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Surface Cristobalite Formation by Mild Hydrothermal Treatment of Silica Gel and Its Effect on the Deposition of Tris(allyl)rhodium and Subsequent Reactivity of (silica)Rh(allyl)$_2$

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Titrimetric analysis of surface silanol sites with methyllithium measures total surface –OH group content. This correlates with simple drying but does not predict organorhodium complex deposition loadings onto the oxide. It is suggested that methyllithium does not discriminate among chemically different types of silanol sites as does tris(allyl)rhodium. Furthermore, there is no correlation between simple silica gel drying procedures and the subsequent reactivity of the supported organometallic. A sequence of mild hydrothermal treatment (hydration), followed by drying of the silica, enhanced organorhodium complex deposition yields and enabled reproducibility of supported complex reactivity. Transmission and photoacoustic FTIR analysis of silicas treated by hydration-drying showed new absorptions in the isolated –OH and Si–O–Si ring deformation regions of the spectra, demonstrating surface cristobalite formation. No change in silica surface area was detected for this process.

Introduction

Hydroxylated oxides are common supports for organometallic complex deposition which can occur by protolytic reaction with a surface hydroxyl group. These oxides are usually pretreated to diminish batch-to-batch aliquot variation by processes ranging from simple drying in vacuo[1] to multistep ones,[2] including washing and oxidation. The surface of silica contains hydrogen-bonded –OH groups (Figure 1, II and III) and isolated –OH ones (I).[3–7] Assignments of –OH groups have been made by IR spectroscopy;[3,5,7] physisorbed water (IV) may also be present, hydrogen-bonded to Si–OH or Si–O–Si functionalities.

We note here that although titrimetric analysis of silica gel surface silanol sites with methyllithium does correlate with simple drying conditions, it is inadequate to predict organorhodium complex deposition yields on aliquots of gels variously treated before final drying. However, a sequence of mild hydrothermal treatment prior to final drying (hydration-drying) gave silica aliquots showing enhanced deposition yields and reproducible supported complex reactivity. Infrared analysis of these aliquots showed the appearance of new bands in the isolated –OH and Si–O–Si group vibration regions.

Experimental Section

General Procedures. Analysis was done on a Hewlett Packard 5840A GC instrument equipped with a flame ionization detector and a direct-injection system. Mass spectral identification of GC components was obtained by using a Hewlett Packard 5992B GC/MS instrument equipped with a variable-voltage ionization gun and a jet separator operating with $^{1}/_{4}$ in. packed glass columns. All air- or moisture-sensitive materials were handled in a nitrogen-filled Vacuum Atmospheres glovebox (residual water content of less than 1.0 ppm). Rhodium trichloride hydrate was purchased from either Engelhardt or Johnson Matthey and was used as received. Allyl chloride (Aldrich Gold Label) was passed through basic alumina just prior to use. Celite, used as a filter aid with moisture-sensitive complexes, was prepared by heating in a standard furnace tube at 10^{-4} Torr, at 280 °C, for 24 h. Diethyl ether and THF were distilled from sodium benzophenone ketyl. Other solvents were dried by distillation from calcium hydride under dry nitrogen in Teflon sleeve-sealed stills. Octane (olefin-free grade, Fluka) was predried over lump sodium, and toluene (spectral grade, Baker) was predried over KOH. Following distillation, the solvent was cannula-transferred into a flask and ca. 70% of the material was passed into a vacuum line valve equipped vessel by bulb-to-bulb distillation. This step was taken to ensure grease-free, degassed solvent.

Hydrogen and CO (UHP grade, MG Scientific and Scott, respectively) were used as received. Methane (UHP grade, Matheson), used for GC calibration of methyllithium titrations, was found by GC and GC/MS to contain water and traces of C_2 and C_3 hydrocarbons. It was passed through a $^{1}/_{2}$ in. × 3 ft column packed with 12-mesh silica gel and condensed into a liquid-nitrogen-cooled trap. The condensed gas was then allowed to warm, and the boil-off was pumped into a lecture bottle which had been purged with "zero" grade helium followed by evacuation. The pressure in the lecture bottle was brought to ca. 5 atm (approximately half the methane which had been condensed into the trap initially; the remaining methane in the trap was vented). The gas was assayed by GC and by GC/MS and found to be free of detectable contaminants. Butane (CP grade, Matheson or AGL), used as an internal standard for methyllithium titrations or for propene assay, had many impurities and was purified in a manner similar to that described for methane, except it was condensed into a trap cooled with a dry ice/acetone slurry and Toepler-pumped into a slurry-cooled sample bulb. The contents of the sample bulb were first frozen in liquid nitrogen. Following proper purging and pumping of the system, the bulb containing the frozen butane was opened to the calibrated sample bulb which was to be filled with standard. The liquid-nitrogen bath was removed, and the storage bulb was gently warmed. When the pressure began to rise, no further heat was applied. When the desired sample pressure was achieved, the storage bulb was sealed off and returned to the liquid-nitrogen bath. The pressure was allowed to equilibrate for a few seconds and then recorded from the mercury manometer. The calibrated sample bulb was subsequently sealed off from the system, and the butane in the system was condensed back into the storage bulb. The system and storage bulb were closed off, and the storage bulb was removed from the system. Material prepared in this manner was found to be >99% *n*-butane by GC and GC/MS analysis. To make standard gas mixtures containing one or more components which had substantial vapor pressure at liquid-N_2 temperatures (such as methane, $p \approx 80$ Torr at −196 °C), for which the final pressure of the sample was less than 800 Torr, measured gases were pumped from sample bulbs into a trap or common vessel. The mixture was then "stirred" by circulating in a loop accomplished by Toepler-pumping for 20–60 min. Gas mixtures in which all components could be condensed at liquid-N_2 temperatures and for which final pressures totaled up to 2 atm were made by condensing measured samples from a calibrated sample bulb into a common vessel. Care was taken that the common vessel had a volume relative to the combined volumes of the two calibrated bulbs such that a total pressure of 2 atm was not exceeded upon thawing the common vessel.

