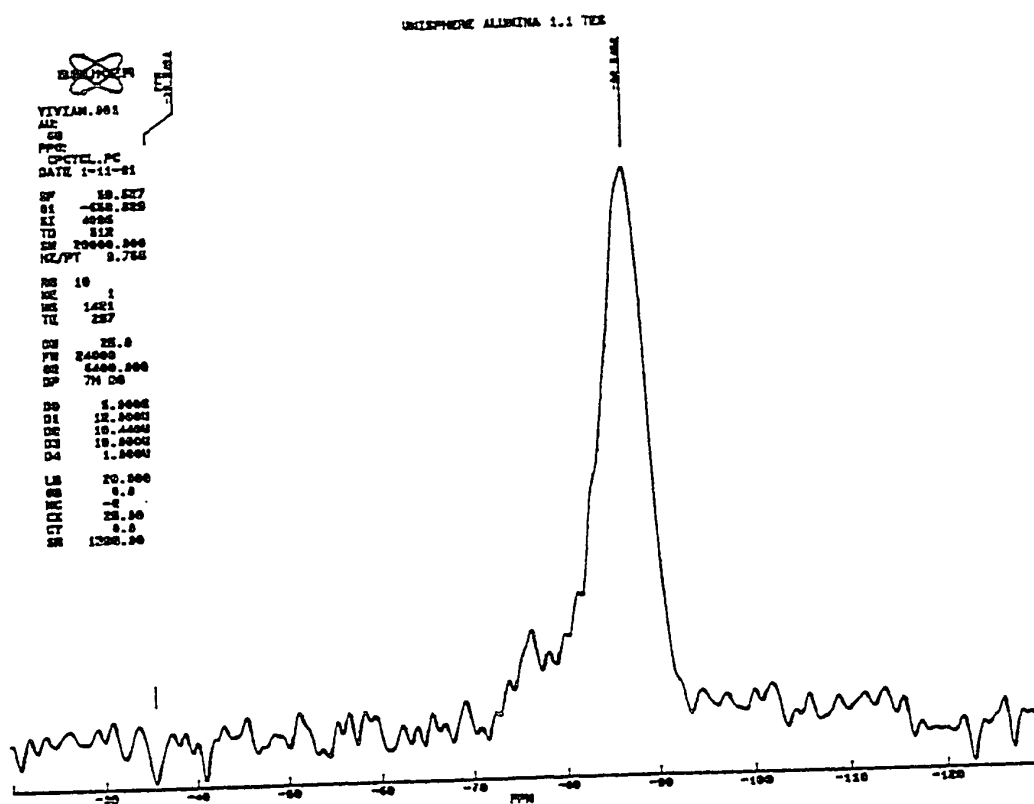
FIGURE 31

^{29}Si CP-MAS NMR Spectrum of Hydride Intermediate

Alumina (UA1) (OH:TES=1:1.1)

UAL TES (1:1.0) V.2
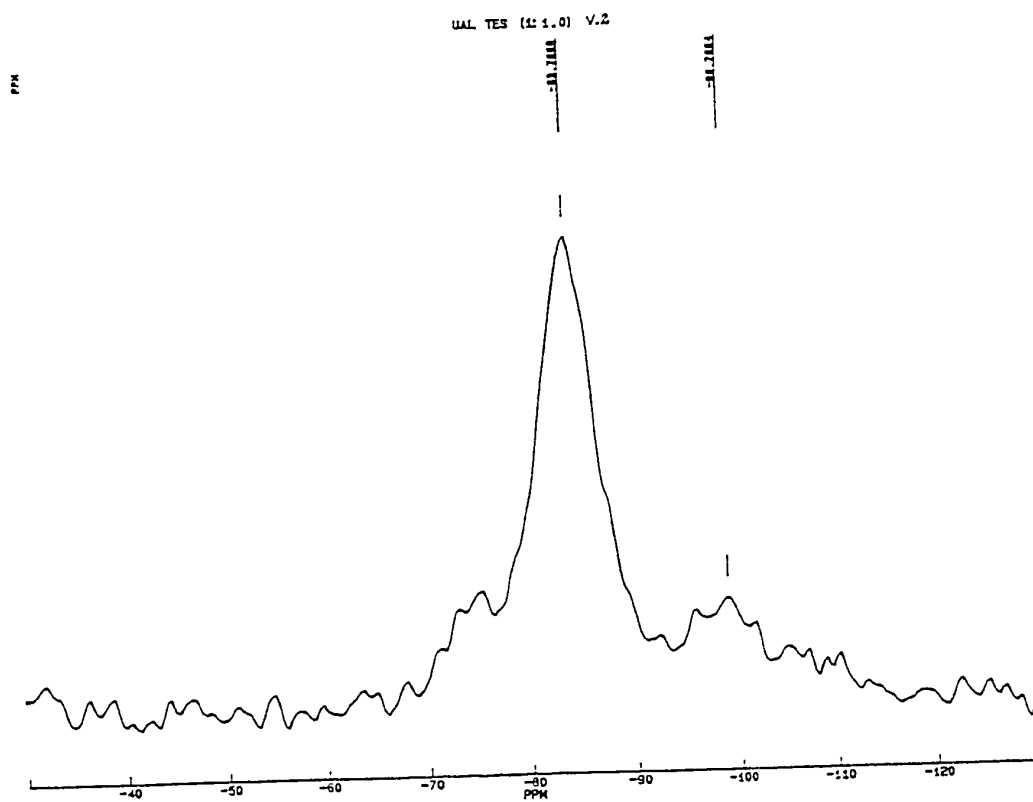
FIGURE 32

^{29}Si CP-MAS NMR Spectrum of Hydride Intermediate
Alumina (UAl) (OH:TES=1:1.0)   Larger Scale
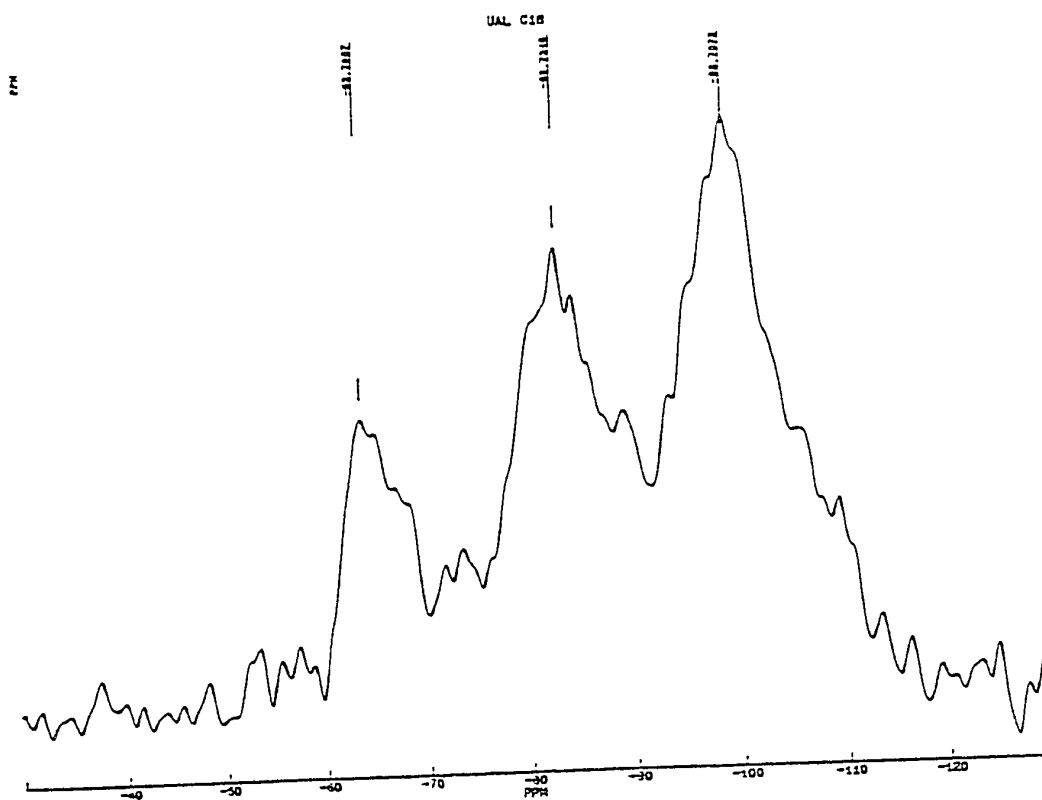
FIGURE 33

