

Vibrational Analysis of H₂ and D₂ Adsorption on Pt/SiO₂

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Vibrational properties of surface species formed upon H₂ and D₂ exposure of silica supported platinum particles have been investigated with in situ diffuse reflection infrared Fourier transform spectroscopy. Experiments have been performed at 50–250 °C, using different platinum loading of the samples in the absence and presence of oxygen. In addition, electronic structure calculations and vibrational analysis have been performed within the density functional theory for H adsorption on a silica cluster, (HO)₃SiOSi(OH)₃. The spectroscopy experiments showed reversible formation of isolated OH and OD groups on the silica surface when the samples were exposed to H₂ and D₂, respectively. In addition to the absorption peak corresponding to isolated OH and OD groups, an intense broad band was observed around 3270 cm⁻¹ (2500 cm⁻¹) during H₂ (D₂) exposure. Supported by the calculations, this band was assigned to perturbed OH groups on the silica surface. The surface coverage of new OH groups was found to correlate to the platinum loading in the samples, indicating that the new silanol groups were formed in the vicinity of the Pt particles. In the investigated temperature interval, the formation rate of OH groups was not found to be temperature dependent.

1. Introduction

For more than 25 years, field effect devices have been used as chemical gas sensors.^{1–3} Applications include leak detectors to monitor hydrogen and the so-called electronic nose.⁴ Due to the large band gap and chemical inertness of SiC, the metal insulator silicon carbide field effect transistor (MISiCFET) has recently been shown to be suitable as a gas sensor in harsh environments such as process flue gases and automotive exhausts.^{5,6} One example is MISiCFET devices as ammonia sensors,^{5,6} with a potential application as an important component in the exhaust abatement system for diesel vehicles. The technical solution to the forthcoming nitrogen oxides (NO_x) emission regulations for heavy-duty diesel vehicles will (at least in Europe) most likely be selective catalytic reduction (SCR) of NO_x using ammonia-releasing urea as the reducing agent.⁷ Today, SCR is a well-established technique for many stationary applications. However, in a vehicle, the flow rate and temperature vary significantly, and without sophisticated control of the SCR process, problems like ammonia slip will arise. Reliable urea injection and ammonia detection methods are thus mandatory for the SCR systems in vehicle applications.

The gas sensitive metal insulator silicon-based field effect transistor (MISFET) may schematically be described as a semiconducting substrate covered with a thin insulating SiO₂ (or other insulator) film with a top gate layer of a catalytic active metal like platinum. The hydrogen sensing mechanism of the MISFET device is assumed to involve dissociative adsorption

of H₂ on the catalytic metal surface followed by atomic diffusion of hydrogen to the metal/SiO₂ interface.⁸ At the interface, hydrogen forms a dipole layer that gives rise to a shift in the capacitance versus voltage characteristics of the device.⁸ Under UHV conditions, the voltage shift has shown to be proportional to the logarithm of the hydrogen pressure. This indicates Temkin adsorption where the heat of adsorption varies with the hydrogen coverage at the interface.⁸ In contrast to the hydrogen response, these types of sensors are sensitive to ammonia only if the catalytic metal film is porous.^{9–12} Hence, exposure of the SiO₂ layer to the gas phase seems to be crucial for ammonia response. In a recent study, ammonia was shown to adsorb and dissociate to NH₂ on Pt, in a sample with dispersed Pt nanoparticles supported on porous SiO₂, thus forming atomic hydrogen.¹³ This implies the possibility for atomic hydrogen species to spill over to the SiO₂ surface to form a dipole layer during ammonia exposure, in similarity to the proposed hydrogen sensing mechanism. This mechanism for ammonia response is in agreement with previous results obtained with the scanning light pulse technique.¹¹ Hence, hydrogen species interacting with the SiO₂ layer seem to play an important role in the sensing mechanism for both ammonia and hydrogen. Interaction between atomic hydrogen and SiO₂ is an important issue for many fields within microelectronics involving Si/SiO₂ interfaces, such as stability and lifetime of semiconductors, and several studies on hydrogen interaction at the Si/SiO₂ interface and bulk SiO₂ have appeared.^{14–20}

The aim of the present study is to enhance the understanding of the sensing mechanism of the MISFET device for hydrogen as well as for ammonia by studying the interaction between hydrogen and SiO₂. Time-resolved in situ diffuse reflection infrared Fourier transform (DRIFT) spectroscopy was used to study the evolution of surface species by exposure of silica supported platinum samples to hydrogen at temperatures where

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TABLE 1: Amount of Chemisorbed CO on Pt at 35 °C, Estimated Platinum Dispersion and Mean Pt Particle Size, Calculated Fraction of the Surface Covered with Pt, and Specific Surface Area (SSA)

sample	Pt loading (wt %)	amount CO on Pt ($\mu\text{mol/g}$ sample)	Pt dispersion ^a (%)	mean Pt particle size ^{a,b} (nm)	Pt surface ^b (% of SSA)	SSA (m^2/g)
20% Pt/SiO ₂	20.0	228	22	5.1	10.1	109
5% Pt/SiO ₂	5.0	56	22	5.2	2.1	126
SiO ₂	0					134

^a From CO chemisorption data assuming a Pt:CO ratio of 1:1. ^b Assuming 0.08 nm²/Pt atom.

both Si- and SiC-based MISFET sensors have shown high response for H₂. Because of the chemical resemblance, dispersed platinum particles supported on high surface area silica is an appropriate model system for the Pt–SiO₂–gas interface. In the present study, this system was used to represent the top layers of the MISFET sensor, which are available for gas-phase adsorption. Moreover, deuterium exchange was employed in the DRIFT experiments to increase the understanding of the observed vibrational modes during H₂ and D₂ exposure.