Silica Support Treatments. Mild Hydrothermal Processing (Hydration). Mild hydrothermal processing of silica gel (hydration) was done in an adaptation of a Schlenk flask fitted with a ball joint, a high-vacuum stopcock, and a 7-mm O-ring connector with a small sample bulb clamped to the side arm (shoulder flask). The vessel was sealed with a ball-to-ball adapter during the hydration run. The flask was usually

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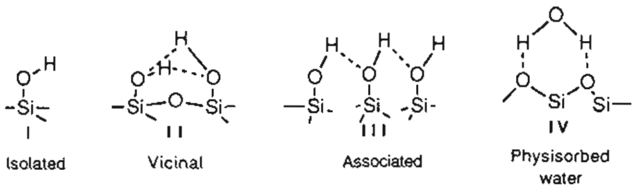

Figure 1. Illustrative types of surface silanol structures for silica gels: (I) 3710–3750 cm^{-1}; (II) 3650–3660 cm^{-1}; (III) 3200–3600 cm^{-1}; (IV) 1620–1630 cm^{-1}.

charged with 6–8 g of silica gel (Degussa Aerosil 300). The small sample bulb typically contained 1.5–3.0 g of H_2O previously degassed by He gas sparging followed by several freeze–pump–thaw cycles. After the flask was charged and assembled, the apparatus, including the side arm up to the sample bulb valve, was evacuated to 10^{-4} Torr. This was accomplished in stages to prevent "bumping" of the oxide due to outgassing. The material was held at this pressure for 30–45 min. The flask was then sealed, and the sample bulb was opened. The entire assembly was placed in an oven. A typical experiment employed temperatures between 80 and 100 °C. The apparatus was removed at 12-h intervals and shaken to "stir" the silica. Care was taken in this step to ensure that the vessel did not cool sufficiently to permit water vapor condensation onto the silica. Hydrothermal treatment was normally done for 2–5 days. The flask was then removed from the oven and was attached to a vacuum line at 10^{-2} Torr drawing through a −78 °C trap. The flask containing the silica was opened to vacuum when condensation appeared at the neck of the flask. Vacuum was applied until condensation was no longer visible; then the flask was closed off again. This was repeated until the material had reached room temperature. Following this, the hydrated silica was handled by using the same procedures as those employed for untreated silica samples.

Drying. Pyrex furnace tubes employed for drying supports were 22 mm in diameter, tapering to 15 mm and terminating in spherical socket connectors. The large-diameter section corresponded to the heated zone of the furnace (either a Lindberg No. 55035 or Fisher No. 10-550-187 was used); care was taken to ensure that all of the support to be dried remained within the large diameter of the tube. Typically, the tube was loaded with use of a powder funnel through one end, with the other closed off by an attached stopcock. The amount of support loaded into the tube (ca. 8 g) was selected to ensure that, when the tube was positioned horizontally in the furnace, there was a 0.5–1.5-cm space along the uppermost portion of the tube side wall. The apparatus was then sealed with another stopcock, and the tube was carefully laid into the furnace. Such precautions provided material which was uniformly dried throughout the batch, as determined by methyllithium titration of randomly selected aliquots: When the silica was packed into a tube, uniform drying did not result; even silica gel loosely packed in a filled tube gave inhomogeneous material. After the tube was inserted into the furnace, vacuum (10^{-2} Torr) was applied slowly. When the operating pressure had been reached, heating was commenced. In this manner the material to be dried was disturbed as little as possible by outgassing accompanying vacuum application. After sufficient drying time (12–24 h), heating ceased and the apparatus was allowed to cool to room temperature under vacuum. The stopcocks on the tube were then closed, and the tube apparatus was transferred into a N_2-charged glovebox. All supports which had been dried were subsequently handled in the glovebox or in airless glassware.

