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Interaction of Titanium Isopropoxide with Surface Hydroxyls on Silica

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Six different silicas, (two aerosils, a hydrophobic aerosil, a silica gel, and Stöber spheres) pretreated at 423 K in vacuum were impregnated with Ti–(O–i-Pr)$_4$ in a N_2 atmosphere and the excess alkoxide washed away in an inert environment. Infrared spectroscopy showed significant differences in the relative proportions of isolated and H-bonded surface hydroxyls on these silicas. The silicas that had a higher proportion of H-bonded hydroxyls picked up a greater amount of titania under our impregnation procedure. Using the route described above, the upper limit of loading appeared to be ≈3.0 Ti/nm^2 on Stöber silica spheres, whose distinguishing feature was that the surface contained exclusively H-bonded hydroxyls. *In situ* infrared spectroscopy was also used to probe the interaction of the titanium alkoxide with the isolated as well as the H-bonded hydroxyls. On the basis of all of these experiments, we conclude that the hydroxyl groups that are capable of H-bonding with neighboring hydroxyls are the preferred adsorption sites, while the isolated hydroxyls are inert, at least at room temperature.

INTRODUCTION

Titanium dioxide is presently used both as a catalyst and as a catalyst support. For example, fumed titania has been shown to be a very effective photocatalyst for oxidation of organics in waste water (1). TiO_2 is also an excellent support for dispersing metal oxides such as V_2O_5 for selective catalytic reduction (SCR) of NO_x with ammonia (2). High surface area titania is therefore desirable for these applications. However, titania tends to sinter easily at elevated temperatures and lose surface area. Furthermore, the titania support is not easy to pelletize or extrude in high surface area forms. Therefore, from a practical standpoint, it is desirable to disperse the titania on other high surface area oxide supports. One approach for dispersing titania on oxide supports is via grafting, such as the reaction of hydroxyl groups on a silica surface with metal precursors like titanium alkoxide. While there is considerable literature on the interaction of metal chlorides and alkyls with the silica surfaces, the interaction of metal alkoxides has not been studied as extensively. The objective of this investigation was to study the reaction of metal alkoxides with silica surface hydroxyls, and in particular the factors that might control the loading and stability of the dispersed titania phase.

In our previous work on immobilizing titania on silica using a titanium alkoxide precursor, we found that there was a remarkable difference between Cabosil HS-5 and Stöber silica spheres (3) in their ability to disperse titania (4). Our procedure involved reacting the silica with the titanium alkoxide compound under a N_2 atmosphere at room temperature, washing away the excess reactant, and then calcining the sample in dry air. We reasoned that the reaction of the alkoxide with surface hydroxyls would be self limiting provided there was no excess water on the silica surface. The maximum weight loading achieved in this manner was therefore considered to be the monolayer capacity of the silica. On Cabosil HS-5 fumed silica, the loading of dispersed titania was limited to ≈1 Ti/nm^2, while loadings of as much as 7 Ti/nm^2 were seen when nonporous Stöber silica spheres were used as support. Adding more than 1 Ti/nm^2 to Cabosil HS-5 led to formation of crystalline TiO_2 as detected by Raman spectroscopy (4). The presence of dispersed as opposed to crystalline titania was confirmed by the absence of features due to crystalline TiO_2 and the presence of a band around 960 cm^{-1} in the Raman spectrum. The dispersed titania was also found to be selective towards partial oxidation of methanol.

The difference in the apparent monolayer capacity of the Cabosil HS-5 and the Stöber spheres could be due to differences in the number and types of surface hydroxyls on the two silicas. Silica spheres are prepared by hydrolysis of tetraethoxysilane in a basic environment and are covered extensively with hydrogen bonded hydroxyls (type B hydroxyls, according to the nomenclature of Ref. (5)) while Cabosil fumed silica contains a greater propor-

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tion of isolated (type A hydroxyls (6)) than hydrogen-bonded hydroxyl groups. It appeared therefore that hydrogen-bonded hydroxyl groups may be better than isolated hydroxyls for stabilizing a dispersed form of titania. Differences in the types of surface hydroxyl groups have been previously suspected to influence the ability to support a dispersed oxide: Weissman *et al.* (7) found that high surface area silica was able to stabilize dispersed niobia, while a silica thin film made by oxidizing a Si wafer at 1273 K was not.

The interaction of specific types of hydroxyl groups on silica with a variety of adsorbates was studied extensively in the late sixties. Hertl and Hair (8) showed that the freely vibrating (isolated) hydroxyls provide the sites for physisorption of hydrocarbon compounds such as benzene, hexane, acetone, and triethylamine. The vibrational frequency of the O–H stretch shifts to lower wavenumbers (energy) upon adsorption. However, water and methanol are very different in that they appear to adsorb on the H-bonded hydroxyl groups exclusively. The suggestion was therefore voiced that the H-bonded hydroxyls may be located in crevices or micropores and may be sterically inaccessible to the more bulky adsorbates. However, steric considerations do not explain why water and methanol do not appear to interact at all with the isolated hydroxyls. It is also interesting that the presence of adsorbed water does not appear to interfere with the adsorption of hydrocarbons on the isolated hydroxyls.