^{29}Si CP-MAS NMR Spectrum of C_{18} Bonded Alumina(UAl)
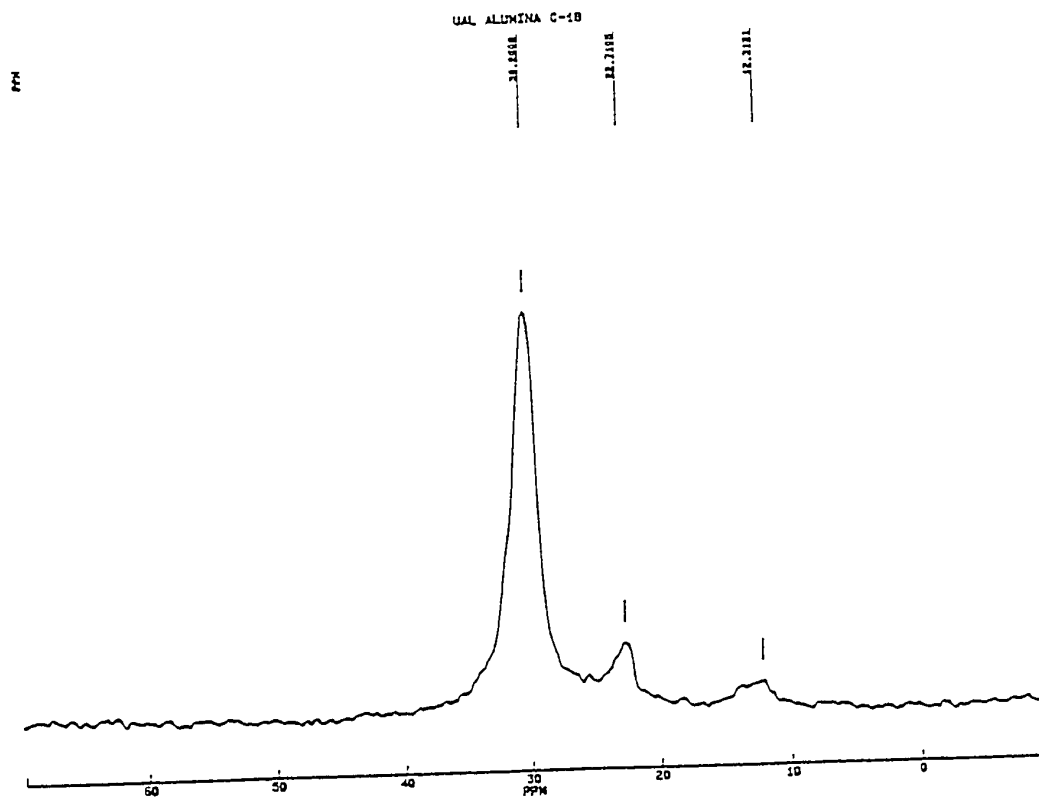
FIGURE 34

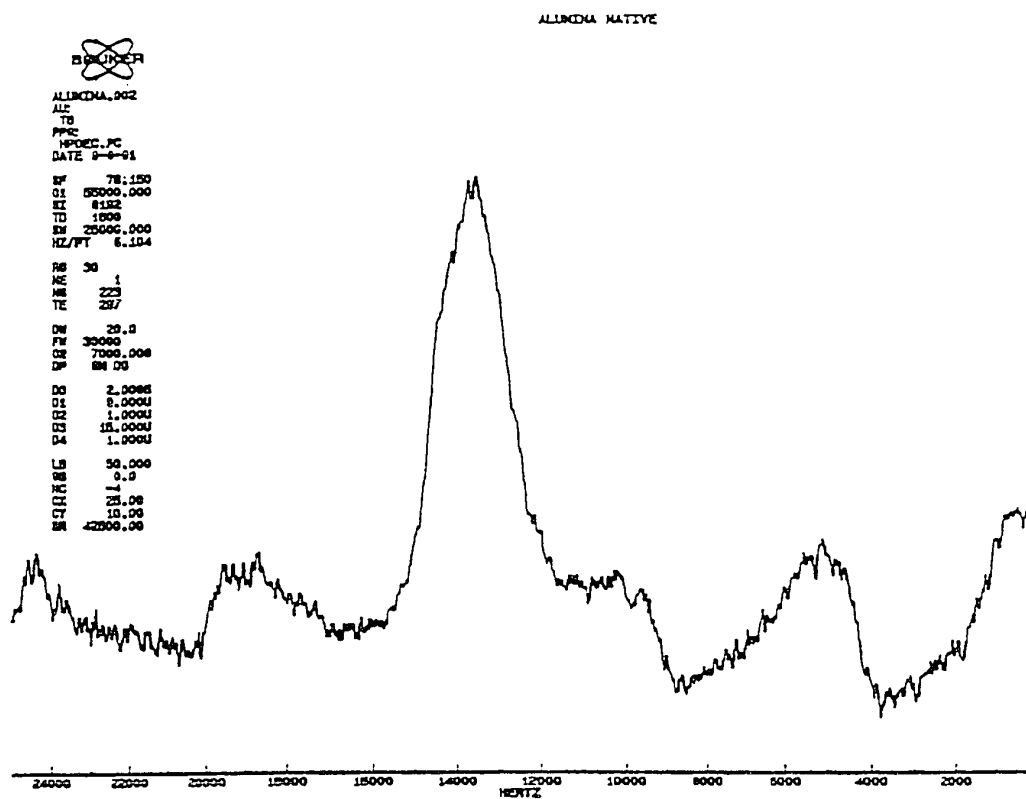13C CP-MAS NMR Spectrum of C18 Bonded Alumina (UAl)
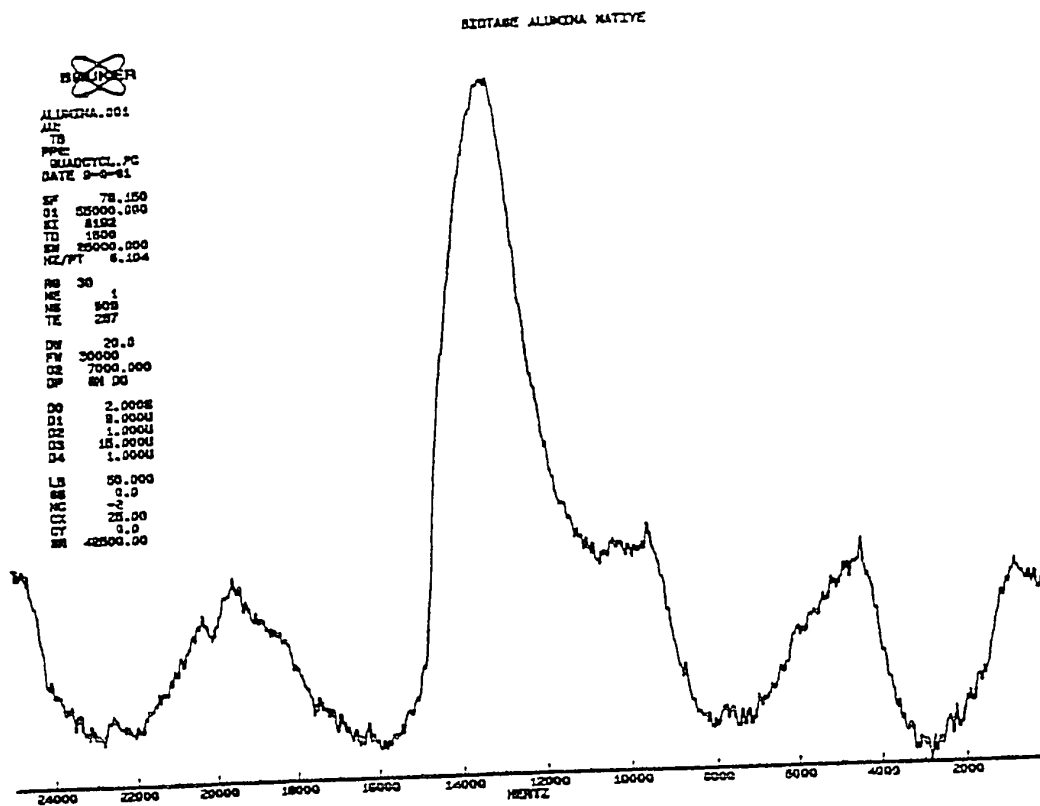
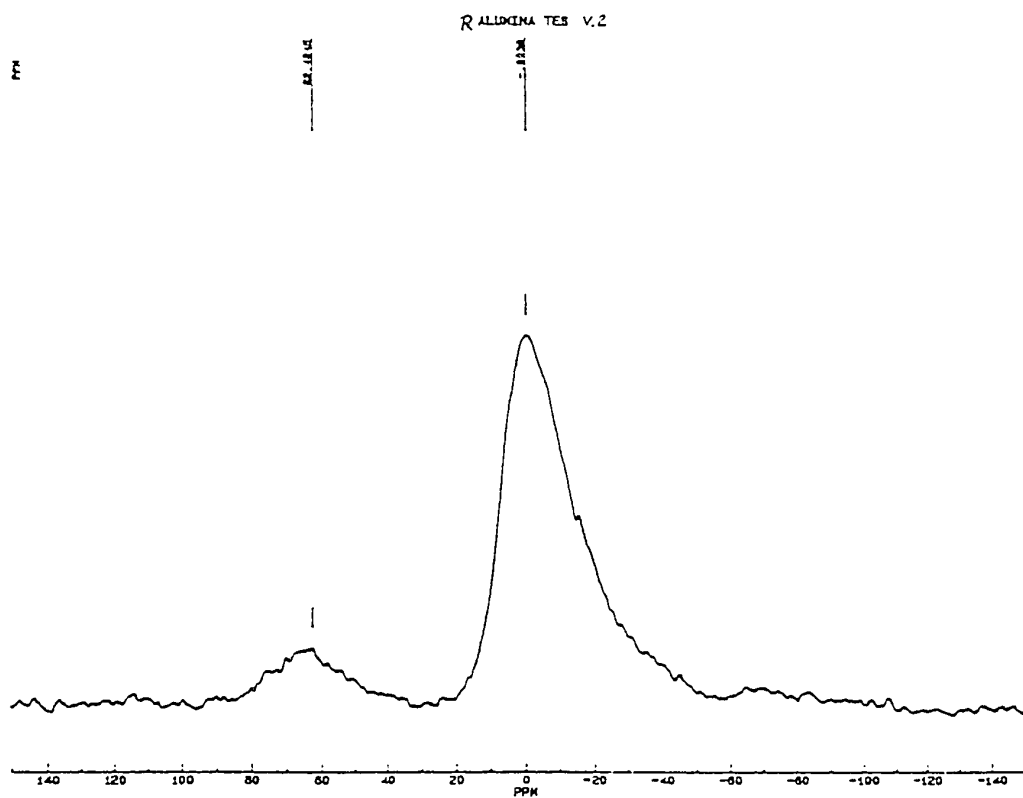FIGURE 35