Hydroxyl Group Content Assay. Silica was assayed for hydroxyl group content by treatment with methyllithium and GC quantification of the evolved methane. A sample bulb was charged with methyllithium solution (1 M, diethyl ether, Aldrich) under N_2 by syringe. The bulb was sealed, transferred to the vacuum line, immersed in liquid N_2 until all contents solidified, and evacuated for 5 min at 10^{-4} Torr, followed by thawing. This was repeated until the solution gave a bubble-free solid upon freezing (usually three times). The sample bulb was then sealed and thawed to room temperature, whereupon it was transferred into the drybox for assembly to a side-arm shoulder flask containing 1 g of silica. The assembled titration apparatus was removed from the glovebox and fitted with an O-ring connector (on the side arm) to a spherical connector (vacuum-line port) adapter. It was then placed onto the vacuum line and supported from beneath with a jack and stirrer assembly. The flask and oxide were evacuated for 30–45 min at 10^{-4} Torr. The flask was then sealed, and the sample bulb containing the methyllithium solution was opened, permitting the solution to run down onto the oxide. When the oxide had been covered by the solution, the stirrer was started and adjusted to spin at a very low rate. The stirring rate was adjusted so that good mixing, but not splashing, was accomplished. Stirring normally continued for 1–3 h. The stirrer motor was then removed, and the reaction flask was inserted into a Dewar flask which was then charged with a dry ice/acetone slurry. When the reaction flask had cooled, it was opened to the Toepler pump, which had been arranged to evacuate the flask through a liquid-N_2 trap and discharge into a reservoir and manometer assembly. Prior to pumping of the evolved methane, the reservoir had been charged with a measured quantity of butane. Toepler-pumping continued for 1–3 h, after which the flask and trap were closed off from the Toepler pump. The manometer containing the methane and butane was connected to the Toepler-pump input. The methane and butane were mixed thoroughly by being repeatedly drawn out through the top of the manometer reservoir with the pump and exhausting the pump into the bottom of the manometer reservoir. When the mixing was complete, a sample was drawn out with a valved gastight syringe through an evacuable needle port attached to the reservoir. The ratio of butane to methane was quantified by GC against a standard mixture using a $^1/_4$ in. × 6 ft glass column packed with 0.19% picric acid on Carbopack C (Supelco) and the Hewlett Packard 5840 GC. Typically, three runs at slightly different sample pressures were averaged. It was determined that the contribution from methyllithium reaction with glass vessel surface hydroxyl sites was negligible.

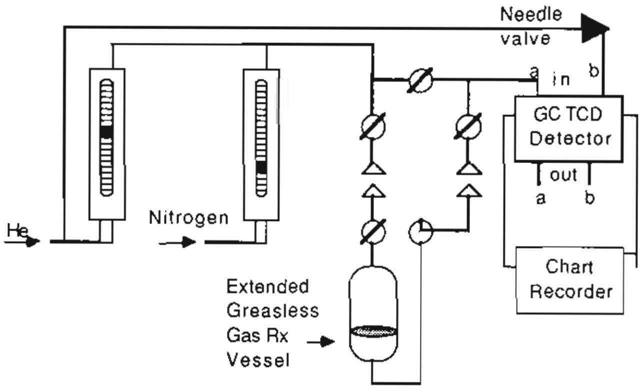

Figure 2. Schematic of apparatus used to determine surface area of silica gels.

Assay of Surface Area. The surface area of hydrothermally treated, dried silica gel was compared with that of Degussa Aerosil 300 by using a modification of a published procedure[8] and was based on surface adsorption of N_2. The material of interest was placed into an extended greaseless gas reaction vessel (GGRV) equipped with a fitting from the oxide-drying apparatus and was evacuated on the vacuum line. The vessel was sealed (under vacuum) and was connected to the thermal conductivity GC (TCGC) as shown schematically in Figure 2. A mixture of N_2 (2% by mass flow) and He was supplied to the GC through flow meters which were connected together at the output. The interconnecting system was purged by allowing the gas mixture to flow through the bypass for 30 min; then the GGRV was opened and the vessel bypass was closed. The gas mixture was allowed to flow over the sample for 30 min to stabilize the pressure in the system and the GC detector. The pen of the chart recorder was adjusted so that the baseline of the graph was set at half full scale. The GGRV was then placed into a Dewar flask filled with liquid nitrogen, and the resulting detector signal was recorded as a positive peak. When the pen had returned to the baseline, the vessel was removed from the liquid-nitrogen bath and was allowed to warm to room temperature, during which time a negative peak was recorded. This procedure was repeated several times for weighed samples of the treated silica gel and of the reference Aerosil 300. A similar measurement was also made for the empty GGRV. The surface area of the treated silica gel was determined by comparing the areas of the peaks resulting from the above procedure carried out on the two different materials. Adjustment was made to each area measurement by subtracting the peak area generated from the empty vessel.

Deposition Reactions. Tris(allyl)rhodium.[9] The title complex was synthesized by reaction of an ethereal solution of bis(allyl)rhodium chloride[10] and (allyl)magnesium chloride. In contrast to the reported preparation,[9] excess Grignard reagent was not hydrolyzed, but the reaction solvent was stripped, and the residue was extracted with pentane. The metal complex was isolated by filtration and evaporation of the pentane. The product was sublimed to purity and was stored at −40 °C in the glovebox. For ease of handling, all reactions and subsequent

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manipulations were conducted in the glovebox.