In parallel with DRIFT experiments, electronic structure calculations were performed within the density functional theory (DFT) for atomic hydrogen, adsorbed on a silica cluster, (HO)₃SiOSi(OH)₃, in the neutral, positively, and negatively charged state. Additional to energetic and structural properties, vibrational analysis supported the interpretation of the DRIFT spectra.

2. Experimental Methods

2.1. Sample Preparation. Two Pt/SiO₂ samples, with 5 and 20 wt % Pt loading, were prepared by impregnating colloidal silica with a halogen-free platinum precursor. 1.0 g of colloidal silica (Bindzil 40NH₃•170, 20 nm spherical particles, Akzo Nobel AB, Sweden) was dispersed in 15 g of double distilled water, and the pH was adjusted to 10.5 by addition of ammonium hydroxide (25% NH₄OH, Merck Eurolab, Sweden). An aqueous solution of Pt(NH₃)₄(OH)₂, (Johnson Matthey, UK) with appropriate concentration to give the desired Pt loading for the sample was added dropwise to the silica sol under continuous stirring. The sol was then left under stirring for 1.5 h. The sol was thereafter instantly frozen with liquid nitrogen and freeze-dried. The resulting powder was calcined at 500 °C for 1.5 h. A sample without Pt, that is, pure SiO₂, was prepared accordingly by diluting 2.0 g of the silica sol used in the preparation of the Pt/SiO₂ samples with 30 g of distilled water, pH adjustment to 10.5, followed by freezing, freeze-drying, and calcination at 500 °C for 1.5 h.

2.2. Sample Characterization. The specific surface area of the samples was measured according to the Brunauer, Emmett, Teller (BET) method by N₂ adsorption at 77 K using a Micromeritics ASAP 2010 instrument. The platinum dispersion and the fraction of the surface covered with platinum were determined by chemisorption of CO at 35 °C using a Micromeritics ASAP 2010C instrument. Prior to CO exposure, the samples were pretreated in O₂ at 350 °C for 30 min followed by 5 min evacuation, exposed to H₂ at 400 °C for 120 min, and evacuated. Sample characteristics are presented in Table 1. The platinum dispersion and the mean Pt particle size, assuming spherical particles, are calculated from the CO chemisorption data using a stoichiometric factor of 1 adsorbed CO molecule per platinum surface atom.

2.3. In situ FTIR Measurements. The in situ FTIR measurements were performed in diffuse reflectance (DRIFT) mode using a BioRad FTS6000 spectrometer equipped with a Harrick Praying Mantis DRIFT cell, described previously,^{21,22} at a spectral resolution of 1 cm^{−1}. Feed gases were mixed from

H₂ (99.998%, Air Liquid), O₂ (99.998%, Air Liquid), D₂ (99.998%, Air Liquid), NH₃ (1.01% in Ar, Air Liquid), and Ar (99.998%, Air Liquid) and introduced to the DRIFT cell via individual mass flow controllers (Bronkhorst HiTech) to yield a total flow of 300 mL/min in all experiments. The powder samples were ground in a mortar and mixed with KBr (10 wt % of sample) and then placed in the DRIFT cell. Before each experiment, the samples were pretreated at 400 °C first with 10% O₂ in Ar for 10 min and then with 4% H₂ in Ar for 10 min. After the pretreatment, the samples were cooled in Ar and background spectra were collected for each temperature used in the experiments. The presented DRIFT spectra are always the difference between the current spectra and the corresponding background spectra.

3. Theoretical Method and Model Systems

Several studies of hydrogen adsorbed on silica have appeared in the literature, using both cluster^{15–17} and bulk SiO₂^{18–20} descriptions. In the present study, the aim is to elucidate some characteristics of atomic hydrogen adsorbed on silica. One is the dependence of the charge state of hydrogen. Presently, it is not known if hydrogen diffuses from the Pt to the silica as a proton or as a neutral atom. The calculations also include vibrational analysis to support the interpretation of the experimental DRIFT spectra. The silica is modeled in the simplest possible manner: as a (HO)₃SiOSi(OH)₃ dimer. This approach stresses the local character of the interaction between hydrogen and hydroxylated SiO₂. It has previously been shown that silica clusters with only a few silica tetrahedrons successfully can be used as model systems for studies of silica surface sites.²³ However, one should bear in mind that possible long-range effects are neglected and that the structural flexibility of the cluster is larger than that for a silica bulk surface.

The density functional theory (DFT)^{24,25} was used with a spin-polarized exchange-correlation functional including gradient correction, the Perdew–Burke–Ernzerhof functional (PBE).²⁶ The one-electron Kohn–Sham orbitals were expanded in a linear combination of atomic orbitals (LCAO) using a numerical atomic basis set.^{27,28} This approach allows for a compact basis set, and a so-called double numerical basis with polarization functions²⁹ was used. All electrons were treated variationally. The geometries of the structures were relaxed to find minima on the potential energy surface, and the wavenumbers corresponding to the vibrational modes were calculated in the harmonic approximation via numerical derivatives.