Reactions of surface hydroxyls on silica were also studied with the aim of quantifying the type of hydroxyl responsible for anchoring the reacting species. Hair and Hertl observed that isolated surface hydroxyls reacted quantitatively with molecules such as hexamethyldisilazane (9), chloromethyl silane (10), and metal chlorides (11), while the H-bonded hydroxyls were completely inert. Contrary to the observations of Hair and Hertl, whose experiments were always performed at elevated temperatures, Kunawicz *et al.* (12) found evidence that at room temperature, it was the H-bonded hydroxyls that were the most reactive. In fact, they suggest that the siloxane bridges created when silica is dehydroxylated are more reactive than the isolated hydroxyl groups.

Interaction of titanium alkoxides with silica has been reported by Smith *et al.* (13), who used a Ti ethoxide precursor and Davison 952 silica gel. They deposited titania by refluxing the alkoxide with the silica and washing several times with n-heptane, and found that the titania weight loading depended on the pretreatment of the silica surface. On a silica pretreated to 873 K containing exclusively isolated hydroxyl groups, they found an almost stoichiometric reaction with 1 Ti deposited per nm^2, whereas on a silica that was pretreated at a lower temperature, where both hydrogen-bonded and isolated hydroxyls were present, the increase in Ti loading was not commensurate with the additional amount of hydroxyl groups present, and the reaction was no longer stoichiometric. The greater reactivity of isolated hydroxyls was thought to be due to the presence of lone pairs of electrons on the oxygen atoms of the hydroxyl groups that are then capable of interacting with molecules having electron acceptor properties. The hydrogen-bonded hydroxyl groups, in contrast, will have their lone pairs participating in a hydrogen bond.

The greater reactivity ascribed to isolated hydroxyls is in contrast to our previous observation of increased apparent monolayer capacity for a silica which had no isolated hydroxyls. Therefore, we have explored further the role of hydrogen bonded and isolated hydroxyls for the immobilization of titania on silica. For this purpose, the interaction of titanium alkoxides with silica has been studied by *in situ* infrared spectroscopy. The morphology and loading of titania was examined by analytical transmission electron microscopy.

EXPERIMENTAL

Infrared spectroscopy was performed in transmission mode by pressing the powders onto a tantalum wire mesh (Unique Wire Weaving Co., Hillside, NJ). The wire mesh was supported on a macor ceramic and stainless steel sample mount that permitted heating the wire mesh resistively and allowed measurement of powder temperature via a chromel–alumel thermocouple spot welded to the wire mesh. The sample was contained in a 2¾″ Conflat UHV stainless steel cube that was connected to a gas handling system and to an EAI (model 1200) mass spectrometer and pumped with a 50 l/s Balzers turbomolecular pump. The vacuum in the sample chamber was generally $\approx 2 \times 10^{-7}$ Torr. The CaF_2 IR windows were mounted on 2¾″ Conflat flanges (Harshaw part no. 8960-1C-CaF_2). When the sample chamber was evacuated, the sample could easily be heated to 1273 K without damage to the CaF_2 windows, allowing us to observe the dehydroxylation and rehydroxylation of the surface. The proportions of the various hydroxyl groups were determined by observing the IR spectra of the surface after evacuation at room temperature for at least 8 hr. For the *in situ* experiments, Ti–(O–i-Pr)$_4$ was dosed from a glass bulb in controlled amounts through a leak valve connected to the vacuum chamber.

Electron microscopy was performed on a JEOL 2000 FX microscope operated at 200 kV. The powders were supported on holey carbon films mounted on 200-mesh, 3-mm TEM copper grids. Elemental analysis was performed using a Tracor Northern 2000 EDS system using a Be window detector. The EDS spectra were analyzed using the standardless analysis program SMTF on the Tracor system using the *K* lines of Ti and Si.

The procedure for coating of titania onto silica was described in detail in an earlier paper (4). Briefly, the silica was dried by heating in air at 383 K, cooled to room temperature with minimal air exposure and introduced into a standard Schlenk apparatus. An excess of Ti-(O-i-Pr)$_4$ dissolved in THF (tetrahydrofuran) was added and after stirring for 15 min, the liquid was filtered through a porous frit. The excess Ti–(O–i-Pr)$_4$ was washed away by rinsing three times with THF. It is noteworthy that this procedure sometimes gave rise to nonuniform weight loadings on individual silica spheres. As a result, for this study a modified pretreatment procedure was adopted as follows: Silica was heated to 423 K in vacuum for 2 h and then cooled back to room temperature in vacuum. It was then treated with a solution of Ti–(O–i-Pr)$_4$ in THF. In a typical experiment, a few gms of silica were added to a solution of Ti–(O–i-Pr)$_4$ (0.4 g, 1.2 mmol) in THF under a dry nitrogen atmosphere. The suspension was stirred for 0.24 hr and filtered under nitrogen on a medium porosity frit. The white solid was washed with three 5-ml portions of THF and then dried *in vacuo*. This procedure does not permit variation in the wt% of titania deposited since the loading is strictly determined by the adsorption and/or the reaction of the silanol groups with the alkoxide.

