The Adsorption of Triethylenediamine on Al$_2$O$_3$-II: Hydrogen Bonding to Al−OH Groups

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Received: August 12, 2004

The hydrogen bonding of the triethylenediamine (TEDA) molecule to isolated Al−OH groups on partially dehydroxylated high area γ-Al$_2$O$_3$ powder has been studied using transmission IR spectroscopy. It has been found that TEDA adsorbs both singly and as multiple species to single Al−OH groups in clearly separable equilibrium stages of adsorption at 300 K. The reversible adsorption of a single TEDA molecule to Al−OH fits the Langmuir adsorption isotherm well, and the enthalpy of adsorption is found to be −15.6 ± 0.5 kJ mol^{-1} in the range of fractional coverage of 0.5−0.6. Red shifts of the Al−OH frequency from $\sim$ −200 cm^{-1} to $\sim$ −1000 cm^{-1} are observed as a result of −OH bonding to the N lone pair in the TEDA molecule.

I. Introduction

The strong bonding of triethylenediamine to Al−OH groups on high area γ-Al$_2$O$_3$ surfaces has been investigated in detail using transmission IR spectroscopy to observe hydrogen bonding to the partially dehydroxylated surface. The mode and strength of surface bonding is of importance because of the use of TEDA to enhance the adsorption properties of various support surfaces used for the adsorption of toxic gases. A previous paper[1] has described certain aspects of the bonding of TEDA to Al$_2$O$_3$ and its stability on the surface.

This paper reports the thermodynamic details of hydrogen bonding of TEDA to surface Al−OH groups. Surprisingly, two stages of TEDA adsorption by hydrogen bonding have been discovered, and these bonding modes are thought to involve the adsorption of either a single TEDA molecule or two TEDA molecules to a single Al−OH group. A key feature of the adsorption of molecules by hydrogen bonding to surface −OH groups is the large red shift in vibrational frequency experienced by the −OH group as well as a significant enhancement in its integrated IR intensity.[1]

II. Experimental Methods

The experimental methods used in this work are described in detail in ref 1. Briefly, a transmission IR cell contains a flat tungsten grid into which the Al$_2$O$_3$ sample is pressed by a hydraulic press. The grid allows the sample to be heated electrically and cooled by a refrigerant, and the grid transmits about 80% of the incident IR radiation. The IR cell is connected to a stainless steel vacuum system with a base pressure < 1 × 10^{-8} Torr. Gas may be dosed quantitatively onto the sample. Al$_2$O$_3$ activation is accomplished by heating the sample in a vacuum to 1200 K to partially remove hydroxyl groups. A MKS capacitance manometer and a Bayard−Alpert ionization gauge are used to measure pressure, and a quadrupole mass spectrometer may be used to measure the gas composition. A Bruker TENSOR 27 FT-IR spectrometer operating at 2 cm^{-1} resolution is used to obtain the absorption spectra.

III. Experimental Results

A. IR Spectral Studies of TEDA Hydrogen Bonding. The spectral developments which occur in the Al−OH stretching
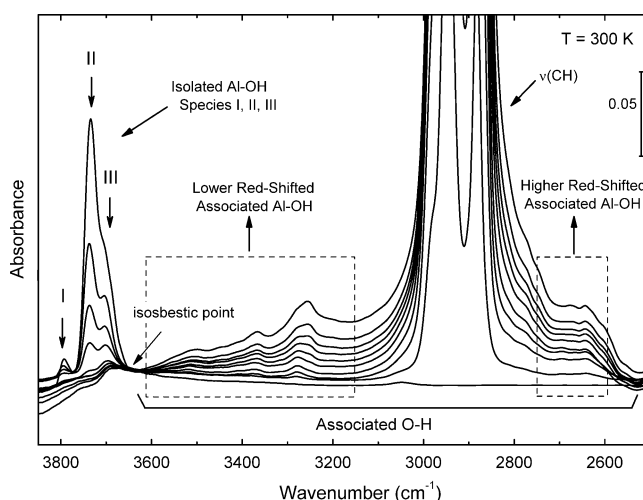