27Al CP-MAS NMR Spectrum of Native Alumina (UAl)

UUL TEI LOW POWER
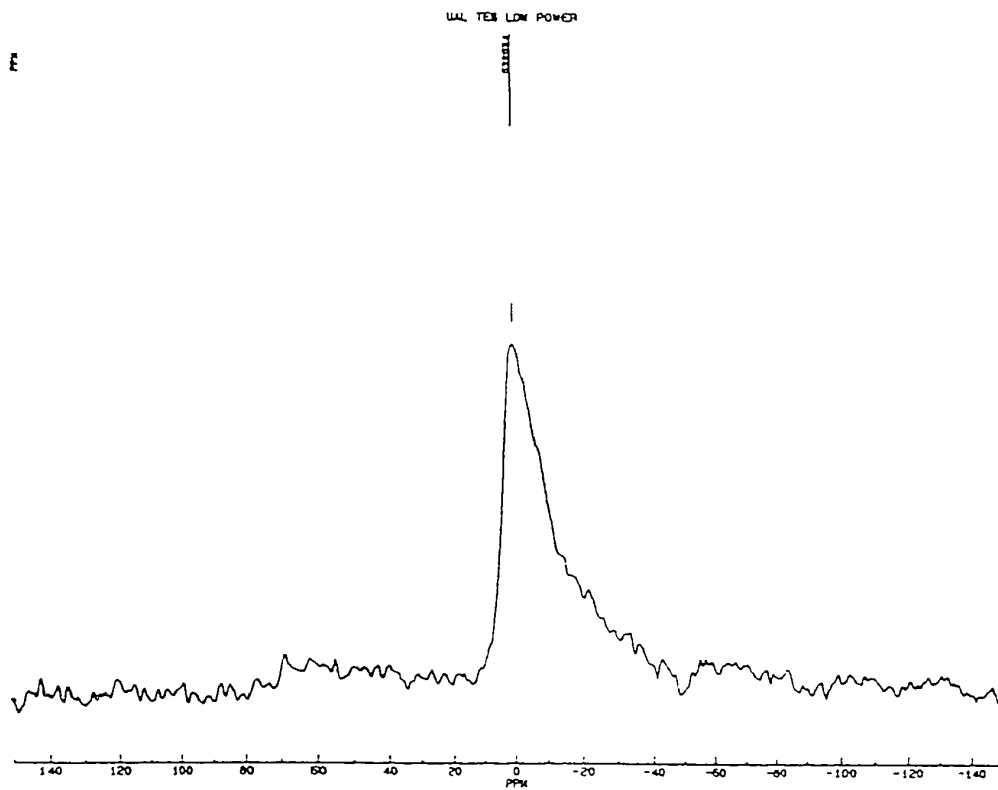
FIGURE 36

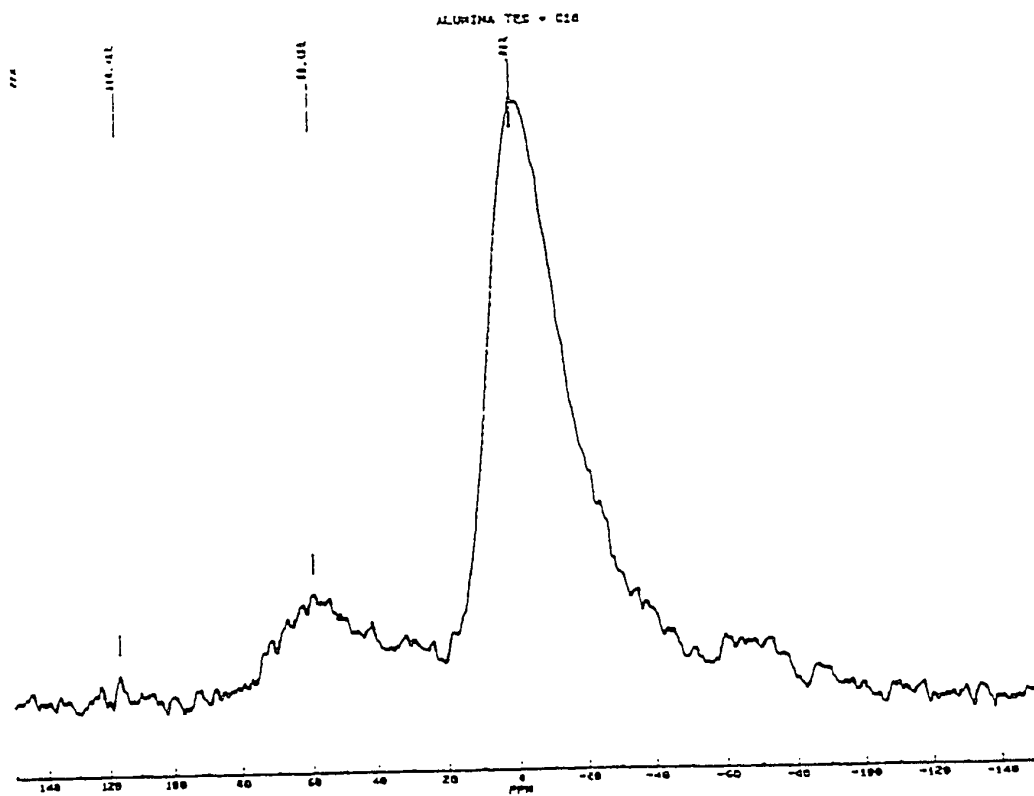^{27}Al CP-MAS NMR Spectrum of Hydride-Intermediate