The following silica samples were studied: model silica spheres (prepared by the method of Stöber *et al.* (3)), acid washed Davison silica gel no. 952 (washed in dilute sulfuric acid as recommended by Williams *et al.* (14)), and Cabosil EH-5 and HS-5 fumed silicas. We also studied two silica samples whose surfaces had been specifically pretreated to modify the concentration of surface hydroxyls: Degussa Aerosil 972, which is a hydrophobic silica prepared by replacing surface hydroxyls with methyl groups and a "hydroxylated" HS-5 which had been treated in excess water at 368 K overnight. Table 1 lists the BET surface areas of the silica samples used in this study. The surface areas were determined after outgassing for 8 hr at 573 K on a Quantachrome Autosorb unit.

TABLE 1

Effect of Primary Particle Size and the Number and the Nature of the Hydroxyls

Silica	Surface area (m^2/gm)	OH/nm^2 by ignition method and from manufacturer's data	Titania wt. loading (%)	Wt loading/surface area (g/m^2) × 10^4	Ti/nm^2
100-nm silica spheres	31.5[a]	6 (24)	1.0	4.21	3.15
EH-5 (Cabosil)	390	3.06 (25)	5.0	1.2	0.9
Aerosil 972 (Degussa)	120	0.75 (27)	0.97	0.8	0.6
Silica gel (Davison 952)	278	3.82[b]	4.0	1.4	1.0
HS-5 (Cabosil)	330	$\sim$2.0–3.5 (25)	$\sim$4.0	1.2	0.9
Hydroxylated (treated) HS-5	308	3.25[b]	4.25	1.4	1.0
Monolayer capacity based on density of anatase (101) plane[c]				13.7	10.3

[a] The calculated value for the surface area of the silica spheres is 26 m^2/gm based on the observed (TEM) primary particle size and $\rho_{silica} = 2.2 \times 10^3$ kg/m^3.

[b] The reported value is based solely on our measurements with a TGA.

[c] The monolayer capacity is based on $\rho_{titania} = 4.25$ g/cm^3 and the *d*-spacing of the (101) plane to be 3.24 Å.

The method of deuteration of the silica surface is a modification of the one followed by Morrow and McFarlan (15) in which the silica is first heated to 423 K for 1 hr with continuous evacuation. It was then exposed to about 2 Torr D_2O for 10 min followed by evacuation for 10 min. This procedure was repeated five times (determined to be sufficient—i.e., until the peak areas corresponding to the hydroxyl and the deuteroxyl peaks showed no change on adsorption and subsequent evacuation). The silicas were then finally heated to 423 K to remove any physisorbed water and D_2O that may be present on the silica surface.

RESULTS AND DISCUSSION

Infrared Spectroscopy of the Silica Samples

The differences in the nature of the hydroxyl groups on the varous silica surfaces were investigated by infrared spectroscopy. The IR spectrum of any silica in the hydroxyl region is known to consist of two components—a sharp band at 3750 cm^{-1} corresponding to freely vibrating, isolated hydroxyls, and a broad band from 3200 – 3750 cm^{-1} which is due to hydrogen bonded hydroxyls. Among the bands whose origins are in the skeletal Si–O stretches and are present on all the silica samples, the 1640-cm^{-1} band has been assigned as an overtone band while the bands around 1875 and 2000 cm^{-1} have been assigned to be combination bands (16). In C–H stretch region, the asymmetric CH_3 and CH_2 stretches exhibit bands in the general vicinity of 2960 and 2925 cm^{-1}, whereas the symmetric stretches exhibit bands around 2870 and 2825 cm^{-1} (17). In the C–H bend region, the CH_2 bend is evidenced by a band around 1465 cm^{-1} while the asymmetric and the symmetric CH_3 bends exhibit bands around 1450 and 1375 cm^{-1}, respectively. The C–H bands on these silica samples are observed because of adsorbed hydrocarbons that may be present on the optical components of the infrared spectrometer and some residual hydrocarbons that may be present in the purge gases. Our silica samples were subjected to at least 8 hr evacuation at room temperature and a vacuum of $\approx 7 \times 10^{-7}$ Torr to remove physisorbed water. Ghiotti *et al.* (18) have shown that an hour of evacuation in a "rough" pump vacuum is sufficient for the removal of physisorbed water and is equivalent to heating the silica to 383 K for 2 hr in flowing dry air.