Reaction of Tris(allyl)rhodium with Silica. An aliquot of dried silica (2–4 g) was placed into a shoulder flask containing a magnetic stir bar and slurried in a minimal amount of deposition solvent (50 mL/g of support). The solvent was added from a graduated cylinder so that the molarity of the metal complex in the deposition solvent could be calculated. Octane or toluene was chosen as the deposition solvent because of good metal complex solubility, high boiling point, and low propene solubility. Tris(allyl)rhodium (20–50 mg/g of support) was dissolved in 10 mL of the deposition solvent. This solution was added to the reaction flask containing the oxide slurry, and the addition vessel and flask port were washed with an additional 10 mL of deposition solvent. The flask was closed at once by clamping an adapter containing a high-vacuum valve into the socket connector that forms the flask opening. Stirring was adjusted to give thorough blending of the materials (demonstrated by a homogeneous color), but without splashing material onto the flask walls. The material was left to stir in the glovebox (ambient temperature, 15–20 °C) for ca. 60 h. When the deposition reaction had run for a sufficient time, the deposition flask was transferred from the drybox to the vacuum line. It was clamped to the main manifold in tandem with two traps. The traps and the vacuum port to which the deposition flask was clamped were evacuated to 10^{-5} Torr. The traps were then cooled, and the manifold valves were manipulated so that the deposition flask was connected only to the inlet of the first trap; the first trap outlet and second trap inlet were connected, and only the second trap outlet was connected to the vacuum manifold. The pressure in the second trap was monitored with a mercury manometer. The trap connected to the deposition vessel (first trap) was immersed in a dry ice/solvent slurry, and the second trap was immersed in liquid nitrogen. When the traps had cooled, the deposition vessel was slowly opened (to prevent bumping of the deposition slurry into the manifold) and the deposition solvent was allowed to distill from the shoulder flask. When all of the deposition solvent had been removed from the oxide (the appearance of the supported material changed from dark brown-black to light brown to golden yellow as solvent was lost), the deposition flask was sealed, and the vacuum port to which it was clamped was closed. The deposition flask was transferred into the glovebox. The supported material was then placed into a fritted funnel and was washed with several aliquots of deposition solvent, followed by two washings with pentane. The supported complex was then placed back into the shoulder flask (which had been rinsed with each wash aliquot prior to being poured over the material in the fritted funnel). The shoulder flask was transferred to a bench line and was evacuated at 10^{-2} Torr until the material had visibly ceased outgassing. The vessel was then sealed and transferred to the vacuum line, where it was evacuated at 10^{-4} Torr for 12–24 h to remove residual wash solvent. No heat source was employed during this step. When postdeposition workup on the vacuum line had been completed, the traps containing the deposition solvent (slurry cooled) and volatile deposition products (liquid nitrogen cooled) were isolated. The trap containing the volatiles was warmed to room temperature and was checked to ensure that no condensate remained. A calibrated sample bulb, charged with a known amount of *n*-butane prior to workup (generally 10–20 cm of pressure; mole content adjusted by choice of the sample bulb volume employed), was connected to the exit of the trap containing the volatiles via an evacuable, valved interconnect. The port was pumped to the main manifold for 10–20 min. At this time, the port was isolated and the volatiles trap was reimmersed in liquid nitrogen. The valve between the trap outlet and the sample bulb was opened, and the contents of the sample bulb were permitted to condense into the volatiles trap. This trap was next isolated and again warmed to room temperature. A syringe adapter was put in place of the empty sample bulb, and a sample of the gas in the trap was obtained through a septum by using a gastight syringe. The quantity of propene in the trap was measured by GC comparison with the added butane against a standard mixture of gases. GC analysis was performed on the Hewlett Packard 5840A GC instrument using a $^1/_4$ in. × 6 ft glass column packed with 0.19% picric acid on Carbopak C (Supelco).

Infrared Studies. All infrared measurements were performed on a Perkin-Elmer 1410 benchtop FTIR spectrometer equipped with a Model 3600 data station and a sample shuttle. Spectra were obtained at 2-cm^{-1} resolution. Analysis of deposited complexes was done with reference to the underivatized oxide. Samples were prepared for IR analysis by hydraulically pressing (1 ton) aliquots (ca. 40 mg) into 25 mm diameter disks by using a hardened die whose working faces had been polished to a mirror finish with graded emery paper and, finally, 3-μ diamond paste. It was necessary to repolish these faces with diamond paste from time to time. All sample disks were made inside a glovebox charged with nitrogen. Disks were examined in gastight cells. Comparison of silicas subjected to different predeposition treatments was performed and care was taken to use equal weights of the materials. Disks were weighed after pressing, and disks were used for comparison only when they were <10% different in pressed weight. Care was also taken to press both disks at similar pressures. Finally, to ensure valid comparison between sample disks, pellets were examined at 2600 cm^{-1} (a featureless region) for equal transmission. Only samples which displayed $\leq$5% difference in transmission values were used.

Table I. Surface –OH Group Titer vs Drying Temperature of Silica Aliquots

drying temp,[a] °C	–OH concn,[b] mmol/g	drying temp,[a] °C	–OH concn,[b] mmol/g
23.5	2.00	99	1.70
32	1.89	105	1.49
50	1.75		

[a] All samples were dried for 19–22 h. [b] By methyllithium titration.

Photoacoustic Infrared Measurements. Photoacoustic infrared (PA) spectra[11] were recorded on a Bomem DA3.002 FTIR instrument equipped with a specially designed acoustic cell.[12,13] The interferometer assembly was modified to provide acoustic isolation from both building vibrations and airborne noise.[12] All spectra were obtained from unpacked powder samples at room temperature under flowing helium. A low mirror velocity of 0.02 cm/s was employed, with 200 scans coadded for each spectrum. Interferograms were phase-corrected, and raw-magnitude spectra were obtained by transformation at 8-cm^{-1} resolution using hamming apodization. Raw spectra were normalized for spectral throughput of the interferometer with the photoacoustic spectrum of graphite as blackbody reference. Normalized photoacoustic spectra of samples were plotted without smoothing. Infrared spectra in the range 450–4000 cm^{-1} were acquired with a globar as the radiation source and KBr as the beam splitter.