4. Experimental Results

4.1. Exposure of Pt/SiO₂ to H₂. In situ DRIFT spectra taken during exposure of the 20% Pt/SiO₂ sample to H₂ at a constant temperature of 150 °C are presented in Figure 1a. At the onset of hydrogen, a sharp absorption peak immediately appears at 3740 cm^{−1}, characteristic for the OH stretching vibration of isolated noninteracting OH groups on a silica surface.^{30–33} In addition to this peak, an intense broad band centered around

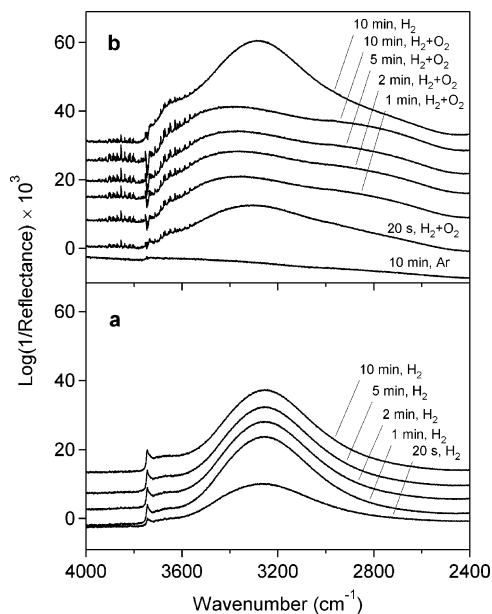


Figure 1. In situ DRIFT spectra of the 20% Pt/SiO₂ sample during exposure to H₂ (a) and H₂ + O₂ (b) at 150 °C. The sample was exposed to 5000 ppm H₂ in Ar for 10 min, flushed with Ar for 10 min, exposed to 5000 ppm H₂ + 10% O₂ in Ar for 10 min, and finally exposed to 5000 ppm H₂ in Ar for 10 min. The spectra are separated by 4×10^{-3} .

3290 cm⁻¹ appears. This band shifts slightly toward lower wavenumbers with increasing intensity. After about 1 min, a maximum in intensity is reached, with the band centered around 3270 cm⁻¹. Mériaudeau et al. have previously observed an intense broad band centered at 3200 cm⁻¹ after exposing Pt/silicalite to hydrogen,³⁴ which the authors suggested to be H bonded to Pt interacting with the silicalite framework. Furthermore, Zholobenko et al. observed a broad band at 3200 cm⁻¹ in a DRIFT study of H-MFI zeolite, which they assigned to OH groups hydrogen-bonded to oxygen in the zeolite framework.³⁵ In general, OH stretching modes of hydroxyl groups on metal oxides are located in the region 3800–3000 cm⁻¹³⁶ and characteristic vibrations of different hydroxyl groups on silica between 3800 and 3200 cm⁻¹.³⁷ It is thus most likely that the broad band observed in the present study arises from the OH stretching vibration of hydroxyl groups. Observations of broad bands centered around 3450–3600 cm⁻¹ have been reported on various silica surfaces, which have been assigned both to OH stretching vibrations of hydrogen-bonded hydroxyl groups and to OH stretching vibrations of adsorbed water.^{30,32,33,37–39} OH stretching vibrations of condensed water are reported to have a broad band centered around 3400 cm⁻¹, and the deformation vibration has a narrow band centered at 1635 cm⁻¹.⁴⁰ Consequently, it can be difficult to distinguish between the OH stretching vibrations of perturbed, hydrogen-bonded surface hydroxyl groups and the OH stretching vibration of adsorbed water molecules due to the heterogeneity of both of these surface groups, with broad overlapping absorption bands. In the present study, only H₂ is present in the feed during the first experiments. However, the presence of trace amounts of oxygen cannot be completely excluded and water would in that case likely be formed on the platinum in the samples.

The formation of surface groups during H₂ exposure is a reversible process. When the H₂ supply is turned off, the broad band centered around 3270 cm⁻¹ completely disappears after 10 min and only a very small peak remains at 3740 cm⁻¹ (bottom spectrum of Figure 1b).

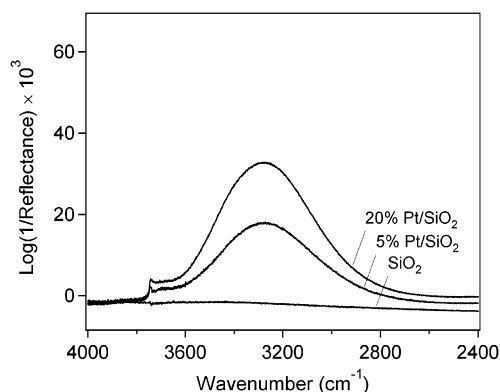


Figure 2. In situ DRIFT spectra of Pt/SiO₂ samples with different Pt loadings after 10 min exposure to 1000 ppm H₂ in Ar at 150 °C.