The infrared spectra of the aerosils—i.e., Cabosils

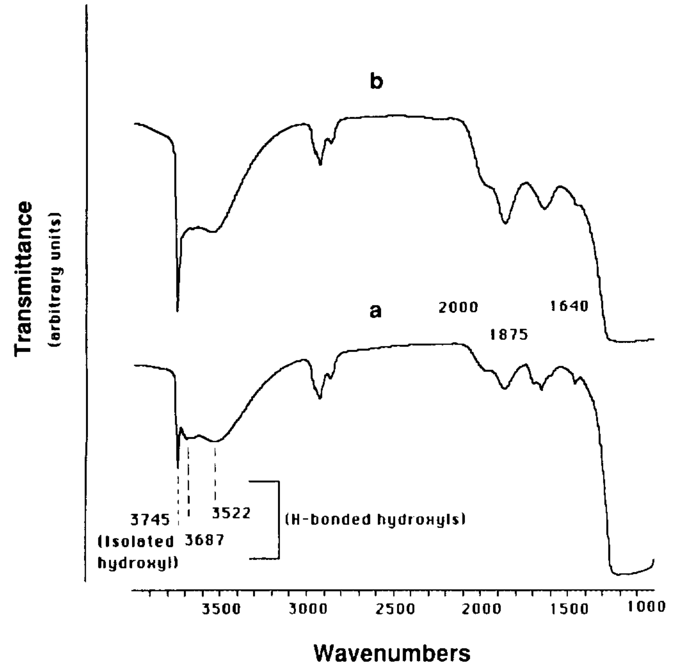

FIG. 1. Transmission IR spectrum of silica after 8 hr evacuation (a) Cabosil EH-5 and (b) Cabosil HS-5.

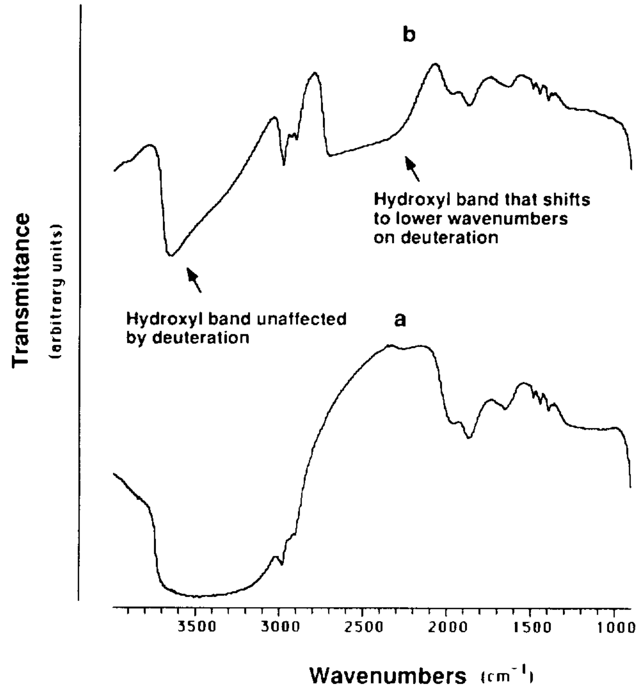

FIG. 3. Transmission IR spectrum Stöber silica spheres obtained after 8 hr evacuation (a) as prepared and (b) after deuteration.

EH-5 and HS-5 made by the vapor phase hydrolysis of $SiCl_4$—are shown in Fig. 1a and 1b. While they show a significant proportion of isolated hydroxyls, we can also observe the presence of hydrogen bonded hydroxyls. In contrast, Fig. 2 shows the infrared spectrum of Degussa Aerosil 972, a silica surface that has been derivatized by reaction with dimethyl dichlorosilane where no isolated hydroxyls are present. This silica is seen to have exclusively hydrogen bonded hydroxyls. Similarly, the infrared spectrum of silica spheres shown in Fig. 3a also shows extensively hydrogen bonded hydroxyls with no evidence for the presence of isolated hydroxyls. The silica spheres are prepared via hydrolysis and condensation reactions of TEOS and are known to contain a significant number of hydroxyls in their bulk. Consequently, the infrared spectrum of the as-prepared silica spheres does not provide direct information on the nature of surface hydroxyls. When the surface hydroxyls are deuterated at room temperature, one can clearly distinguish hydroxyls that may be present in the bulk or be in some way be inaccessible to exchange (19). As can be observed from Fig. 3b, a broad envelope corresponding to hydroxyl groups that could not be exchanged with D_2O is in the region that extends from around 3050 to 3800 cm^{-1}. The hydroxyl groups that have been exchanged with D_2O, i.e., the ones that are indeed the true surface (accessible) hydroxyls are seen around 2100–2800 cm^{-1}. One can immediately note that they are all "hydrogen" (deuterium) bonded to one another. The results of this deuteration experiment confirms that the hydroxyls on the *surface* of the silica sphere are indeed all hydrogen bonded.

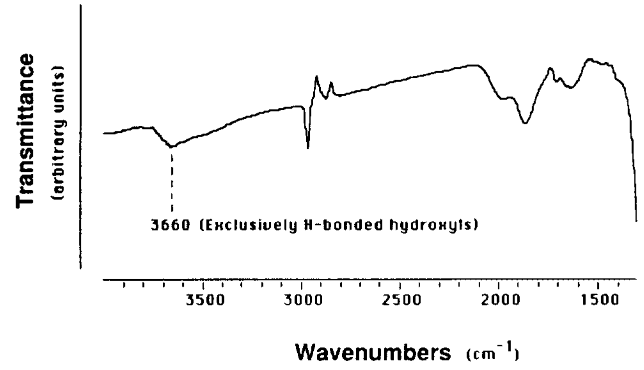

FIG. 2. Transmission IR spectrum of Degussa Aerosil 972 obtained after 8 hr evacuation.