Figure 1. FT-IR spectra of adsorbed TEDA on Al$_2$O$_3$ at 300 K with increasing equilibrium pressure of TEDA. P = 0, 1, 2, 3, 5, 18, 44, 82, 135, 246 mTorr.

region as TEDA is adsorbed to various coverages at increasing equilibrium partial pressures at 300 K are shown in Figure 1. It is observed that the absorbance of the isolated Al−OH modes are monotonically attenuated as the TEDA coverage increases, and that a broad band due to hydrogen-bonded Al−OH groups is produced. Superimposed on the broad hydrogen-bonded modes is the absorbance due to ν(CH) bands for adsorbed TEDA. Two spectral regions due to associated Al−OH species are designated by dotted boxes in Figure 1. Three different kinds of isolated Al−OH species are observed prior to TEDA adsorption: (1) a terminal OH group (I) being coordinated to a Al^{3+} cation with ν(OH) $\cong$ 3800 cm^{-1}; (2) a bridging OH group (II) being coordinated to two neighbor Al^{3+} cations with ν(OH) $\cong$ 3740 cm^{-1}; and (3) a 3-fold bonded OH group (III) being coordinated to three Al^{3+} cations in octahedral coordination with ν(OH) $\cong$ 3700 cm^{-1}.[2] The observation of an isosbestic point suggests that a stoichiometric conversion from free −OH to isolated −OH groups is occurring. The shift in −OH frequency due to hydrogen bonding to TEDA occurs down to $\sim$2600 cm^{-1}, over an amazingly large frequency range for hydrogen bonding. The three types of Al−OH group exhibit somewhat different kinetics for TEDA adsorption. As TEDA is adsorbed, the
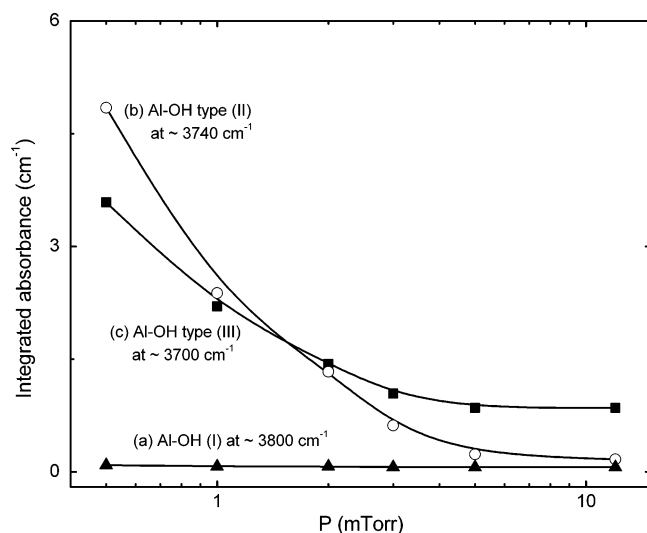
Figure 2. The decrease in the integrated absorbance of: (a) type (I) Al−OH species observed at ∼3800 cm^{-1}; (b) type (II) Al−OH species observed at ∼3740 cm^{-1}; (c) type (III) Al−OH species observed at ∼3700 cm^{-1}.

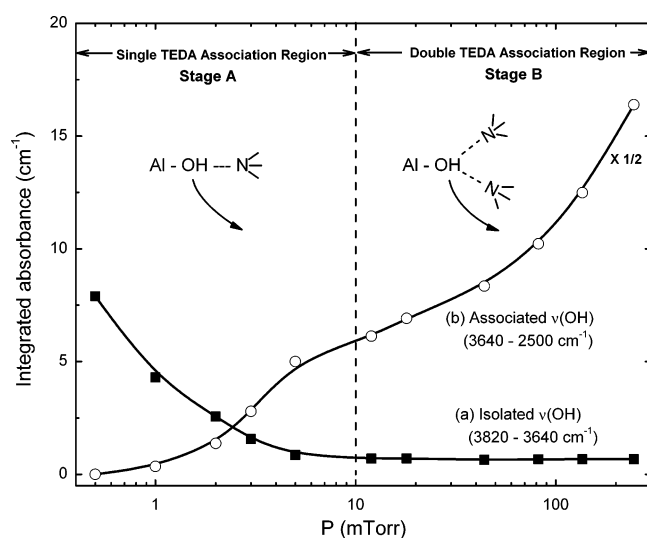**Figure 3.** Relationship between: (a) the decrease of the isolated Al−OH integrated absorbance in the 3820−3640 cm^{-1} region; and (b) the integrated absorbance of the associated Al−OH species in the 3640−2500 cm^{-1} region with increasing coverage of TEDA at 300 K.