To further investigate the influence of water, the Pt/SiO₂ sample was exposed to hydrogen, but this time in the presence of 10% oxygen. The collected DRIFT spectra are presented in Figure 1b. A sharp negative peak is observed at 3740 cm⁻¹, indicating that the isolated OH groups present before the simultaneous exposure to H₂ and O₂ are perturbed or removed. Furthermore, a very broad positive feature appears in the range 3800–2400 cm⁻¹ immediately at the onset of hydrogen and oxygen. Initially, this broad feature consists of one band centered around 3320 cm⁻¹. However, with increasing exposure time, two overlapping bands, centered around 3400 and 2800 cm⁻¹, respectively, can be resolved. Thus, it seems likely that the perturbed silanol groups formed during H₂ exposure initially are formed also in the presence of oxygen. However, with increasing exposure time, the band due to condensed water around 3400 cm⁻¹ increases and overlaps the band at 3270 cm⁻¹, which corresponds to perturbed OH groups. Rotational bands between 3950 and 3550 cm⁻¹, which are characteristic for gaseous water,⁴¹ are also observed during the simultaneous exposure to H₂ and O₂. Furthermore, at lower wavenumbers, a positive peak is observed at 1630 cm⁻¹, which overlaps with rotational bands for water between 1900 and 1350 cm⁻¹. The peak at 1630 cm⁻¹ corresponds to the reported deformation vibration of condensed water,⁴⁰ indicating the formation of adsorbed water when both H₂ and O₂ are present. When oxygen is removed from the feed and the sample is exposed to only H₂, the broad band of the perturbed OH groups reappears overlapping the observed broad bands of adsorbed water and shifts slightly to 3320 cm⁻¹ (top spectrum in Figure 1b). Thus, the origin of the band at 3320 cm⁻¹ seems to be different from adsorbed water.

DRIFT spectra collected after 10 min exposure to hydrogen of Pt/SiO₂ samples with different Pt loading are presented in Figure 2. A striking observation is that no new IR active surface species are formed without Pt in the sample. The very small negative peak at 3740 cm⁻¹ observed in the spectrum of pure SiO₂ can be caused by species very weakly adsorbed to the isolated silanol groups. The intensities of the 3740 and 3270 cm⁻¹ bands in the DRIFT spectrum of the 5% Pt/SiO₂ sample are significantly lower as compared to the corresponding bands for the 20% Pt/SiO₂ sample. Although it is difficult to quantify absorption peaks in DRIFT spectra, this indicates that the amount of new isolated silanol groups is correlated to the amount of platinum in the samples.

Exposure of the 20% Pt/SiO₂ sample to hydrogen was performed at different temperatures (see Figure 3), and it is clear, by the appearance of the two bands discussed above in all spectra, that new silanol groups are formed in the entire

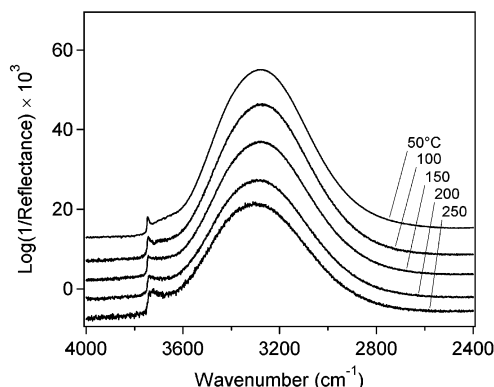


Figure 3. In situ DIRFT spectra of the Pt/SiO₂ sample with 20% Pt after 10 min exposure to 1000 ppm H₂ in Ar at different temperatures. The spectra are separated by 4×10^{-3} .

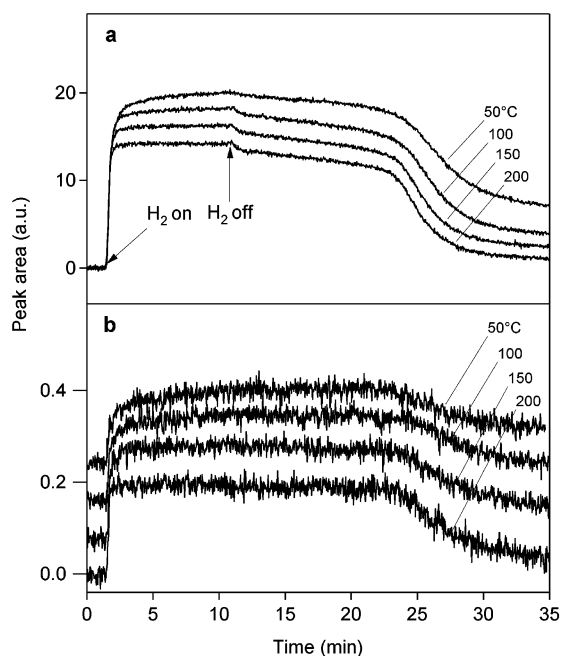


Figure 4. The peak area intensities as a function of time for (a) the broad band centered at 3270 cm⁻¹ and (b) the 3740 cm⁻¹ peak, during experiments performed at different temperatures where 1000 ppm H₂ in Ar was added to the feed after 1 min and removed from the feed after 10 min. The graphs are separated by 0.08 in (b).

investigated temperature interval. A slight shift of the band to higher wavenumbers with higher temperatures can be observed for the broad band at 3270 cm⁻¹. In this experiment, the DRIFT spectra are continuously collected with a frequency of 0.5 Hz. In Figure 4, the evolution of surface species during exposure of the 20% Pt/SiO₂ sample to hydrogen is followed by investigating the integrated area under each band (i.e., 3740 and 3270 cm⁻¹). [The peak areas under the band at 3270 cm⁻¹ were calculated between 3650 and 2630 cm⁻¹ using a baseline drawn from 3800 to 2500 cm⁻¹ in the spectra, and under the peak at 3740 cm⁻¹ the areas were calculated between 3765 and 3710 cm⁻¹ using a baseline drawn from 3820 to 2440 cm⁻¹]. The hydrogen was always added to the feed after 1 min and removed again 10 min later. A first observation is that the formation of the new silanol groups is rapid and without temperature dependence. A more thorough investigation of the initial formation rate of the two bands (i.e., 3740 and 3270 cm⁻¹) shows minor temperature dependence. By analyzing the Arrhenius plot, a rough estimation indicates that the activation barrier in both cases is only 2 kJ/mol. A further observation