The infrared spectrum of acid washed Davison 952 silica gel seen in Fig. 4a shows the presence of isolated as well as hydrogen-bonded hydroxyls. This silica could be described as being intermediate in its degree of hydroxylation; i.e., it could be described as between a Cabosil silica which shows a large proportion of isolated hydroxyls and silica spheres which show exclusively hydrogen bonded hydroxyls.

We also attempted to increase the number of hydroxyl

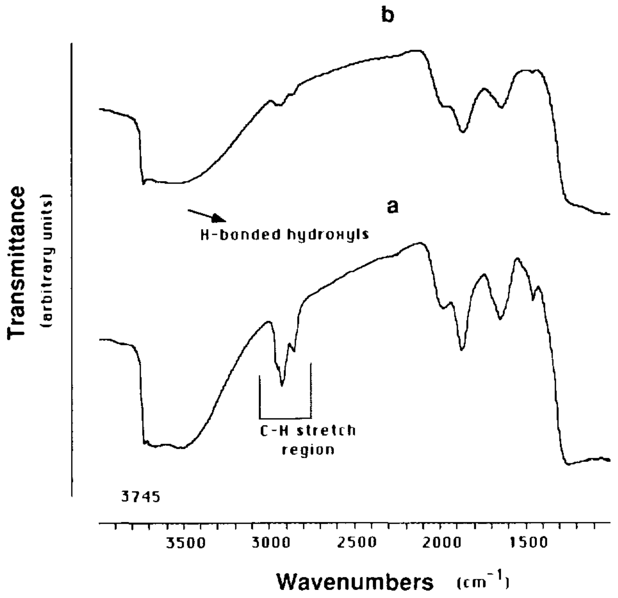

FIG. 4. Transmission IR spectrum of (a) acid-washed Davison 952 silica gel and (b) "hydroxylated cabosil HS-5", after 8 hr evacuation.

groups on the Cabosil HS-5 silica surface by heating the silica in water at 368 K for 8 hr. We hoped that this would increase the number of hydroxyls as well as the proportion of hydrogen bonded hydroxyls. The IR spectrum of this sample, designated as "Hydroxylated HS-5" is shown in Fig. 4b and shows that this treatment has succeeded in making the hydroxyls on cabosil silica look more silica gel-like in character while resulting in a slight loss of surface area.

The Loading of Titania on Silica

Our preparation involved heating the silica to 423 K in vacuum before being exposed to a THF-solution of the titanium alkoxide under a N_2 atmosphere. Excess alkoxide was washed away with THF. The sample was subsequently exposed to the air and transferred to the TEM. Elemental analysis was performed on the samples using the EDS facility available in the electron microscope. Table 1 shows the weight loadings of titania on various silica samples. In no case did we detect any crystalline titania on these samples. In previous work (4), we also showed that heating these samples to 773 K in dry air does not transform the titania into a crystalline phase, provided the titania is introduced by impregnation and the excess alkoxide removed by washing. It is important to emphasize that our method of coating involves removal of all physisorbed water on the silica, and the impregnation of the alkoxide under dry N_2 atmosphere. Therefore, the loading of titania is limited by the interaction of surface hydroxyls with the titanium alkoxide.

Table 1 shows that all of the high surface area silicas have a titania loading of approximately 1.0 Ti/nm^2 after reaction with the alkoxide, regardless of their hydroxyl content. This table also lists the surface areas and hydroxyl concentration on the silica samples. The hydroxyl content was determined by the ignition method, which involves measuring the weight loss between 383 K where there is a change in the slope of the sample weight vs temperature curve, and 1373 K. The sample was first pretreated by heating in air at 383 K for 2 hr before transferring to the thermogravimetric analyzer (TGA). We did not attempt to quantify the relative proportions of isolated and vicinal hydroxyls due to the difficulties in deconvoluting the peak corresponding to the isolated hydroxyl from the broad peak corresponding to the H-bonded hydroxyls. A further complication is that hydroxyls in the bulk of the silica are also contained within the broad band corresponding to H-bonded hydroxyls. The differences in the nature of the hydroxyls on the various silicas do not seem to affect the amount of titania they pick up except for the Aerosil 972 and the silica spheres. Aerosil 972 which has a lower hydroxyl content picks up only about 0.6 Ti/nm^2, while the loading for the silica spheres is almost 3.0 Ti/nm^2. The higher loading on the silica spheres is consistent with observations we reported previously (4). The Stöber silica spheres possess exclusively H-bonded hydroxyls as seen by IR spectroscopy and appear to pick up the highest amount of titania per unit surface area.