efficiency of hydrogen bonding to species (II) (∼3740 cm^{-1}) is highest as shown in Figure 2.

Figure 3 shows a plot of the integrated absorbance of the isolated Al−OH modes compared to the integrated absorbance of the hydrogen-bonded Al−OH modes. The integrated absorbance of the hydrogen-bonded Al−OH modes is obtained in the 3640−2500 cm^{-1} region assuming a smooth contribution under the ν(CH) bands due to TEDA adsorption. At an equilibrium pressure of about 10 mTorr at 300 K, the isolated Al−OH species have been completely complexed by TEDA adsorption and the integrated intensity of the associated Al−OH modes has reached a plateau in absorbance. This region of adsorption is designated Stage A and is associated with the bonding of a single TEDA molecule to an isolated Al−OH group. Even after all the isolated −OH groups disappear in Stage A adsorption, the integrated intensity of associated Al−OH bands continues to increase during Stage B adsorption. At equilibrium pressures of TEDA above about 10 mTorr, Stage B of TEDA bonding is observed. Here, the integrated intensity
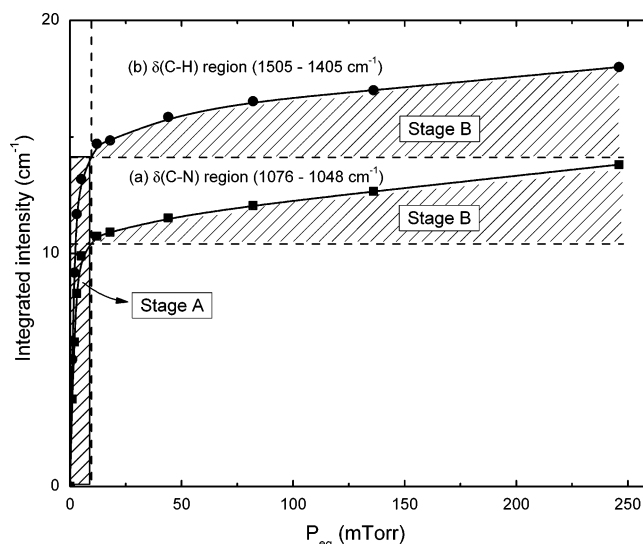

Figure 4. Plots of the integrated absorbance of the several TEDA modes with increasing coverage of TEDA at 300 K: (a) δ(C−N) region (1076−1048 cm^{-1}); (b) δ(C−H) region (1505−1405 cm^{-1}).

of the associated Al−OH groups rises by more than a factor of 2 above its intermediate plateau value as a second TEDA molecule is adsorbed onto the Al−OH group. The two stages of TEDA adsorption may also be correlated with the increase of TEDA coverage.

Figure 4 shows the integrated absorbance for two vibrational bands associated with the TEDA molecule as the equilibrium TEDA coverage is increased at 300 K. For both of the δ-CN skeletal deformation mode and the δ-CH deformation modes (1505−1405 cm^{-1}), two stages of adsorption are also observed. Stage A occurs below 10 mTorr; Stage B occurs above 10 mTorr, and both stages are designated by the crosshatched regions on each isotherm in Figure 4. These integrated absorbance measurements indicate that approximately 30% of the adsorption up to 250 mTorr occurs in stage B, after all Al−OH groups have been converted in Stage A adsorption to associated Al−OH groups by the adsorption of a single TEDA molecule.