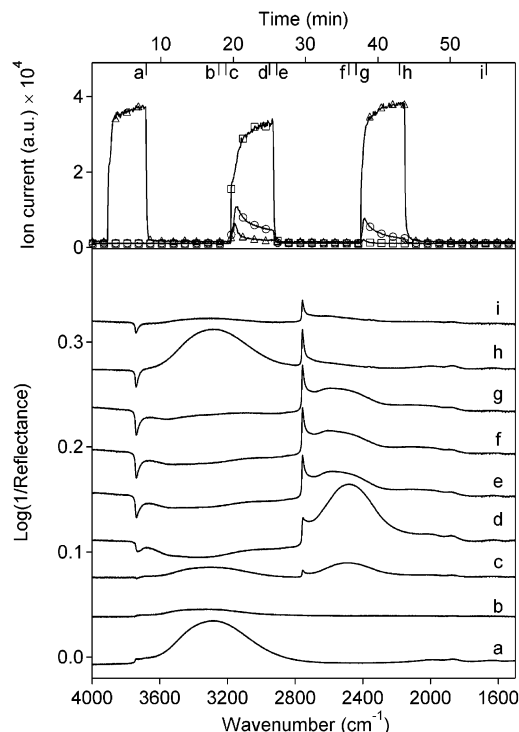


Figure 5. (Top) Corresponding MS ion currents of masses $m/e = 2$ (Δ), $m/e = 3$ (\circ), and $m/e = 4$ (\square) representing the outlet gas composition. (Bottom) In situ DRIFT spectra of the Pt/SiO₂ sample with 20% Pt collected at 150 °C (a) after 5 min exposure to 1000 ppm H₂ in Ar, (b) after 10 min exposure to Ar, (c) at the onset of 1000 ppm D₂ in Ar, (d) after 5 min exposure to 1000 ppm D₂, (e) at the removal of D₂, (f) after 10 min exposure to Ar, (g) at the onset of 1000 ppm H₂, (h) after 5 min exposure to 1000 ppm H₂, and (i) after 10 min exposure to Ar.

from these experiments is that the removal of the perturbed silanol species, the broad band at 3270 cm⁻¹, seems to proceed in a two-stage process. After the removal of hydrogen, a slow decrease of the peak area during 10–13 min is followed by a much faster decrease. This behavior is not seen when analyzing the evolution of the peak area of the isolated silanol groups at 3740 cm⁻¹. However, the removal of these groups seems to be correlated to the second fast process.

4.2. H/D Exchange. To further analyze the origin of the hydrogen related absorption bands, an experiment was performed where the 20% Pt/SiO₂ sample initially was exposed to H₂, evacuated, and subsequently exposed to D₂ at 150 °C. In addition to the DRIFT spectra collected at different times during the experiment (Figure 5a–i), the outlet gas composition from the DRIFT cell was continuously analyzed by mass spectrometry and the ion currents of masses $m/e = 2$, 3, and 4 representing H₂, HD, and D₂, respectively, are displayed in the top graph of Figure 5. The letters representing each DRIFT spectrum show in this graph at what time the spectrum was collected. After 5 min of H₂ exposure (Figure 5a), the two features discussed above, at 3740 and 3270 cm⁻¹, are observed, and after 10 min of Ar exposure they almost completely disappear (Figure 5b). When D₂ is added to the feed (Figure 5c), two new vibrational bands are observed, one sharp peak at 2755 cm⁻¹ and a broad band centered around 2500 cm⁻¹. These features correlate with the expected shift ($\omega_D \approx 0.7 \omega_H$) toward lower wavenumbers for new isolated and perturbed surface OD groups. After 5 min of D₂ exposure (Figure 5d), the intensities of the new bands increase and negative bands are observed at 3740 and 3400 cm⁻¹, indicating exchange of H with D in OH groups initially present on the sample surface. The H/D exchange is

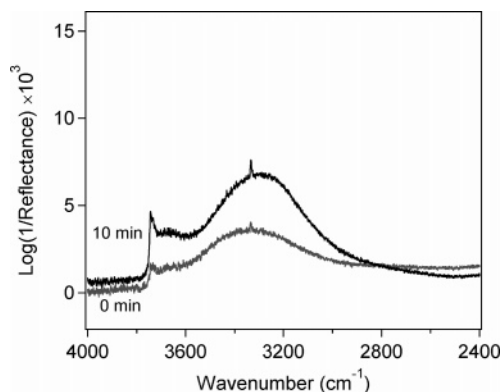


Figure 6. In situ DRIFT spectra of the Pt/SiO₂ sample with 20% Pt collected directly after onset and after 10 min exposure to 1000 ppm NH₃ in Ar at 225 °C.