The Interaction of Titanium Alkoxides with Surface Hydroxyls on Silica

In order to better understand the interaction of the silica hydroxyls with the alkoxide, we performed *in situ* IR spectroscopy. Figure 5a shows a spectrum of EH-5 silica heated to 923 K to remove all H-bonded hydroxyls. A sharp band corresponding to isolated hydroxyls can be seen. Due to residual hydrocarbons in the spectrometer, and problems with background subtraction, we see negative peaks in the C–H stretch region in spectrum (a). When the sample was exposed to 0.088 Torr of Ti–(O–i-Pr)$_4$ for 17 min and evacuated (Fig. 5b), the presence of adsorbed alkoxide caused an increase in the intensity in the C–H stretch region and a broad feature centered around 3450 cm^{-1}. When this sample was heated to 463 K under vacuum, as shown in Fig. 5c, the alkoxide desorbed, leaving behind a silica surface very similar to the one before pretreatment. Repeated exposure of the silica to the alkoxide did not change the results markedly. When the titania content of this sample was determined by removing the sample from the IR cell and analyzing by EDS, no Ti peak could be detected. We can conclude from this experiment that the titanium alkoxide is only weakly physisorbed on the isolated silanol groups.

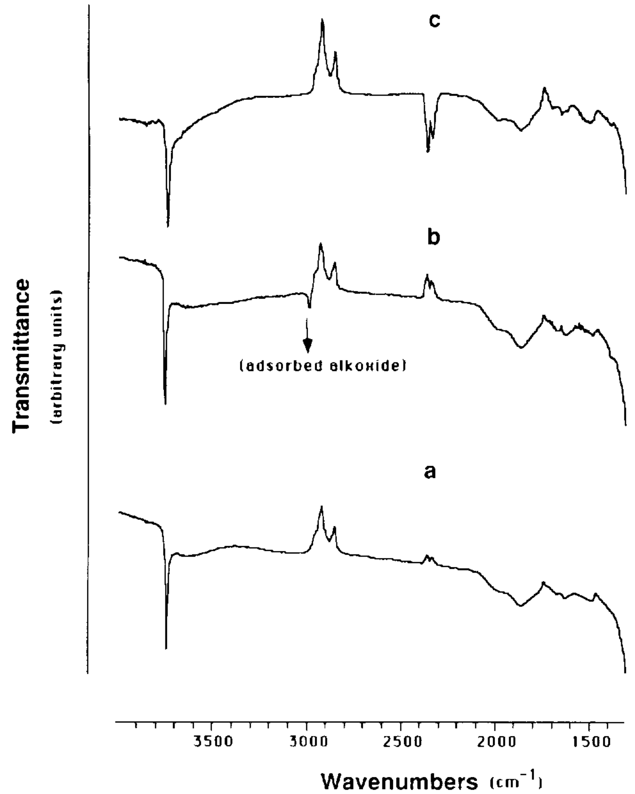

FIG. 5. Transmission IR spectrum of EH-5 silica (a) after heating to 923 K at an ambient pressure of 2×10^{-7} Torr to retain only isolated hydroxyls, (b) exposed to 0.088 Torr Ti isopropoxide, and (c) evacuated at 463 K to a pressure of 1×10^{-6} Torr.

A similar series of experiments was performed with a sample of EH-5 where the population of surface hydroxyl groups was representative of that after exposure to amospheric air. As seen in Fig. 6a, the sample shows a significant proportion of H-bonded hydroxyls. This sample was evacuated at a vacuum of 7×10^{-7} Torr for 8 hr after having been heated to 423 K for 40 min. It has been shown that such a treatment (i.e., evacuation in vacuum for a period of at least an hour) very effectively removes all molecular water from the silica surface at least for those silicas that are nonporous (18). We recognize that the removal of adsorbed H_2O would be hindered by any closed porosity when the pellet is presssed, but we can assume that the titanium alkoxide does not penetrate the closed pores either. Figures 6b and 6c show the IR spectra of this sample after exposure to the titanium alkoxide and evacuation at 433 K. We can see that the exposure to the Ti-alkoxide leads to a significant increase in the ν(C–H) bands, indicating the presence of adsorbed Ti-alkoxide. When the sample was heated to 433 K, there was a significant decrease in the ν(C–H) band. We interpret this as the loss of some of the physisorbed alkoxide but the residual ν(C–H) vibrations show that not all of the alkoxide has desorbed. This is confirmed by EDS elemental analysis of the specimen after removal from the IR cell which shows 4–6 wt% of TiO_2 on this sample. We conclude that the titanium alkoxide interacts more strongly with the H-bonded silanols so that it cannot be pumped off by room temperature evacuation.