The relative rate of TEDA adsorption by hydrogen bonding to the three types of Al−OH groups (I, II, and III) differs, as shown in Figure 2. Also, the reactive rate of producing hydrogen-bonded Al−OH⋯TEDA species varies as the TEDA coverage is increased. Figure 5 shows the integrated −OH absorbance behavior of the two categories of associated Al−OH⋯TEDA species. We focus only on Stage B TEDA adsorption, where a second TEDA molecule is postulated to adsorb on an Al−OH group already containing a single TEDA molecule. It may be seen that Stage B of adsorption is more associated with the production of hydrogen-bonded Al−OH groups with lower red shifts. In Stage A of TEDA adsorption the higher red shifted Al−OH⋯TEDA species seem to be favored compared to the lower red-shifted species.

B. Detailed Isotherm Studies. In the previous paper, TEDA adsorption on Al−OH sites at 300 K was fitted to the Langmuir adsorption kinetic model.[1] Figure 6 shows the isotherms for TEDA absorption on Al−OH groups as a function of equilibrium pressure at various temperatures. These isotherms were measured in a special way in order to investigate bonding of TEDA specifically to the Al−OH groups. We assume that the decrease in integrated absorbance of the isolated Al−OH groups is linearly dependent on the coverage on the single Al−OH⋯TEDA complex. Other measures of TEDA coverage might not be so specific to the Al−OH⋯TEDA species coverage.

TEDA Adsorption on Al$_2$O$_3$: II

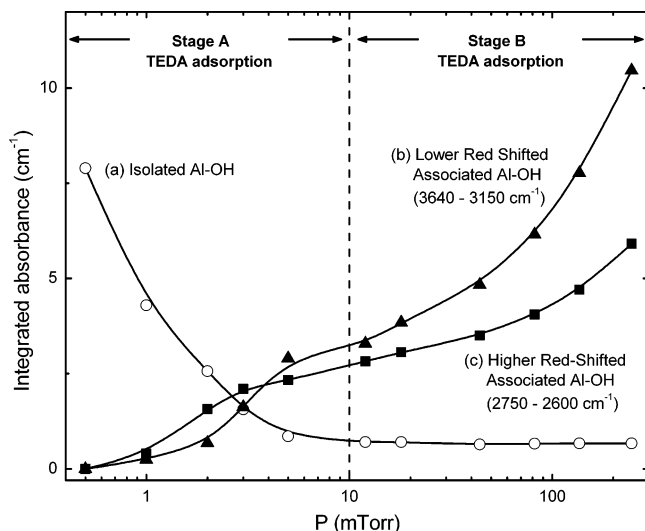*J. Phys. Chem. B, Vol. 109, No. 8, 2005* **3509**

Figure 5. The relationship between loss of (a) the isolated Al−OH species and (b) the gain of associated OH species in the lower red-shifted associated region (3640−3150 cm^{-1}) and (c) in the higher red-shifted associated region (2750−2600 cm^{-1}).
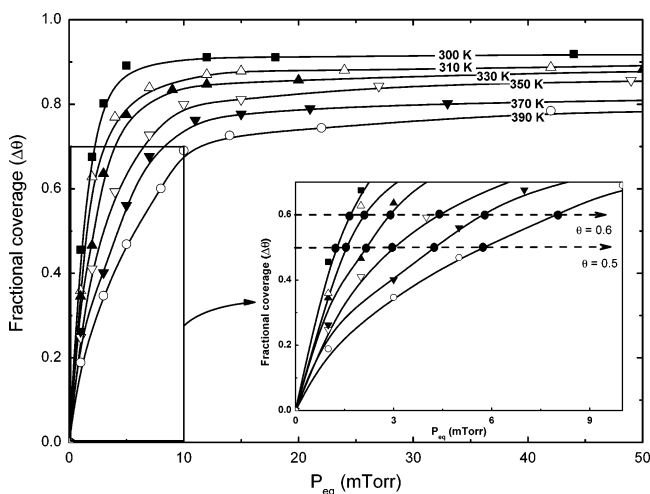

Figure 6. Isotherm plots of TEDA adsorption on Al−OH groups at various temperatures. The insert shows a magnified view in the region below 10 mTorr (Stage A) and the cuts at $\theta = 0.5$, and 0.6.