Results

Simple Drying. Surface Si–OH groups are lost thermally,[4] which has been studied by IR and ^{1}H NMR spectroscopy[6,14] and confirmed by titration techniques sensitive to surface hydroxyl groups.[7] Different drying environments (heating under vacuum or in a gas stream) and, to a lesser extent, drying times are known to affect the observed concentration of residual hydroxyl groups for a given thermal condition. Physisorbed molecular water is usually lost at $\leq$105 °C.[4] Above this temperature, water is lost from the surface by condensation of silanol groups, which becomes a major process at $\geq$200 °C[15] and which leaves, primarily, vicinal silanol sites. Heating at >400 °C is required for isolated silanol sites to dominate the total –OH distribution.[14] The onset of liberation of water trapped in pores and subsurface sites occurs above 200 °C.[4]

Samples of Degussa Aerosil 300 were subjected to a variety of mild drying temperatures for varying lengths of time in a tube evacuated to 10^{-2} Torr. Following drying, these materials were assayed by methyllithium titration.[7,16] This method produces 1 equiv of methane for each acidic proton available on the surface, is easy to execute with a minimum of laboratory equipment, and is sensitive only to surface species. However, this method makes no distinction between chemical types of silanol sites or even other proton sources present on the surface (such as water). For a given sample of silica, an obvious trend relates decreasing proton content (at comparable drying time) with drying temperature (Table I). Provided short times (<1 h) were not involved, there was no significant correlation between the length of time a sample was treated at a given temperature and the residual hydroxyl content measured. To ensure homogeneity of an aliquot used for de-

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Table II. Comparative Titrable –OH Group Content and Rh Complex Deposition Yields for Variously Prepared Silica Aliquots

batch	hydration temp, °C; time, h	drying temp, °C	–OH content,^{a,c} mmol/g	Rh content,^{b,c} mmol/g	mmol of Rh/mmol of –OH, %
1		99	1.73*	0.040*	2.3
	110; 48	94	1.84	0.105	5.7
2		112	1.40	0.055	3.9
	100; 72	113	2.05†	0.085†	4.1
3		130	1.40	0.020	1.4
	105; 93	125	1.74*,†	0.165*,†	9.5

[a] By methyllithium titration. [b] By Rh(allyl)$_3$ complex deposition. [c] ✱, †: see text.

positions (vide infra), at least 10–15 h of treatment was employed for a given sample; times up to 24 h were commonly used.

Mild Hydrothermal Treatment of Silica Gels Followed by Drying. Surface silanol groups can be generated on silica by reaction with water;[5,17] adventitious atmospheric moisture could variably create surface silanol sites on silica aliquots drawn from a given preparation batch of the oxide at different storage time intervals. If silica samples could be rehydrated to saturation, a standard starting point for conditioning would exist, thus improving the reproducibility of this material as a reaction substrate. Accordingly, samples of silica gel were placed in a vessel which was connected to an evacuated, sealed glass tube containing degassed water. The entire apparatus was evacuated, the tube containing the water was opened to the silica gel, the apparatus was placed in an oven, and the silica gel was treated with water vapor under various conditions. Hydrated material was then initially dried at ≤100 °C prior to use to remove as much physisorbed molecular water as possible without promoting silanol condensation. Under various subsequent drying conditions, the hydroxyl content of rehydrated silica was measured to be greater than that of aliquots of similarly dried material which had not been hydrothermally treated; samples taken randomly from a given batch of treated silica reproducibly showed total –OH content by methyllithium titration. The maximum titrable hydroxyl content measured for a given aliquot increased with reduction in hydrothermal treatment temperature and with increased time (at a given hydration temperature), although the theoretical maximum silanol content, 3.00 mmol/g (300 m^2/g of Degussa Aerosil),[8] was not achieved (see Table II). Hydrothermal treatment was usually performed ca. 100 °C as a compromise between hydroxyl content gain and time requirement. Subsequent drying was performed at various temperatures. Surface areas were measured by using thermal adsorption and desorption;[18] samples of simply dried and hydrated-dried silica gel were compared and were found to have similar surface areas (±5%).

Three batches of a given lot of silica gel were hydrothermally treated under different conditions and then dried, and each was compared for total –OH content with a second portion of the same silica which was simply dried under comparable conditions. For each case, it was found that the hydrothermally treated material had a somewhat higher hydroxyl group content than did the simply dried aliquot (Table II). Comparative IR analysis (by either dispersive reflectance or transmission, Figure 3) showed some depletion of isolated –OH absorption at 3749 cm^{-1} and the appearance of prominent new, isolated –OH absorption at 3734 cm^{-1} for the hydrothermally treated, dried aliquot. A similar band appearance, noted[5] on ambient hydration of Cabosil, has been attributed to a local structural change of the silica surface. This shift to lower frequency can be ascribed to a densification of the underlying lattice, consistent with surface crystallite formation.[12]

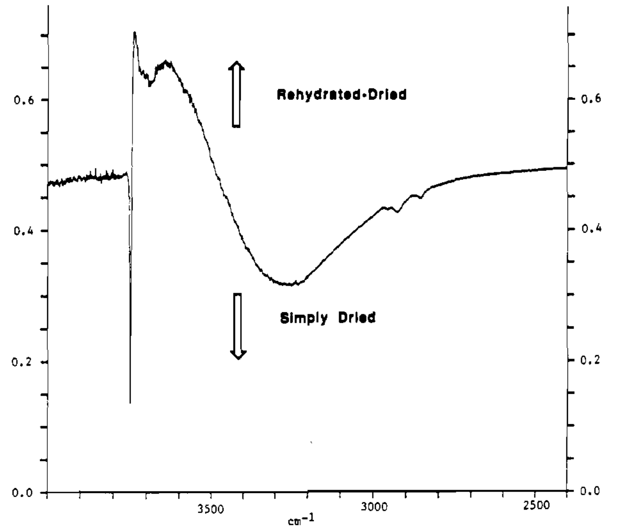

Figure 3. Transmission IR analysis of hydrated-dried Aerosil 300 versus the simply dried gel: simply dried, 3749 cm^{-1}; hydrated-dried, new peak at 3734 cm^{-1}.