also demonstrated in the MS signals (top Figure 5) where loss of hydrogen from the sample surface is observed by the formation of HD ($m/e = 3$) and a slight increase of the outlet H₂ signal ($m/e = 2$). It is also observed that the maximum exchange is achieved within the first minute after the switch from Ar to D₂ and continues during the D₂ exposure. When the D₂ supply is turned off, the intensities of the H₂ and HD signals ($m/e = 2$ and 3) rapidly decline and the exchange ceases. The DRIFT spectra show that after removing D₂ from the feed (Figure 5e and f) the intensity of the broad band at 2500 cm⁻¹ decreases and shifts to 2610 cm⁻¹, while the intensity of the peak at 2755 cm⁻¹ remains constant. When the sample once again is exposed to H₂ (Figure 5g), the broad band at 3270 cm⁻¹ reappears; however, the peak at 3740 cm⁻¹ is still negative but with decreased intensity. The intensity of the peak at 2755 cm⁻¹ remains constant or decreases slightly during the 5 min of H₂ exposure (Figure 5h); however, the broad band at 2610 cm⁻¹ disappears. Formation of HD is observed during the H₂ exposure by the increase in the HD ion current $m/e = 3$, indicating that deuterium in the OD groups, corresponding to the stretching band at 2610 cm⁻¹, is exchanged with hydrogen. When H₂ is removed from the feed and the sample is exposed to Ar for 10 min (Figure 5i), the broad band at 3270 cm⁻¹ disappears; however, the negative peak at 3740 and the positive peak at 2755 cm⁻¹ both remain, although with decreased intensity, indicating that the H/D exchange occurs also for isolated OH groups originally present on the silica surface.

In addition to the two bands discussed above, weak vibrational bands can be observed at 2000, 1875, and 1640 cm⁻¹, during both H₂ and D₂ exposure, which disappear after turning off the H₂ or D₂ supply. As no shift of the position of these bands could be observed during D₂ exposure, the most likely assignment of these bands is to vibrations in the SiO₂ lattice. Absorption bands observed for dry silica at 2000, 1870, and 1635 cm⁻¹ have previously been suggested to be overtones and/or combination bands of Si–O lattice vibrations.⁴²

4.3. Exposure of Pt/SiO₂ to NH₃. Ammonia adsorption on Pt/SiO₂ samples has recently been investigated by in situ DRIFT spectroscopy.¹³ In this study, it was observed that NH₂ groups are formed on the Pt surface upon NH₃ exposure at 50 and 150 °C. Thus, it is likely that atomic hydrogen would be present in the sample also during ammonia exposure.

Figure 6 presents the DRIFT spectra collected when the 20% Pt/SiO₂ sample is exposed to ammonia at 225 °C, a temperature at which the Pt-based MISiCFET sensor has shown high sensor response for NH₃.⁶ A clear resemblance with the DRIFT spectra collected during exposure of the same sample to H₂ is observed where a peak at 3740 cm⁻¹ and a broad band at 3270 cm⁻¹

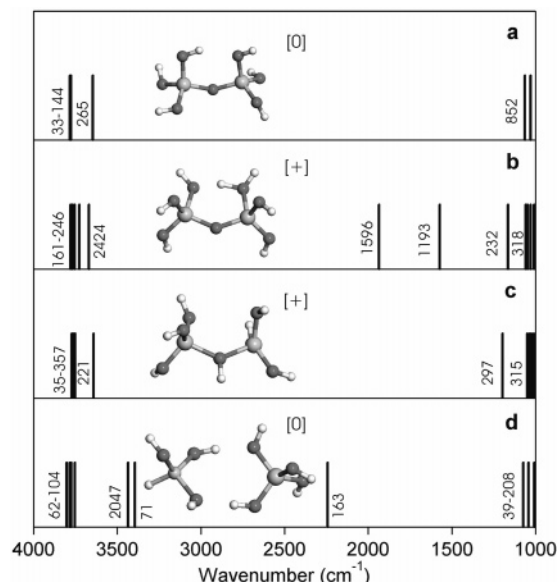


Figure 7. Geometry optimized structures and vibrational analysis results from the DFT calculations of (a) the silica dimer, (HO)₃SiOSi(OH)₃, of positively H species adsorbed (b) on one of the OH groups and (c) on the oxygen bridge, (HO)₂SiOHSi(OH)₃, and (d) adsorption of two neutral hydrogen species on the (HO)₃SiOSi(OH)₃. The calculated wavenumbers are presented as a stick with corresponding intensities (km/mol) next to each stick.

appear when NH₃ is added to the feed, although not as intense as during the H₂ exposure. This indicates that hydrogen species adsorbed on the platinum particles spill over to the silica surface both during H₂ exposure and during NH₃ exposure. The additional sharp peak, observed at 3336 cm⁻¹, is characteristic for NH stretching of gas-phase ammonia.⁴¹

5. Computational Results

5.1. Structure and Energetics. Electronic structure calculations of hydrogen species adsorbed on silica, represented by the (HO)₃SiOSi(OH)₃ cluster, have been performed to gain further understanding of the surface species formed upon hydrogen adsorption on Pt/SiO₂. For the system studied in the present work, hydrogen adsorbs and dissociates on Pt and the formed hydrogen species can spill over to the silica surface. The picture that has emerged from the DRIFT study is that H₂ adsorbs and dissociates on the Pt or Pt/SiO₂ interface. The H species thereafter diffuse to the silica surface. The character (charged state) of these species is, however, unknown. In fact, the character of H spilling over from metal to metal oxide is under debate.^{43,44} The structure of the geometry optimized silica cluster is presented as the inset in Figure 7a. The bond length between the silicon and oxygen atoms varies between 1.64 and 1.66 Å, and the bond length between the oxygen and hydrogen atoms varies between 0.97 and 0.98 Å.