Figure 6 shows, as would be expected, that the saturation equilibrium coverage of TEDA decreases monotonically as the temperature increases. The insert shows a magnified view of the isotherm behavior in the region below 10 mTorr (Stage A adsorption) where only a single TEDA molecule bonds to a single Al−OH group. Cuts across this isotherm at relative coverages of $\theta = 0.5$ and $\theta = 0.6$ are shown, and these cuts will be used to construct a van't Hoff plot to determine the enthalpy of adsorption, as will be shown later. Rather than fitting to the Langmuir model, the isotherm curves are spline fits to the equilibrium data. For the simple Langmuir equilibrium relationship, linear fits by plotting P_{eq}/θ vs P_{eq} should be obtained. In the initial region (up to ∼10 mTorr) of the isotherm, the plots of P_{eq}/θ as a function of P_{eq} with a linear fit at each temperature are shown in Figure 7. We believe that the data support the operation of a Langmuir equilibrium during Stage A adsorption within the limits of accuracy of measurements.

Figure 8 shows the van't Hoff plot for the equilibrium between an Al−OH group and a single TEDA molecule in Stage A adsorption. The data are shown for two relative coverages, as indicated in Figure 6. It may be seen that to within the
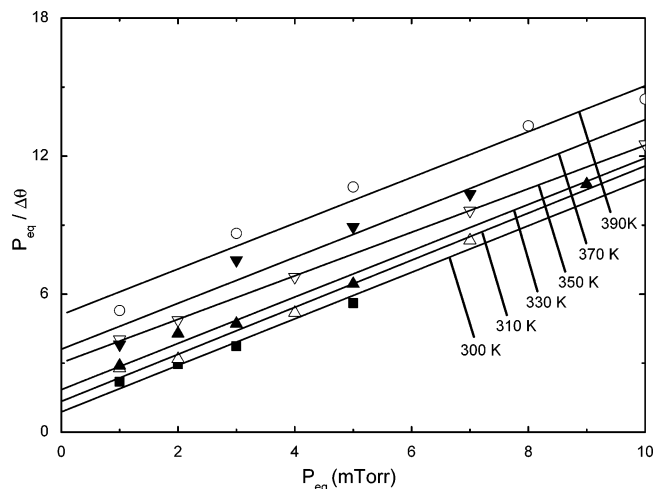

Figure 7. Linear fitting of $P_{eq}/\Delta\theta$ vs P_{eq} in the Langmuir fit to isotherms shown Figure 6 in the region below 10 mTorr (Stage A), corresponding to single TEDA molecule adsorption on Al−OH groups.
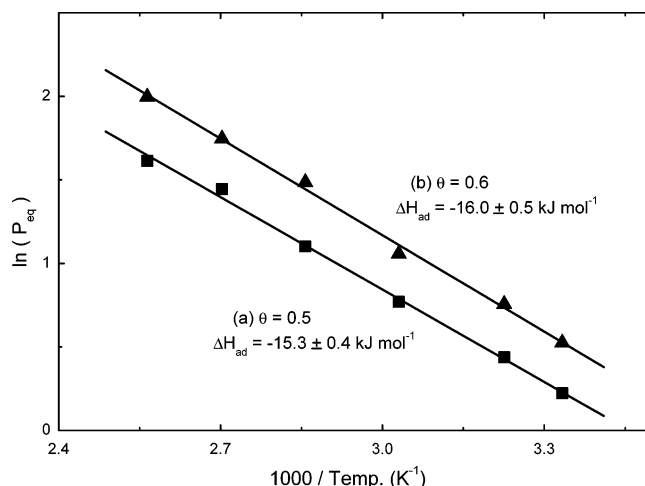

Figure 8. van't Hoff plots for the equilibrium between Al−OH species and TEDA molecules at: (a) $\theta = 0.5$; and (b) $\theta = 0.6$.

experimental error, the values of ΔH_{ad} are equal at the two coverages, and the average value of $\Delta H_{ad} = -15.6 \pm 0.5$ kJ mol^{-1}. The data used in Figure 8 are for equilibrium pressures of TEDA below 7.5 mTorr, clearly in the Stage A region of adsorption.