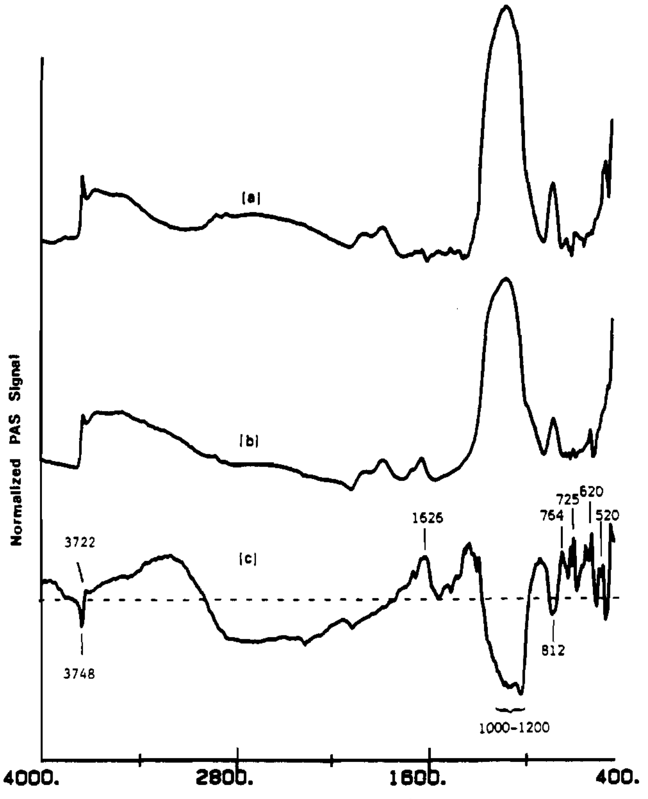

Figure 4. Photoacoustic IR analysis of hydrated-dried Aerosil 300 versus the simply dried gel: characteristic cristobalite ring deformation absorptions at 725, 620, and 520 cm^{-1}.

Infrared photoacoustic spectroscopy (PAS) of solids is ideal for analysis of high surface area materials, such as powdered oxides, since its useful range is limited only by the spectrometer, not by strong lattice absorptions below 1200 cm^{-1}, which preclude analysis below this energy using conventional procedures. Problems of radiation scattering and reflection inherent in transmission spectroscopy of particulate samples are also avoided.[12] Since PAS does not require transmission of light, spectra of ground samples are easily studied. The photoacoustic FTIR signal arises from pressure waves in a bath gas near the sample surface. These are due to the periodic heating of the sample by the absorption of modulated light.[11] The amplitudes of the pressure waves depend on the optical absorption coefficient and the thermal diffusion length of the sample. The surface signal is proportional to the optical absorption coefficient, α, when $1 > \alpha\mu$ (μ is the sample thermal diffusion length). For silica, $\mu \approx 10^{-5}$ m, which is much smaller than the thickness of typical pressed disks.

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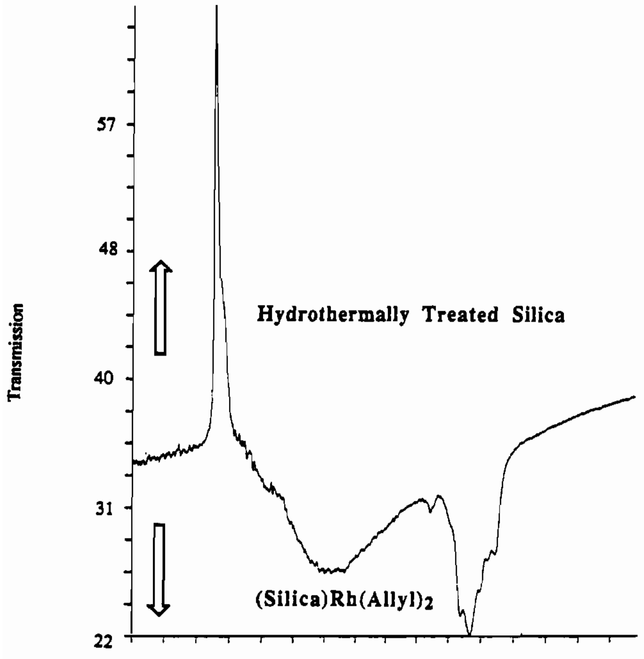

Figure 5. IR analysis of the reaction between $Rh(allyl)_3$ and silica occurring at isolated silanol sites. Unloaded silica: 3749, 3734 (sh), 3650 (broad), 3540 (broad), 1870, and 1630 cm^{-1}. $(silica)Rh(allyl)_2$: depletion of support features, 3749, 3734, and 3540 cm^{-1}; unchanged, 3650 and 1630 cm^{-1}. Metal complex: 3055, 3024, 2993, 2966, 2944, 2901, 2872, and 2854 cm^{-1}.