Alumina (UAl) Larger Scale
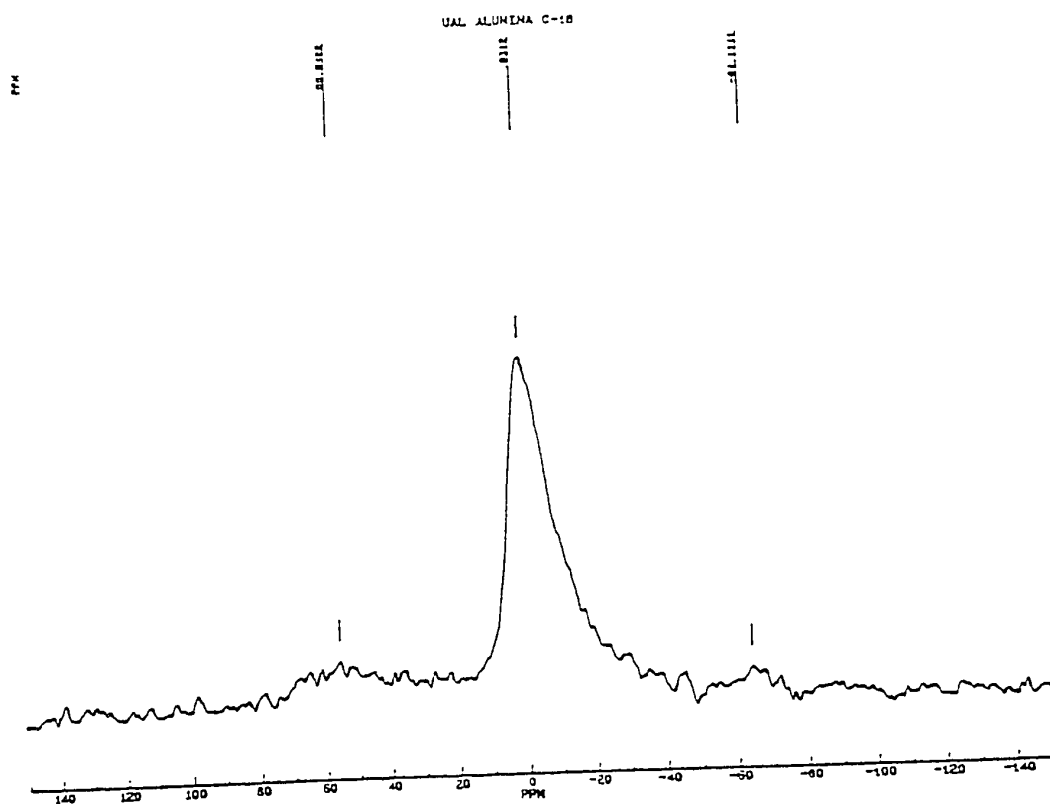
FIGURE 37

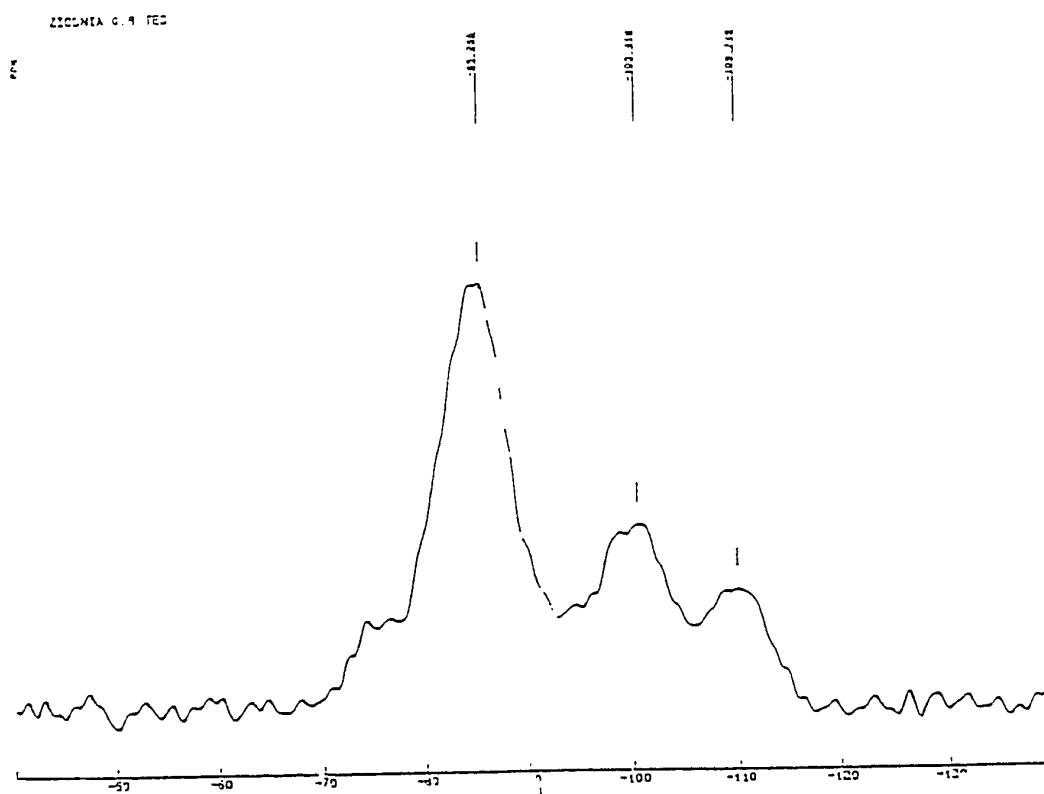^{27}Al CP-MAS NMR Spectrum of C_{18} Bonded Alumina (UAl)
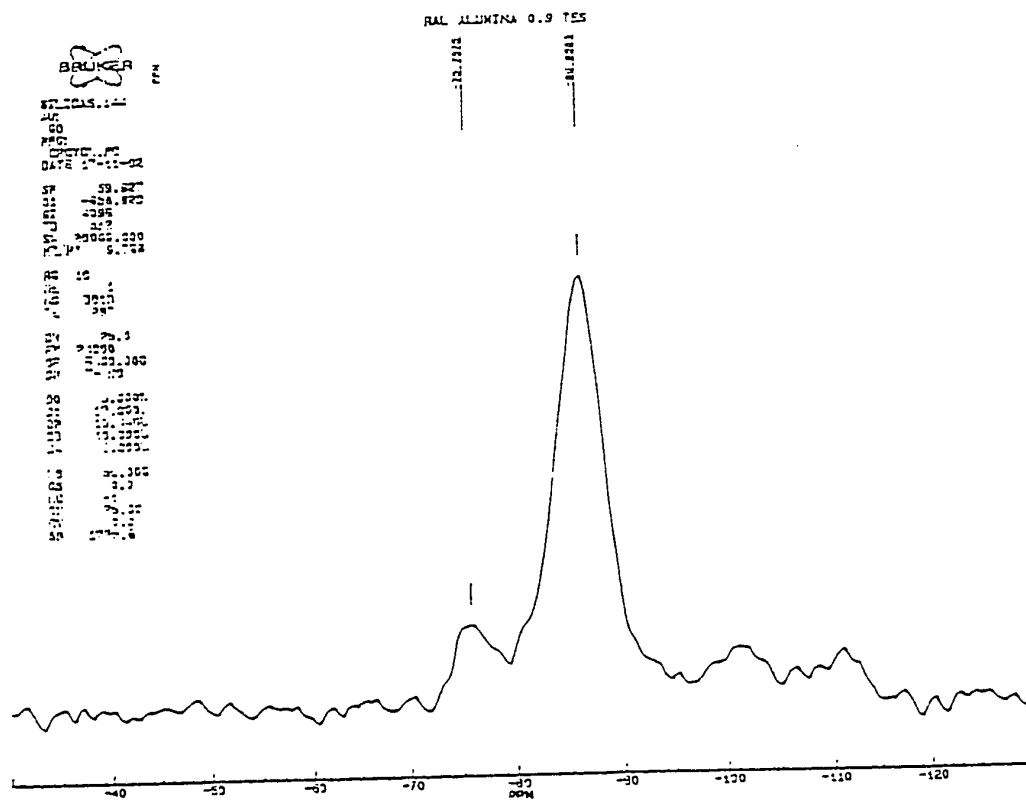
FIGURE 38

^{29}Si CP-MAS NMR Spectrum of Hydride Intermediate
Alumina (RAl) (OH:TES=1:0.9)
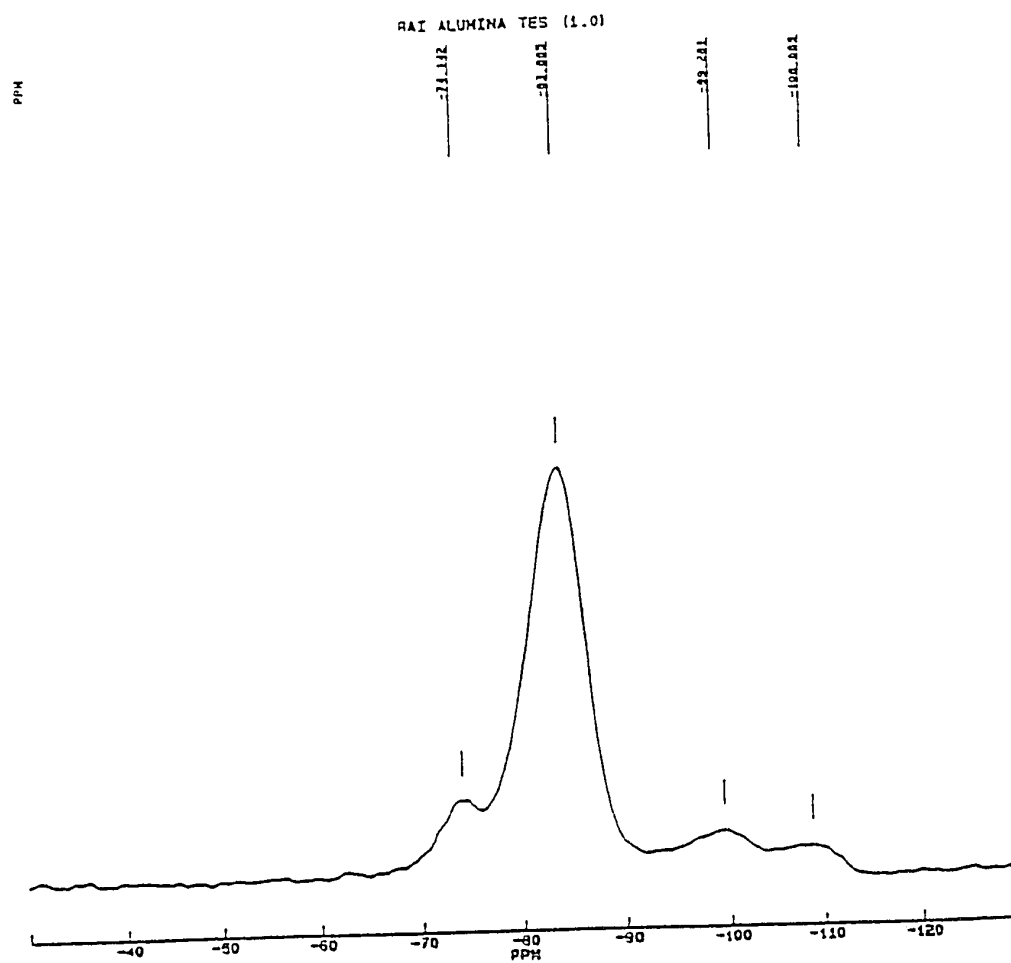
FIGURE 39