Anchoring Sites for the Titanium Alkoxide

The *in situ* experiments provide support for the hypothesis that when isolated OH groups are the only species present on silica, they do not interact strongly with the adsorbed alkoxide at room temperature. Our *in situ* IR experiments do show a weak interaction of the isolated silanols with the adsorbed alkoxide. Hair and Hertl (8) have previously shown that hydrocarbons do interact with isolated hydroxyls and cause a shift in vibrating frequency of the OH group. However, the weak physisorption of the alkoxide on the isolated hydroxyls appears to be reversible. On the other hand, when H-bonded OH groups are present along with the isolated silanols we do see evidence of a stronger interaction with the adsorbed

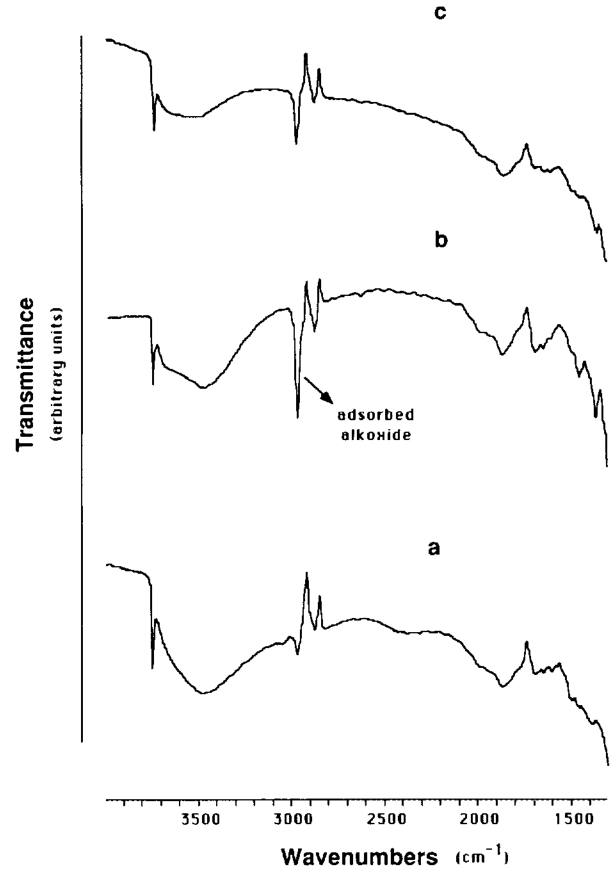

FIG. 6. (a) Transmission IR spectrum of Cabosil EH-5 silica (a) after pretreatment at 423 K for 40 min to remove molecularly adsorbed water, (b) exposed to 0.0688 Torr Ti isopropoxide, and (c) evacuated for 15 min at room temperature and heated to 433 K.

alkoxide and the alkoxide cannot be pumped off at room temperature. We therefore conclude that the primary adsorption sites for the alkoxide at room temperature must be the H-bonded hydroxyls.

On Aerosil 972, where all of the isolated hydroxyls have been reacted away, we were still able to disperse 0.6 Ti/nm^2. This is approximately 60% of the loading achieved on the other silicas despite the total hydroxyl content being only 25% of that of the other silicas. This observation further confirms the remarkable effectiveness of the H-bonded hydroxyls in providing anchoring sites for the alkoxide.

These results suggest that if we want to increase the loading of the dispersed titania we should increase the proportion of H-bonded hydroxyls on a given silica surface. One method for doing this would be by refluxing the silica in water, which causes an almost complete loss of the isolated hydroxyl band as shown in Fig. 4b. However, when this hydroxylated Cabosil HS-5 was impregnated with the titanium alkoxide, it was found to be no more effective in picking up the titanium alkoxide in the room-temperature impregnation. It is possible that the HS-5 fumed silica transforms into a gel during the hydrothermal treatment, losing its open fractal-like nature. The additional H-bonded hydroxyls which are created by the hydrothermal treatment may actually be inaccessible to the isoproxide. We have seen some evidence for inaccessible hydroxyls on the acid washed Davison 952 silica gel sample where only about two-thirds of the hydroxyls present on the surface could be deuterated (20). Hence, the lower loading on the silica gel sample compared with the Stöber spheres despite the abundance of H-bonded hydroxyls must be related to the decreased accessibility of the bulky titanium alkoxide molecule to the hydroxyls within the tortuous pore structure of the silica gel. The silica spheres, on the other hand, have a convex surface which would be very readily accessible to the titanium alkoxide.

Comparison of Our Results with Previous Work

The titania loadings obtained by us are lower than those reported by previous workers, i.e., Wachs (21), Smith *et al.* (13), Fernandez *et al.* (22), and Vogt *et al.* (23), due in part to the different procedure used for loading the titania on silica. The distinguishing features of our method are (a) *pretreatment in vacuum* at a temperature (423 K) higher than that used by previous workers, which would correspondingly result in a lower hydroxyl content on the surface; and (b) *room temperature* contact with the titanium alkoxide dissolved in THF, followed by washing with the same solvent to remove the unreacted alkoxide. Wachs (21) observed a loading of about ~10 wt% of dispersed titania on Cabosil EH-5 silica, but they used air exposed silica samples and did not wash off any weakly held alkoxide. Smith *et al.* (13) deposited titania by refluxing the alkoxide with a silica suspension in *n*-heptane whose boiling point is around 371 K. The higher temperature could have led to better reactivity of the alkoxide with the hydroxyls on the silica surface, compared with room temperature impregnation done by us. Their loading corresponds to 3.0 Ti/nm^2. Fernandez *et al.* (22) report a coverage of about 7 wt% (which corresponds to ~2.6 Ti/nm^2) after incipient wetness impregnation using titanium isopropoxide on an untreated silica. However, from their results it is not clear whether all the titania is present in a dispersed form since they report UV–vis diffuse reflectance spectra characteristic of small particles of TiO_2. Finally, in the study of Vogt *et al.* (23), A $TiCl_3$ precursor was used whose interaction with the silica may be much stronger than the alkoxide and may indeed give rise to complete coverage of the silica by the titania as reported by them.