The PA spectrum of simply dried silica is shown in Figure 4a. The strong absorption band between 1000 and 1200 cm^{-1} is attributed to transverse and longitudinal lattice vibrations of Si–O–Si;[19] it is broadened due to the amorphous structure of the silica and the small particle size of the sample.[20] Other lattice vibrations were found at 468 and 812 cm^{-1}, and overtones of the fundamental lattice vibrations, at 1625, 1860, and 2004 cm^{-1}. As in transmission IR studies, hydrogen-bonded Si–OH groups gave a broad stretching band at 3520 cm^{-1} with a long tail (3700–3400 cm^{-1}) attributed to a small amount of residual water adsorbed on the surface. A sharp peak at 3748 cm^{-1} was noted for stretching of free Si–OH groups.[21] The PA spectrum of hydrated-dried silica (Figure 4b) shows a distinct band due to adsorbed water (1626 cm^{-1}). The difference spectrum (Figure 4c) was obtained, and a pattern in the isolated –OH region, similar to that found by transmission FTIR spectroscopy, was noted. Bending modes due to –OH of adsorbed water and Si–OH were also recorded in the hydrated-dried silica at 1626 and 764 cm^{-1}, respectively.[22] The simply dried silica showed stronger Si–O–Si absorption bands at 1000–1200 and 812 cm^{-1}. Most significantly, the difference PA spectrum reveals features due to cristobalite ring deformation at 520, 620, and 725 cm^{-1} for the hydrated-dried silica, which are not present in the simply dried oxide.[23,24] Thus, even mild hydration-drying of silica gel can locally change the structure of the silica surface.

Reaction between $Rh(allyl)_3$ and Silica. Three batches of silica gel were compared for reactivity with $Rh(allyl)_3$ as a function of oxide pretreatment. Samples taken randomly from a given batch of treated silica showed reproducible Rh complex loading. Rhodium complex loading trends did not follow methyllithium-titrable hydroxyl group contents (see Table II, ✱ and † cases). For similar drying conditions, hydrated-dried silica was more reactive toward $Rh(allyl)_3$ than was simply dried material. A somewhat larger fraction of methyllithium-titrable hydroxyl groups of the hydrated-dried silica reacted with $Rh(allyl)_3$ than did those of simply dried material (see Table II for each "batch"). For either hydrated-dried or simply dried supports, IR analysis of reaction products with $Rh(allyl)_3$ showed preferential attack on the *isolated* silanol sites (3749, 3734 cm^{-1}; Figure 5), even though hydrogen-bonded sites clearly dominated the –OH group distributions. Yields for deposition of $Rh(allyl)_3$ should therefore correlate with the amount of reactive, isolated surface –OH groups present, yet these are indistinguishable from hydrogen-bonded ones by total surface silanol titration with methyllithium. Perhaps reaction of $Rh(allyl)_3$ occurs at isolated –OH groups because these are most efficient for coordination to the metal center in a deposition process in which ligand protonolysis occurs intramolecularly[25] (see Figure 6).

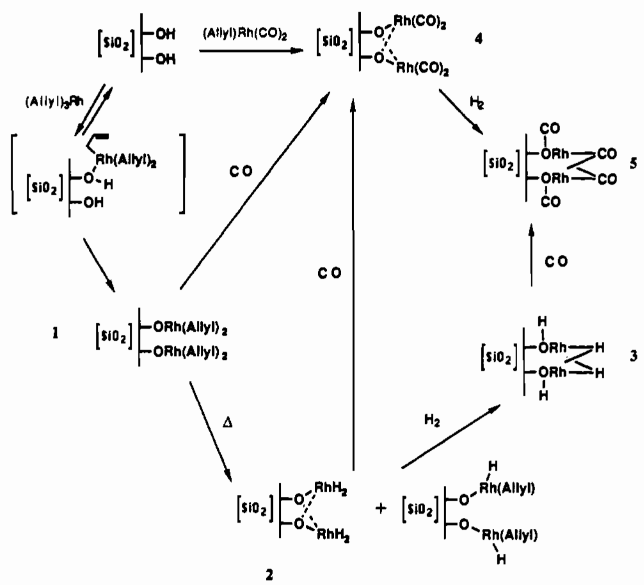

Figure 6. Ligand transformations of silica-supported rhodium complexes.

Thermal Chemistry of Silica-Supported Rhodium Complexes. Synthesis and ligand conversions of silica-supported Rh(allyl) complexes have been described.[26-28] Deposition of $Rh(allyl)_3$ onto silica[26] gives $Rh(allyl)_2$ species **1** which reacts with CO to give a weakly interacting dimer containing no bridging carbonyl ligation, studied by IR spectroscopy.[27,29] This suggests that **1**, too, is a dimer. Deposition of monomeric $Rh(allyl)_3$ to give this aggregate may be due to the location of reactive, non-hydrogen-bonded –OH groups on the silica surface. Transformations studied were (a) thermolysis of $(silica)Rh(allyl)_2$ to (silica)Rh(allyl)H and $(silica)RhH_2$ and (b) "migration" of $(silica)RhH_2$ and $(silica)Rh(CO)_2$ under H_2 (Figure 6).[27]

Influence of Support Pretreatment on Migration and Thermal Ligand Transformations. The relationship between silica gel pretreatment and reactivity of the supported organorhodium complex was investigated, and the five reactions shown in Figure 6 were monitored (Table III). Thermal and "migratory" chemistry of the supported Rh complexes was only poorly reproduced when silica used for deposition was simply dried. Hydration prior to drying, regardless of times and temperatures employed, gave supported complexes showing easily reproducible behavior, for all complex loading values examined.