^{29}Si CP-MAS NMR Spectrum of Hydride Intermediate Alumina (RA1) (OH:TES=1:1.0)
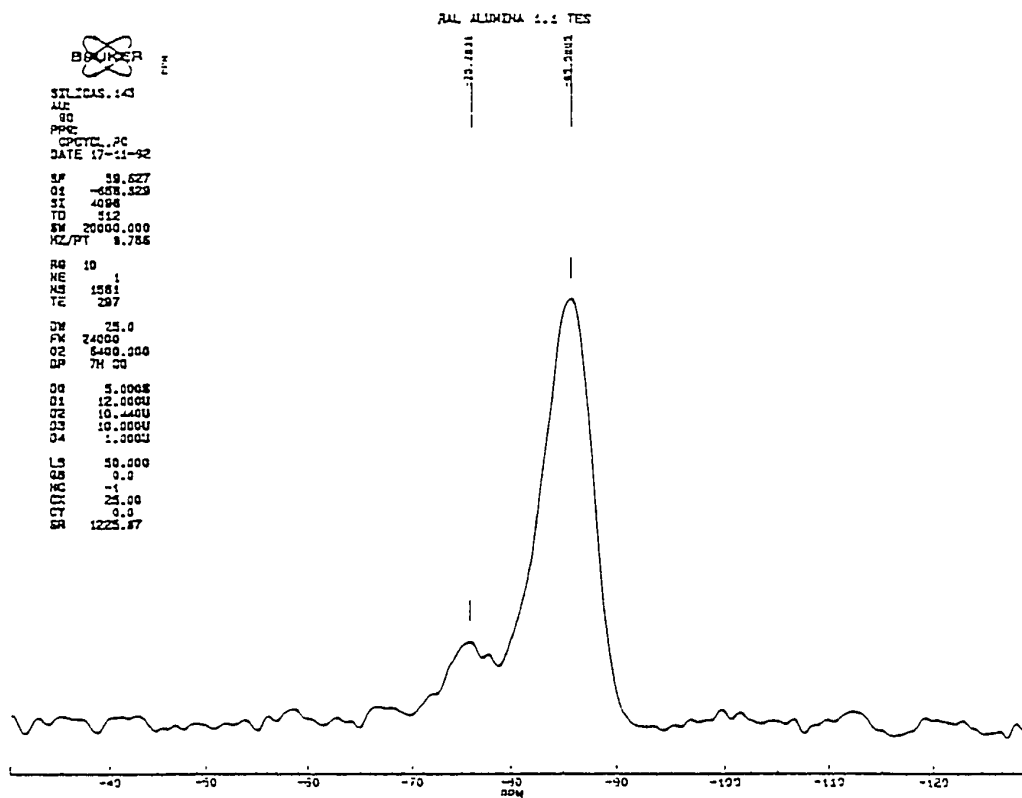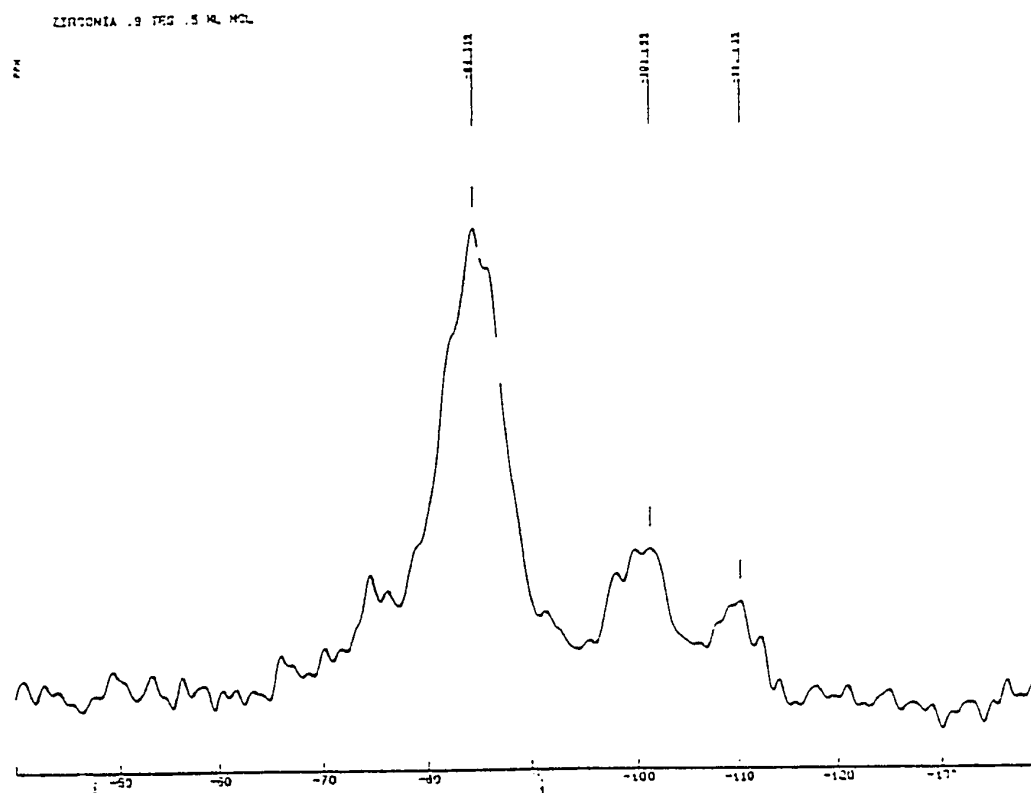
FIGURE 40

^{29}Si CP-MAS NMR Spectrum of Hydride Intermediate
Alumina (RA1) (OH:TES=1:1.1)
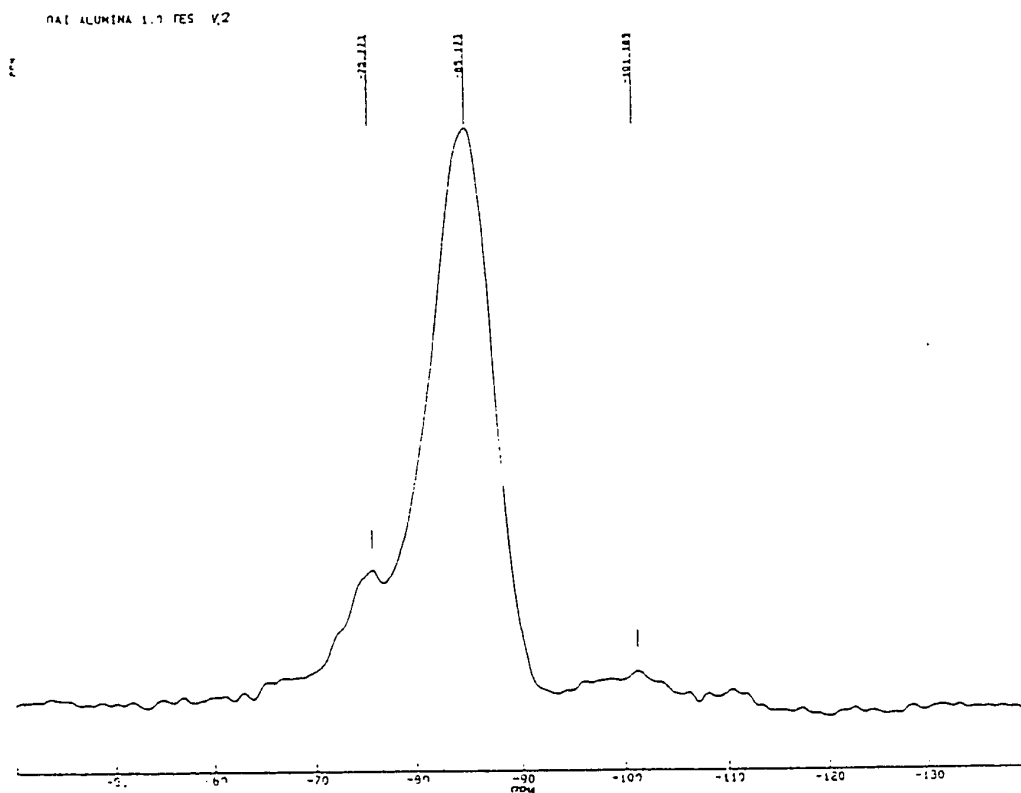
FIGURE 41