The calculations of adsorbed hydrogen revealed a very weak interaction between the silica dimer and the neutral hydrogen atom. This is in agreement with previously reported calculations of weak or no interaction between neutral hydrogen species and bulk silica.^{18,19} Different adsorption geometries of H⁺ on the dimer were investigated. The two lowest energy configurations are presented in Figure 7b and c. In Figure 7b, a “water” species is found, whereas H⁺ binds to the bridging O in Figure 7c. Figure 7b shows the stable configuration with binding energy of 8.9 eV. The structure in Figure 7c is ~0.4 eV higher in energy, that is, a binding energy of 8.5 eV. In the case of negatively charged hydrogen species, a local minimum was

obtained with H^- adsorbed on Si. However, this configuration is unstable (by 0.5 eV) with respect to $\text{H}_2 + [(\text{HO})_3\text{SiOSi}(\text{OH})_3]^-$. Previous electronic structure calculations of charged species in bulk SiO_2 , where no OH groups are present, show that the most stable configuration for the positively charged hydrogen species is adsorption on the oxygen of the siloxan bridge. For the negatively charged hydrogen, adsorption on one of the silicon atoms is the most stable configuration.^{18,19}

5.2. Vibrational Modes. The calculated vibrational modes of the silica cluster and for the adsorbed hydrogen species are presented in Figure 7. In all cases, there are vibrational modes between 3750 and 3780 cm^{-1} , corresponding to the OH stretching vibrations of isolated silanol groups. These are slightly higher wavenumbers than the reported experimental value of the isolated OH stretching mode at 3740–3750 cm^{-1} .^{30–33} Modes of SiO vibrations are calculated to be in the lower wavenumber region below 1100 cm^{-1} . For the silica dimer (Figure 7a), there is a 130 cm^{-1} shift of one OH stretching mode of isolated silanol groups to 3646 cm^{-1} , caused by weak interaction between the oxygen of one OH group in the silica dimer close to a hydrogen of another OH group. This correlates well with the reported experimental values of weakly bonded (vicinal) silanol groups at 3650–3660 cm^{-1} .^{31–33} In Figure 7b, the calculated vibrational modes for the case with a positively charged hydrogen species adsorbed on a hydroxyl group are presented. Two vibrational modes are observed at 1935 and 1571 cm^{-1} , which correlate to deformation modes relating to the HOH group. The group resembles adsorbed water, and experimentally reported deformation modes of condensed water show two bands, one with low intensity centered at 2130 cm^{-1} and one more pronounced band at 1635 cm^{-1} .⁴⁰ Additionally, there are small shifts of two OH stretching modes, again correlated to perturbed OH groups. In the second case of the adsorbed positively charged hydrogen species, the calculated vibrational modes are presented in Figure 7c. The vibrational mode at 3641 cm^{-1} corresponds to the OH stretching mode of the OH species formed on the oxygen bridge. In the lower wavenumber region, a vibrational mode at 1197 cm^{-1} corresponds to the deformation mode of the adsorbed H species.

In summary, the vibrational analysis of adsorbed hydrogen species, in the neutral, positively, and negatively charged state, only reveals wavenumber shifts of about 130 cm^{-1} for the OH stretching vibration modes and some features corresponding to a water-like surface species. There are no vibrational modes corresponding to the larger shift of OH stretching vibrations observed in the DRIFT experiments during exposure of Pt/ SiO_2 to H_2 .

Calculations were performed for two neutral hydrogen species adsorbed on the silica dimer. The optimized structure is presented as the inset in Figure 7d, and the calculation reveals that the oxygen bridge of the silica dimer is broken and one silica monomer, $\text{Si}(\text{OH})_4$, is formed together with one $\text{HSi}(\text{OH})_3$ species. The closest distance between the two molecules is 1.79 Å, and the weak H bonding of ~0.5 eV between the two clusters gives rise to perturbation of the OH stretching modes of the involved silanol groups resulting in shifts of the vibrations to 3395 and 3434 cm^{-1} . Thus, wavenumber shifts of OH stretching modes due to this type of hydrogen bonds can be found in the same order as the experimentally observed shift. Additionally, the intensity is very strong for one of the calculated vibrational bands, which is consistent with the experimentally observed bands. The vibrational mode at 2245 cm^{-1} corresponds to the SiH stretching in the $\text{HSi}(\text{OH})_3$ cluster. The structure in Figure 7d is 0.22 eV less stable than $\text{H}_2 + (\text{HO})_3\text{SiOSi}(\text{OH})_3$.

However, although the formation of the species in Figure 7d is an exothermic process, it is not an impossible scenario, as atomic hydrogen, and not hydrogen molecules, is present in the Pt/ SiO_2 system. Moreover, the experimentally observed bands of new H species on silica disappeared when H_2 was removed. Consequently, the H species on silica are in equilibrium with the H_2 partial pressure.

We note that the perturbed vibrational mode at 3400 cm^{-1} can be present within the framework of a silica cluster. This was verified by explicit calculations for a larger $\text{Si}(\text{OSi}(\text{OH})_3)_4$ cluster. These calculations revealed vibrations in the 3405–3511 cm^{-1} region due to perturbed OH stretching modes.

6. Discussion

The DRIFT experiments in the present study have shown that new hydroxyl groups are formed on silica during H_2 exposure only when Pt is present on the surface. Thus, new OH groups are not produced by molecular hydrogen interacting directly with the silica surface. Instead, atomic hydrogen species, formed by dissociation of hydrogen molecules on the Pt surface, spill over to the silica surface and form new hydroxyl groups. Estimation of the activation barrier (2 kJ/mol) shows that this is a nonactivated process. From the peak observed at 3740 cm^{-1} , it is clear that one type of new OH group is isolated silanol groups. However, the origin of the perturbed OH stretching vibration observed in the DRIFT measurements at 3270 cm^{-1} is not obvious. Considering the calculated shifts of vibrations for the adsorbed neutral, positively, or negatively charged H species on the silica dimer, it is not likely that any of these species form surface groups that directly cause this perturbation. However, the calculations show that two neutral hydrogen species are able to break a SiO bond of the siloxan bridge to form $\text{Si}(\text{OH})_3$ and $\text{HSi}(\text{OH})_3$ clusters. The interactions between these two clusters cause wavenumber shifts similar to the experimentally observed shift. This implies that perturbations such as the ones observed in the DRIFT spectra may arise from interactions between the OH groups in the silica surface, caused by structural changes of the surface.