Conclusions

Methyllithium titration of silica provides one measure of total surface –OH content which varies with silica drying conditions. However, determining total surface hydroxyl content is not ad-

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Table III. Chemistry of Rh Complexes on Variously Treated Silica Aliquots

hydration *temp, °C; time, h*	drying *temp, °C*	Rh content,[a] *mmol/g*	-OH content,[b] *mmol/g*	**1 → 2**[c]	**2 → 3**	**1 → 4**	**4 → 5**
85; 63	72	0.091	2.40	+	+	+	+
85; 63	116	0.186	2.37	+	+	+	+
95; 96	105	0.061	2.26	+	+	+	+
110; 48	155	0.133	1.87	+	+	+	+
110; 48	94	0.098	1.83	+	+	+	+
none	130	0.021	1.40	X	X	+	X
none	99	0.038	1.70	O	O	+	X
none	50	0.071	1.75	+	[+]	+	+
none	74	0.193	1.77	+	X	+	X
none	32	0.055	1.89	+	X	+	X

[a] Rh complex loading determined by propene evolution. [b] -OH group content determined by methyllithium titration. [c] + = reaction observed; [+] = weak reaction observed; X = reaction did not occur; O = inconclusive result for the reaction.

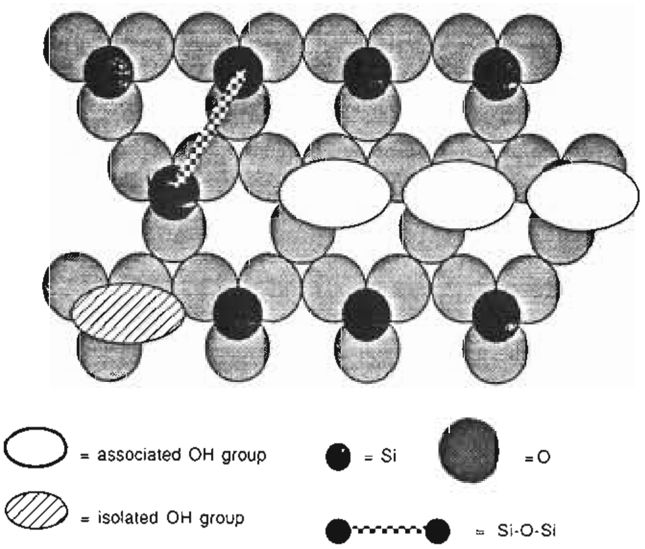

Figure 7. [111] cristobalite model for the amorphous silica surface following partial dehydration showing how an isolated site can be created. (A saturated surface would contain one OH group over every silicon atom; only selected OH groups are shown.)

equate to predict rhodium metal complex reactivity with the surface of silica: Whereas methyllithium reacts with all accessible surface hydroxyl sites, IR analysis shows that $Rh(allyl)_3$ reacts only with "isolated" ones. Therefore, it is the distribution of free and hydrogen-bonded -OH sites on the silica surface, discernible by IR spectroscopy, which is the best indicator of rhodium complex deposition.

Various crystal plane models, including [111] cristobalite (Figure 7), have been proposed for small regions of the amorphous silica surface on the basis of similarities of density and area-normalized hydroxyl group occurrence.[5,6,30] In fact, vigorous hydrothermal treatment of silica gel has long been known to yield cristobalite, but in the absence of catalysts, complete conversion requires high temperatures.[5,31] The hydrothermal processing described herein was done under thermally much milder conditions than those typically used for complete conversion of silica gels to cristobalite. Nonetheless, transmission and, especially, photoacoustic IR analyses, but not diffraction, reveal that at least local regions of surface crystallinity (cristobalite) have been made in these silica samples, yet without surface dehydroxylation or loss in surface area. Surface organometallic species formed by deposition onto these locally crystalline surface regions would involve more regular ligation environments than would be realized on an amorphous gel, and this should foster qualitatively reproducible chemistry of deposition and subsequent reactivity, which is reminiscent of other crystalline supports.

Note Added in Proof. The proposed hydride intermediate **3** in Figure 6 has recently been challenged: Dufour, P.; Sántini, C. C.; Houtman, C.; Basset, J. M. *J. Mol. Catal.* **1991**, *66*, L23–L26. The assignment of this species on bulk oxides[26] and on single-crystal oxide surfaces under ultrahigh vacuum has already been addressed: see Chang, T.; Bernasek, S. L.; Schwartz, J. *J. Am. Chem. Soc.* **1989**, *111*, 758. Smith, P. B.; Bernasek, S. L.; Schwartz, J.; McNulty, G. S. *J. Am. Chem. Soc.* **1986**, *108*, 5654. Smith, P. B.; Bernasek, S. L.; Schwartz, J. *Surf. Sci.* **1988**, *204*, 374. Further discussion is beyond the scope of the present study.

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Registry No. Degussa Aerosil 300, 7631-86-9; methyllithium, 917-54-4; tris(allyl)rhodium, 12082-48-3; cristobalite, 14464-46-1.

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