^{29}Si CP-MAS NMR Spectrum of Hydride-Intermediate
Alumina (RA1) (OH:TES=1:1.0) Larger Scale
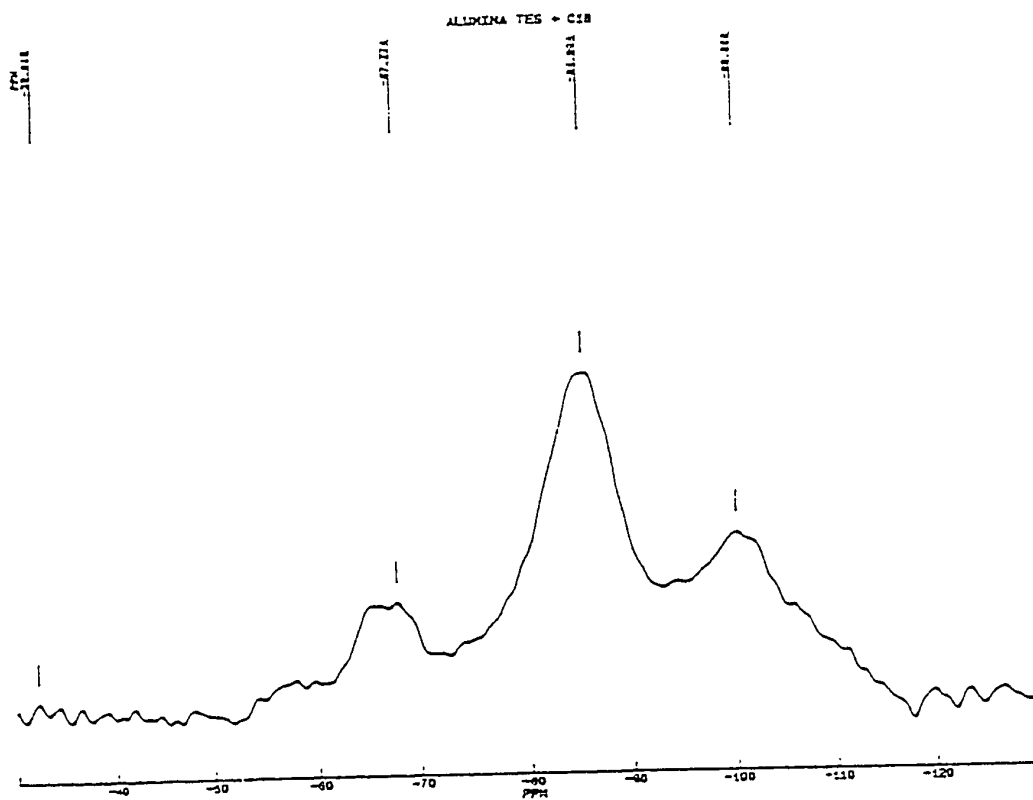
FIGURE 42

^{29}Si CP-MAS NMR Spectrum of C_{18} Bonded Alumina(RA1)
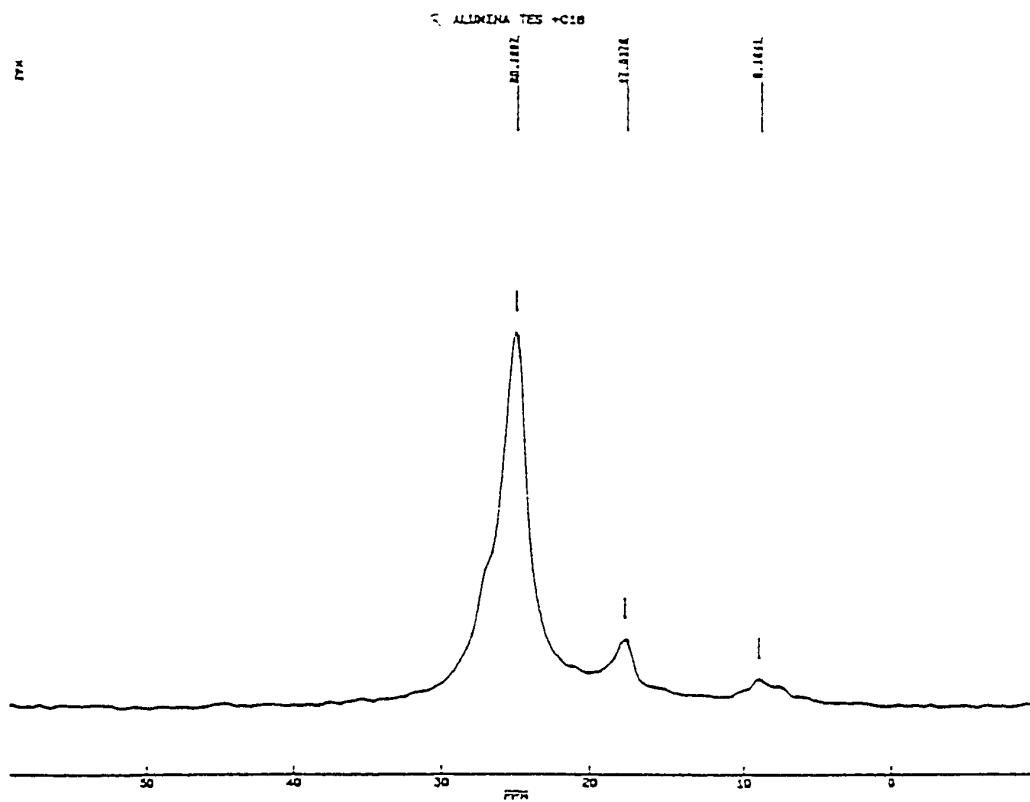
FIGURE 43

^{13}C CP-MAS NMR Spectrum of C_{18} Bonded Alumina(RA1)

ALUMINA NATIVE

FIGURE 44

^{27}Al CP-MAS NMR Spectrum of Native Alumina (RA1)

FIGURE 45

^{27}Al CP-MAS NMR Spectrum of Hydride-Intermediate
Alumina (RAl) Larger Scale

FIGURE 46

^{27}Al CP-MAS NMR Spectrum of C_{18} Bonded Alumina(RA1)
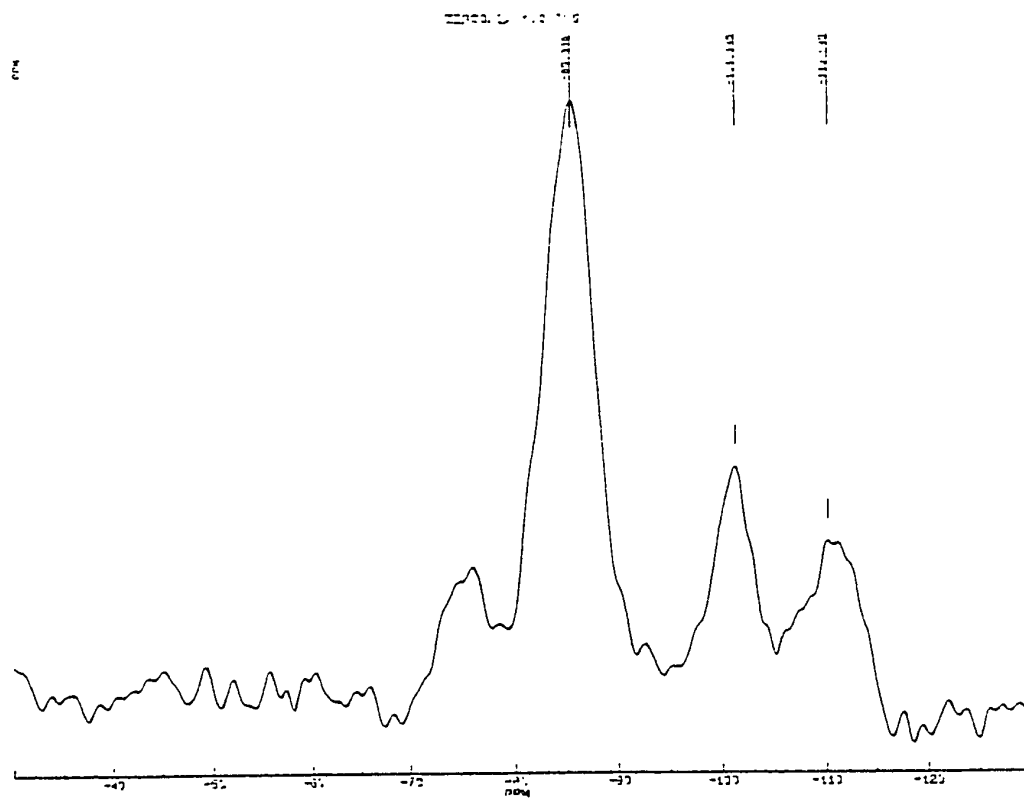
FIGURE 47

^{29}Si CP-MAS NMR Spectrum of Hydride Intermediate

Zirconia   (OH:TES=1:0.8)

FIGURE 48

^{29}Si CP-MAS NMR Spectrum of Hydride Intermediate

Zirconia   (OH:TES=1:0.9)