The DRIFT experiments show that the sample surface is saturated with new OH species within the first minutes of H_2 exposure (Figure 4). Although the sample with a higher amount of Pt has lower available silica surface area, the coverage of new OH groups is higher as compared to the sample with a lower amount of platinum. The number of new OH groups is thus correlated with the surface coverage of Pt. The calculated platinum dispersions as well as the mean platinum particle size for the two Pt-containing samples are very similar. Thus, the total interfacial area, between Pt and SiO_2 , is considerably higher in the sample with high Pt content. Because the new OH groups most likely are formed on the silica surface, this indicates that the Pt–silica interface is of major importance for the formed OH groups. A possible explanation for the higher OH coverage with higher Pt content is that migration of atomic hydrogen species is limited to a certain distance from the Pt particles. However, an IR study by Cevallos-Candau et al. showed that hydrogen in OH groups on a Pt-free silica sample were exchanged by atomic deuterium, migrating from a Pt/ Al_2O_3 point source, as far away as 9 mm.⁴⁵ Hence, an explanation for the dependence on the interface area would more likely be that the new OH groups observed in the DRIFT spectra are formed only very close to the Pt–silica interface. In a study of hydrogen adsorption to a Pt/silicalite sample, Mériaudeau et al. proposed that a broad band observed at 3200 cm^{-1} in the infrared spectra is due to hydrogen bonded to Pt interacting with the silicalite

framework.³⁴ However, our results suggest that the band could be due to formation of hydroxyl groups at the Pt–silica interface, interacting with OH groups on the silica surface.

The DRIFT experiments in the present study show that the new OH species are reversibly formed on the silica surface when platinum is present. A puzzling behavior of the system is, however, the observed two-stage process when the new OH groups disappear after gaseous hydrogen is removed from the feed. The first slow decrease, or delay time, is equally long for the Pt/SiO₂ samples with 20 and 5% Pt, respectively. The delay time is therefore not dependent on the interfacial area. A hypothesis for this behavior is that the new OH groups are formed only near the Pt–silica interface at the same time as hydrogen species are able to migrate over the entire silica surface and possibly also in the bulk. The activation barrier for diffusion of atomic hydrogen in an amorphous silica film has been reported to be only 0.3 eV.^{46,47} These weakly bound surface species would not be observed in the DRIFT spectra. Desorption of hydrogen may follow different paths, and one is recombination to H₂ on the silica surface, followed by desorption to the gas phase. Another path is a spillover process of hydrogen species from the silica to the Pt surface followed by recombination and desorption of H₂. There is also a reversed step for the OH formation at the Pt–silica interface, when the hydrogen feed is turned off. However, as long as hydrogen species are present, there may be re-formation of OH groups. When all H species in the silica are removed, the DRIFT band corresponding to the interfacial OH groups disappears.

The charged state of the hydrogen species participating in the spillover process is not clear. Experimental support for both H atoms and H⁺ species is found for similar catalytic systems, that is, transition metals supported on silica.⁴³ Recently, Roland et al. argued that the hydrogen species should not be defined as an invariable species but rather a species that may change charge state depending on the support. They concluded that the hydrogen participating in the spillover process should be regarded as a chemisorbed surface electron donor.⁴³ According to the present computational result, a neutral hydrogen atom would not be expected to adsorb on silica. It is probable that the experimentally observed formation of new OH species involves this kind of electron-transfer process to form charged adsorbed species. At the Pt surface, the hydrogen is not expected to form H⁺, and it is not likely that there would be transfer of an electron from a hydrogen atom to the insulating bulk SiO₂. Therefore, if electrons are transferred from the hydrogen atoms, it would most likely be at the Pt–silica interface, where platinum might change the local structure of the silica or act as an electron sink. This assumption correlates well with the indications that the new OH species are formed at or near the Pt–silica interface.

7. Concluding Remarks

In the present study, vibrational properties of surface species formed upon hydrogen adsorption on Pt/SiO₂ have been investigated with in situ DRIFT spectroscopy at different temperatures. Additionally, deuterium exchange experiments and electronic structure calculations within DFT for adsorbed hydrogen species on silica clusters were performed to support the assignments of the absorption bands in the DRIFT spectra.

During exposure to hydrogen, new isolated as well as perturbed OH groups were observed on Pt/SiO₂, whereas no detectable surface species were formed on pure SiO₂. The new OH species appeared at all of the measured temperatures, 50–250 °C. The surface coverage of OH groups correlated to the Pt surface coverage, indicating that the new OH groups were formed at, or in the vicinity of, the Pt–SiO₂ interface.

Adsorption of ammonia was performed at a temperature relevant to the MISiCFET sensor response for ammonia, 225 °C. This experiment showed formation of the same surface OH groups as observed during hydrogen exposure, and this strongly indicates that hydrogen spillover occurs also during exposure of Pt/SiO₂ to NH₃. For the understanding of the sensor mechanism for ammonia detection, this supports the suggestion in a previous report¹³ that it resembles the mechanism for hydrogen response.

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