IV. Discussion

A. The Surface Hydrogen Bond of TEDA to Isolated Al−OH Groups. The complexation of a donor molecule to Al−OH groups occurs by hydrogen bonding, which is primarily an ionic form of bonding.[3] Many factors influence both the red shift in frequency as well as the increase in integrated absorbance of hydroxyl groups which experience hydrogen bonding,[3] including the polarizability of the adsorbate,[2] and the ionization potential of the adsorbate.[4] The spectroscopic development of Al−OH groups associated with the TEDA molecule results in a large range of −OH stretching frequencies from about 3600 cm^{-1} to about 2600 cm^{-1}, suggesting that Al−OH groups with different degrees of coordination to the Al$_2$O$_3$ substrate experience large differences in their modification by hydrogen bonding.[2] A slightly higher efficiency of hydrogen bonding of TEDA to OH species II (∼3740 cm^{-1}) having less positive net charge than species III (∼3700 cm^{-1}) at OH is observed, as shown in Figure 2.

(a)   (b)

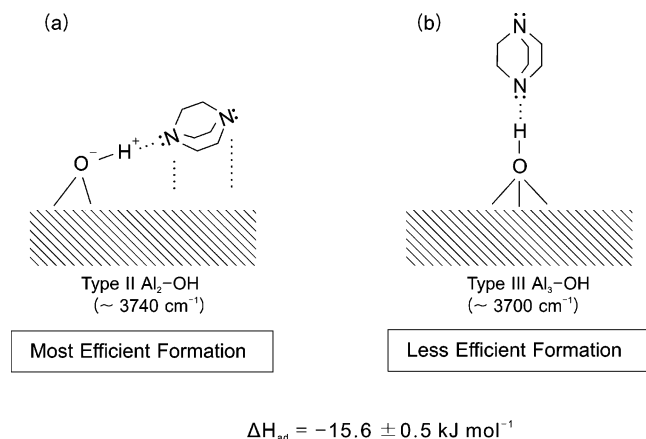**Figure 9.** Schematic picture of TEDA adsorption on: (a) type (II) Al−OH species at ∼3740 cm^{-1}; (b) type (III) Al−OH species at ∼3700 cm^{-1} during Stage A adsorption.

Figure 9 schematically illustrates the difference between Type II and Type III Al−OH species. Type II (∼3740 cm^{-1}) Al−OH species are bridge bonded to two Al^{3+} ions according to the assignment of Knözinger and Ratnasamy,[2] where Type III (∼3700 cm^{-1}) is coordinated to three Al^{3+} ions. On this basis, one might expect for Type II Al−OH species that dispersive adsorption forces would cause the TEDA molecules to become more parallel to the surface as a result of bending of the bridged Al−O−Al type moiety. In contrast, little or no bending of the Al$_3$−O moiety could occur since three Al−O bonds are involved. We postulate that hydrogen binding of TEDA to Type II Al−OH species would result in the production of the highest red shift of ν(OH), where type III Al−OH···TEDA binding produces a lower red shift. This postulate then suggests, for Stage A adsorption, a larger efficiency of complexation of type II Al−OH groups to TEDA, and the more efficient formation of the least red-shifted Al−OH···TEDA species, correlating the observations in Figure 2 and Figure 5.

Other physically adsorbed molecules have also been observed to produce a wide range of red shifts for Al−OH groups upon hydrogen bonding.[5,6] This is a distinct behavior for Al−OH groups, not observed for Si−OH groups on SiO$_2$ surfaces, which undergo hydrogen bonding to molecules such as CO and N$_2$ at low temperatures, producing only 100 cm^{-1} to 50 cm^{-1} red shifts respectively in −OH frequency.[7,8]