ZIRCONIA TES .9 1M HCL
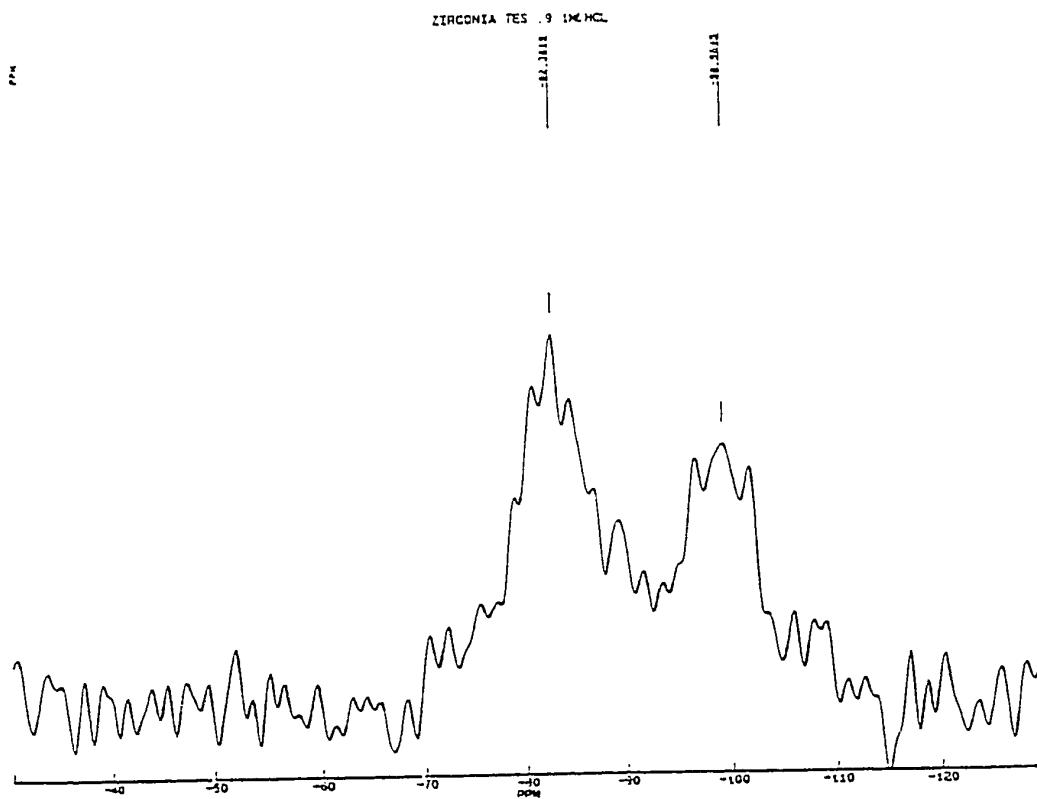
FIGURE 49

^{29}Si CP-MAS NMR Spectrum of Hydride Intermediate
Zirconia   (OH:TES=1:0.9, in 1.0 mL HCl)

FIGURE 50

^{29}Si CP-MAS NMR Spectrum of Hydride Intermediate
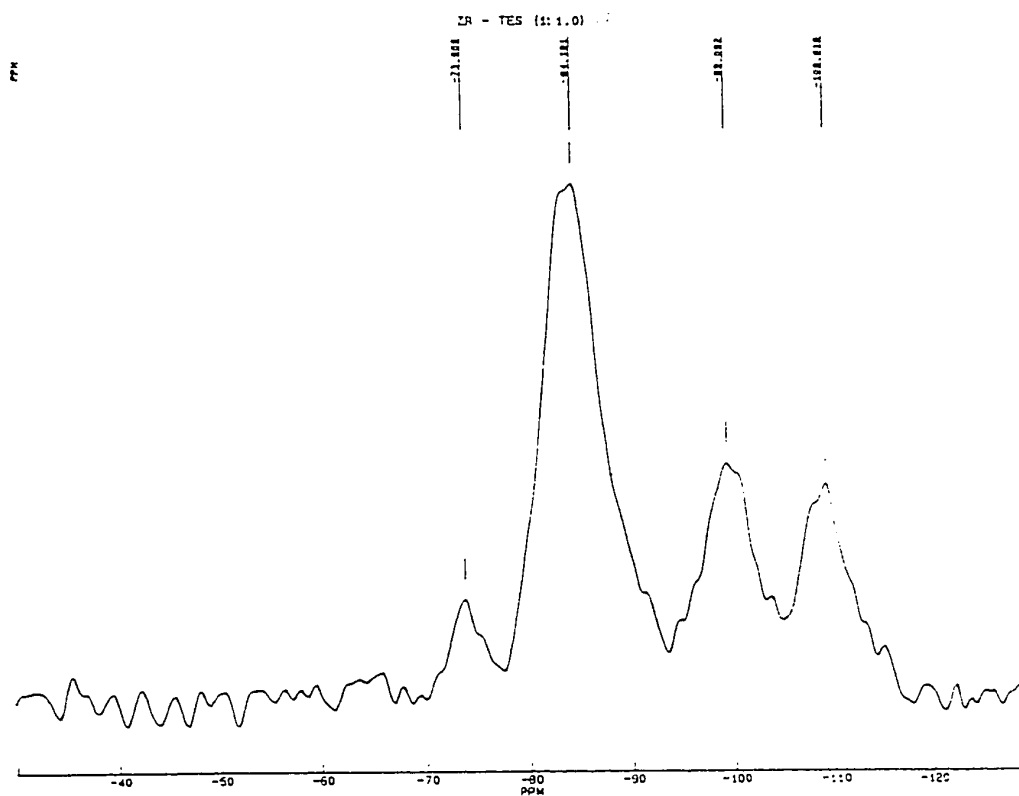Zirconia   (OH:TES=1:1.0)

FIGURE 51

^{29}Si CP-MAS NMR Spectrum of Hydride Intermediate
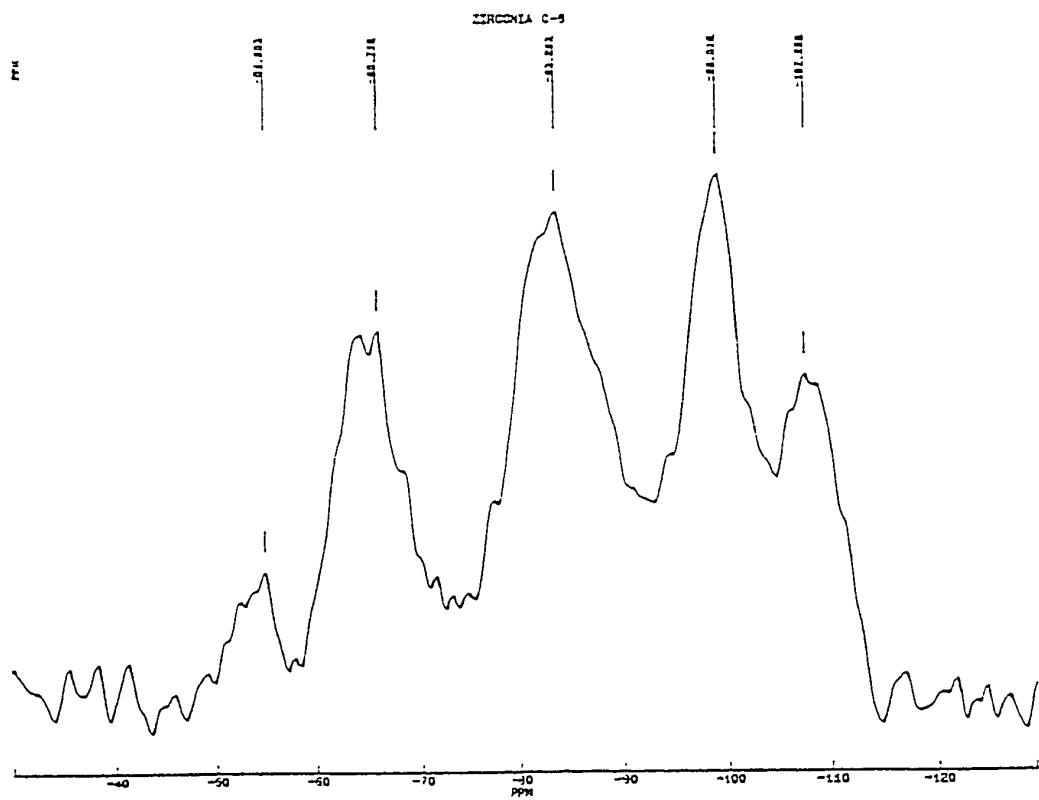
Zirconia   (OH:TES=1:1.0)   Larger Scale

FIGURE 52
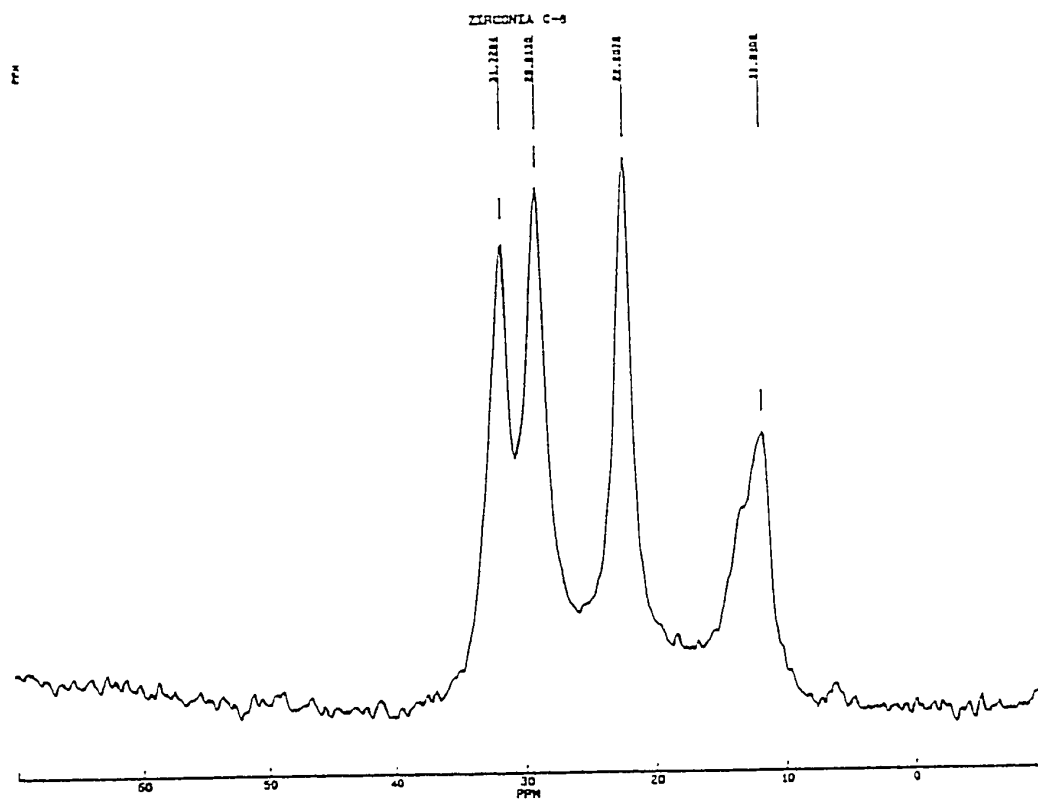
^{29}Si CP-MAS NMR Spectrum of C$_8$ Bonded Zirconia