The literature data suggests an upper limit of 3 Ti/nm^2 for a dispersed form of titania where the Ti^{4+} octahedra are present as isolated structures on the surface. On the Stöber spheres, we may assume that the Ti^{4+} is coordinated with the silica surface via two –O–Si bonds from two neighboring silanols which were H-bonded. Since the surface concentration of such silanols is ≈6 OH/nm^2, this would correspond with 3 Ti/nm^2. It is possible that isolated hydroxyls also provide anchoring sites, particularly during high temperature preparation. On a typical high surface area silica such as a silica gel, the surface concentration of a fully hydroxylated surface is expected to be ≈4.6 OH/nm^2 (1.6 isolated silanols and 3.0 silanols that are close enough to H-bond). This would lead to a surface loading of 1.6 Ti/nm^2 on isolated hydroxyls and 1.5 Ti/nm^2 on the hydroxyl pairs, an overall loading of 3.1 Ti/nm^2. Depending on the heat treatment of the silica, we may find a lower concentration of surface hydroxyls, and consequently a lower loading of titania. This would explain the loading of 1 Ti/nm^2 seen by us on high surface area silicas.

While our study suggests that H-bonded hydroxyls may be exclusively responsible for providing anchoring sites during room temperature preparation, there is other work in the literature showing that isolated silanols may play a significant role, particularly during high temperature deposition. For example, a recent study by Roark *et al.* (26) has shown that isolated silanols can assist in spreading supported molybdena on silica. When molybdena is dispersed on silica at concentrations of ≈1 Mo/nm^2, the Mo^{6+} is found to spread upon dehydration and consume all of the isolated surface hydroxyls. This is a result of a corrosive chemisorption of the molybdena on the silica. However, the process is reversible and upon rehydration the isolated silanols are restored. Our study has not specifically addressed the effect of dehydration on the dispersed titania species. However, while our pretreatment temperatures were comparable to those used by Roark *et al.*, we did not observe a migration of titania or consumption of surface hydroxyls after heating in vacuum at 773 K.

SUMMARY AND CONCLUSIONS

In summary, based on our work and that reported in the literature, the loading of 3 Ti/nm^2 seems to be the upper limit for a dispersed titania on silica. However, we are unable to achieve a loading greater than 1 Ti/nm^2 on the high surface area silicas using our room temperature deposition procedure. The deposition procedure differs from that used by previous workers in that it involves pretreatment of the silica to remove molecularly adsorbed water, contact with a THF-solution of titanium isopropoxide for 15 min and subsequent washing away of the weakly held alkoxide. Only on the Stöber silica spheres that contain almost exclusively H-bonded hydroxyls are we able to achieve the loading of 3 Ti/nm^2. When we used a similar deposition procedure for silica samples devoid of H-bonded hydroxyls, no titania was deposited on the silica. Therefore, we conclude that the titanium alkoxide is strongly adsorbed on H-bonded hydroxyls, whose geometric arrangement on the surface helps to provide multiple sites for interaction with the metal alkoxide. For instance, these could involve the interaction of oxygen atoms from neighboring hydroxyl groups with the Ti^{4+} in the isopropoxide. Under such a scenario, a group of H-bonded hydroxyl groups would bind the $Ti\text{–}(O\text{–}i\text{-}Pr)_4$ more strongly than an isolated hydroxyl and therefore prevent it from being washed away during filtration or prevent it from desorbing during evacuation.

While our work has shown dramatic differences in the ability of isolated and H-bonded hydroxyls to retain the titania on the surface during room temperature impregnation, the *in situ* IR spectroscopy experiments did not provide any direct evidence for reactions of the hydroxyl groups with the metal alkoxide at room temperature. We suspect that the reaction between the alkoxide and the hydroxyl may actually take place at elevated temperature during calcination of the sample. The role of H-bonded hydroxyls could be to provide strong adsorption sites that prevent loss of the adsorbed alkoxides before reaction actually takes place. Therefore, when impregnation is performed at room temperature, a temperature too low to allow appreciable reactivity between the alkoxide and surface hydroxyls, it is possible that the H-bonded hydroxyls act as strong adsorption sites and influence the amount of titania that is retained on the surface. If the loading of the titanium oxide is to be maximized during room temperature impregnation, the number of vicinal hydroxyl groups should be increased. Room temperature impregnation should therefore yield the highest titania loading only on those silica surfaces that are fully hydroxylated and have a significant number of vicinal hydroxyl groups. Accessibility of the hydroxyls to the alkoxide is also important, and for this purpose the fumed silicas with their open, fractal nature would be desirable. Among the fumed silicas we investigated, we find the EH-5 silica to have a significant number of H-bonded hydroxyls and should therefore yield the highest loading of dispersed titania.

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