It is very clear from the spectroscopic data as a function of the equilibrium pressure of TEDA that two rather distinct stages of adsorption occur. In Stage A, the isolated Al−OH groups are almost completely converted to hydrogen-bonded groups, and this is complete at an equilibrium pressure of ∼10 mTorr at 300 K. The integrated absorbance of the complexed Al−OH groups produced by a single TEDA molecule is approximately twice the original intensity of the isolated Al−OH species before adsorption, as may be seen in Figure 3. In the equilibrium pressure range 10−250 mTorr, Stage B of TEDA adsorption mainly occurs. Figure 3 shows that Stage B adsorption results in more than a factor of 2 increase in integrated −OH absorbance, compared to that achieved at the end of Stage A. By correlation to the integrated absorbance changes for two vibrational bands associated with the TEDA molecule (Figure 4), it may be seen that Stage B adsorption occurs during the last ∼ 30% of the coverage of TEDA which develops up to an equilibrium pressure of 250 mTorr. Thus, the effect of the adsorption of a second TEDA molecule on a TEDA-complexed Al−OH group exceeds, by a factor of about six, that of the

first TEDA molecule is-so-far as measured by the integrated −OH absorbance.

The hydrogen bonding of more than a single species to −OH groups (bifurcated or trifurcated bonding) has been observed in carbohydrates or amino acids.[9,10] For adsorption on −OH groups, the bonding of one and then a second CO molecule to Si−OH groups on SiO$_2$ surfaces has also been reported,[7] and well-defined stages of CO adsorption by hydrogen bonding were observed by IR spectroscopy.

B. Thermodynamics of Hydrogen Bonding of Al−OH Groups to TEDA. The equilibrium adsorption of TEDA on isolated Al−OH groups on Al$_2$O$_3$ occurs according to the Langmuir adsorption isotherm, based on the fits to the Langmuir model, as shown in Figure 7. These fits have been made only in the Stage A region, where single TEDA molecule adsorption occurs on single isolated Al−OH groups. Fitting these data to the van't Hoff equation yields the value of $\Delta H_{ad} = -15.6 \pm 0.5$ kJ mol^{-1}.

This value of ΔH_{ad} is in the range often found for hydrogen bonding, where values from −25.2 kJ mol^{-1} to −12.6 kJ mol^{-1} are reported.[3] The physical adsorption of smaller molecules, having lower polarizability and less electron donor capability than TEDA gives slightly lower values for the adsorption enthalpy. For example, ΔH_{ad}(CO) on Si−OH groups is −11.3 kJ mol^{-1},[7] and ΔH_{ad}(N$_2$) on Si−OH groups is −13.4 kJ mol^{-1}.[8] Our method of measuring the fractional coverage of TEDA in the isotherm study measures only single TEDA molecules adsorbed on Al−OH groups, and is therefore specific to this mode of surface bonding.

C. Other TEDA Bonding Sites. The experiments reported here have almost exclusively focused on the behavior of the Al−OH groups which initially form a hydrogen bond to a single TEDA molecule. At higher coverage a fraction of the hydrogen-bonded species involve two TEDA molecules. Other more detailed studies (to be published) find minor spectroscopic differences in the TEDA spectrum for different levels of hydroxyl group coverage. This suggests the presence of TEDA binding to Lewis acid Al^{3+} sites via the N atom lone pair electrons. Because of the focus of this paper on the Al−OH mode during TEDA adsorption, the results do not address TEDA binding to Lewis acid sites.

V. Summary

The bonding of the TEDA molecule to partially hydroxylated γ-Al$_2$O$_3$ has been studied by transmission IR spectroscopy and the formation of Al−OH···TEDA hydrogen bonds has been characterized. The following results are found. (1) Single TEDA molecules adsorb selectively on isolated Al−OH groups with an enthalpy of adsorption of $\Delta H_{ad} = -15.6 \pm 0.5$ kJ mol^{-1} at $\theta = 0.5 - 0.6$. (2) Equilibrium adsorption on Al−OH groups follows the Langmuir adsorption isotherm. (3) A second TEDA molecule can bind to an Al−OH···TEDA species as the coverage is increased at 300 K. (4) The hydrogen bonding of TEDA to Al−OH groups causes large red shifts in the −OH stretching frequency ranging up to −1000 cm^{-1}. (5) The largest efficiency of hydrogen bonding of TEDA occurs with type (II) −OH species (∼3740 cm^{-1}) compared to type (III) −OH species (∼3700 cm^{-1}).

References and Notes

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