FIGURE 53

13C CP-MAS NMR Spectrum of C8 Bonded Zirconia
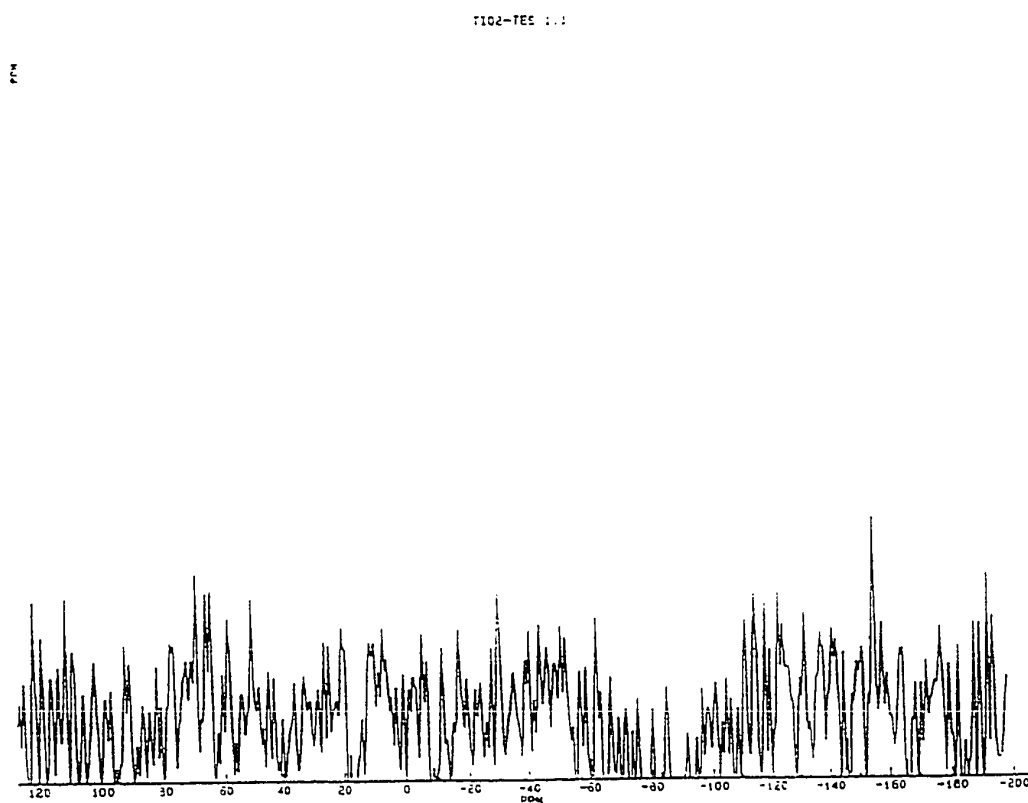
TiO2-TES 1:1

ppm

Figure 54

^{29}Si CP-MAS NMR Spectrum of Hydride Intermediate
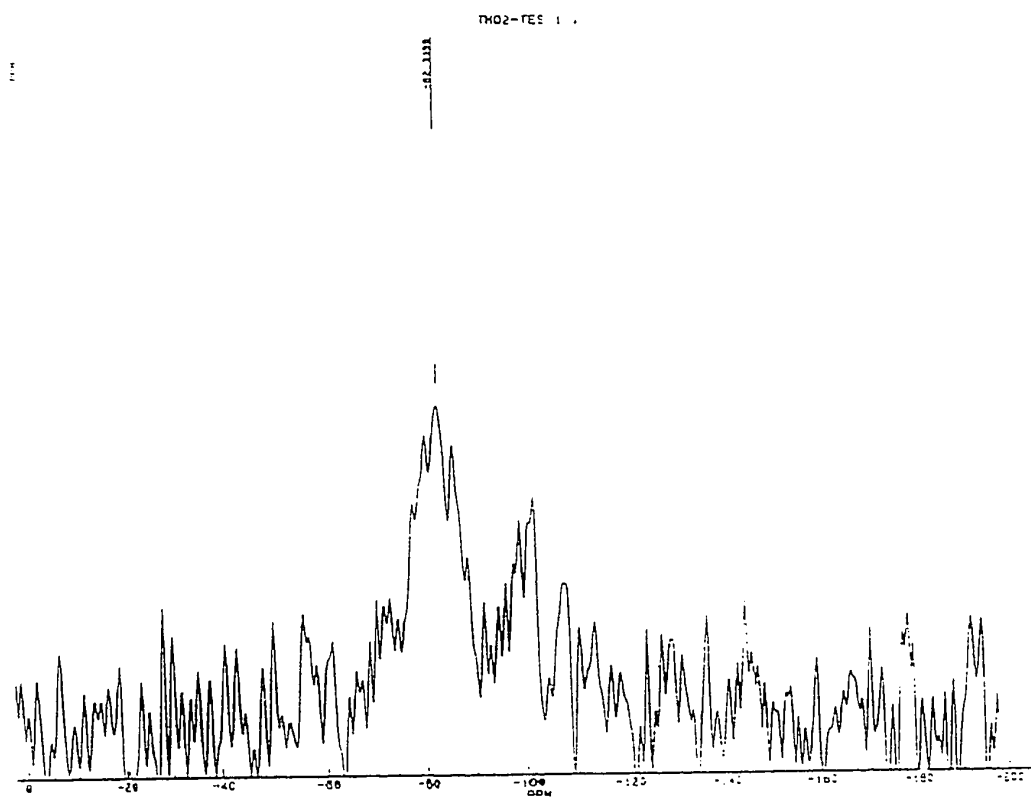
Titania (OH:TES=1:1.1)

Figure 55

^{29}Si CP-MAS NMR Spectrum of Hydride Intermediate

Thoria (OH:TES=1:1.1)

BIBLIOGRAPHY

1. Berthor, Alan *J. Chromatography*, **1991**, 549:1-28.

2. Halasez, I.; Sebestian, I. *Angew. Chem.* (int. ed.) **1969**, 8(6), 453.

3. Kirkland, J. *J. Chrom. Sci.* **1971**, 9, 206.

4. Chu, C. H. Thesis, San Jose State University, Unpublished, **1991**.

5. Sandoval, J. E.; Pesek. J. J. *Anal. Chem.*, **1989**, 61, 2067-2075,

6. Blackwell, J. A. *J. Chromatogr.* **1991**, 549, 59-75.

7. Pesek, Joseph J.; Graham, *J. Anal. Chem.* **1977**, 49(1), 133.

8. Hubner, E. Dorre. H.; Heidelberg, Springer-Verlag, Berlin *Alumina*, MRS, **1984**.

9. Kaliszan, R.; Petrusewicz, J.; Blain, R. W.; Hartwick, R. A. *J. Chromatogr*, **1988**, 458, 359.

10. Knox, J. H.; Pryde, A. *J. Chromatogr.* **1975**, 112, 171.

11. Pesek, J. J.; Lin, H. D. *J. Chromatographia*, **1989**, 28: 11/12, December.

12. *The Merck Index*, 11th. edition, published by Merck & Co., Inc. N. J., U.S.A. **1989**.

13. Smith, A. L.; Angelotti, *N. C. Spectrochim. Acta* ,, 1959, 15, 412-420.

14. Macdiarmid, A. G., Ed.; *Organometalic Compounds of the Group IV Elements*, The Bond to Carbon; Marcel Dekker: New York, 1968, 1, Part I.

15. Morterra, C.; Low, M. J. D. *J. Phys. Chem.* , 1969, 73, 327-333.

16. *Principles of Instrumental Analysis*, 3rd Ed. Douglas A. Skoog, by CBS College Publishing, 1985.

17. Becker, E. D. *High Resolution NMR*, 2d Ed., Academic Press: New York, 1980.

18. Harris, R. *Nuclear Magnetic Resonance Spectroscopy*, Pitman Publishing: Marshfield, MA, 1983.

19. Cox, R. H. *Analytical Applications of NMR*, Wiley: New York, 1977.

20. King, Roy W.; Williams, Kathryn R. *Topics in Chemical Instrumentation*, The Fourier Transform in Chemistry, Part 1, NMR, 1989, 66(9), A213, September.

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

22. Pesek, J. J.; Sandoval, Junior E.; Su, Minggong *J. Chromatogr.* 1993, 630, 95-103.