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Determination of surface OH acidity from the formation of acid/base complexes on ultrathin films of γ-Al_2O_3 on NiAl(100)

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Abstract

The interactions of benzene, toluene, acetonitrile, pyrazine, and pyridine with hydroxylated ultrathin films of γ-Al_2O_3 were investigated using vibrational spectroscopy (high-resolution electron energy-loss spectroscopy). These molecules act as Lewis bases, forming acid/base complexes with the surface hydroxyl groups. Complex formation shifts the frequency of the isolated O–H-stretch vibration (3711 cm^{-1} on the clean surface) to lower frequency. The magnitude of the frequency shift depends on the strength of interaction between the basic probe molecule and the surface OH groups. The strength of interaction is dependent on both the acidity of the surface OH groups and the basicity of the isolated probe molecule. Our data indicate that there are two distinct types of surface hydroxyl groups, which differ in surface acidity, on our thin films of hydroxylated γ-Al_2O_3 [J. Phys. Chem. B 107 (2003) 8538]. To determine the surface OH acidity for the surface hydroxyl groups on the hydroxylated γ-Al_2O_3, we followed the approach of Hair and Hertl [J. Phys. Chem. 74 (1970) 91] and developed a calibration plot using existing data available in the literature for silica, silica–alumina, magnesia, and phosphate on silica. Using this calibration plot, we determine a $pK_a = 6.5 \pm 1.1$ for the more acidic surface OH groups and a $pK_a = 8.4 \pm 1.1$ for the less acidic surface OH groups.

Keywords: Alumina; Surface hydroxyl; Acidity; Acid–base complex; Vibrational spectroscopy; Hydrogen bond; Metal oxide film

1. Introduction

The catalytic activity of metal oxides, such as Al_2O_3, depends on the concentration, nature, and acidity of the catalytic active sites. Thus, the determination of surface acidity is of great utility in the development of a detailed picture of the surface chemistry of this widely used metal oxide. The chemistry of γ-Al_2O_3, which is used as an industrial acid–base catalyst [3–8] and metallic catalyst support [9–11], depends on the surface composition, particularly the quantity, types, and acidity of the surface catalytic sites [12–14]. Perhaps, the most important sites are the surface hydroxyl groups because they provide the sites for Brønsted acid-catalyzed reactivity, as we have reported for the dimerization of 1,3-butadiene on hydroxylated thin films of γ-Al_2O_3 [15,16]. Additionally, Heemeier et al. have also shown that increasing the concentration of surface hydroxyl groups increases metal dispersion on metallic supported catalysts [17], presumably due to the addition of more nucleation sites for the initiation of metal particle growth. Recently, a number of research groups have developed the use of ultrathin films of Al_2O_3 that can be grown on the surfaces of single crystals of the intermetallic compounds of Ni and Al as models for Al_2O_3 catalyst supports [1,15,16, 18–25]. Such ultrathin films have a number of advantages for fundamental studies utilizing modern surface spectroscopies. These Al_2O_3 ultrathin films are highly ordered (thus providing substantially simpler surfaces than that of powdered Al_2O_3) and they exhibit much of the chemistry associated with γ-Al_2O_3. In addition, since the films are only 10–15 Å thick, electron spectroscopies can be utilized without undue charging effects. Since it is well known that surface hydroxyl groups have a large impact on the chemistry of Al_2O_3 catalyst supports, we have carried out a number of studies of the impact of surface OH groups on the surface chemistry on these ultrathin film models of Al_2O_3 [1,15,16].

As many as 5–7 distinct OH environments have been identified on the surface of powdered γ-Al_2O_3 as distinguished by the OH-stretching vibration. On the somewhat simpler (structurally ordered) ultrathin films described here, we observe only a single OH-stretching frequency at

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3711 cm^{-1} using HREELS [1,15]. The spectral resolution of HREELS is limited and we have shown previously that the OH-stretching mode we observe at 3711 cm^{-1} corresponds to two distinct types of OH groups [1]. The aim of the present work is to quantify the acid properties of the OH groups that can be formed on the surface of these ultrathin Al_2O_3 films.

The adsorption of basic probe molecules on metal oxide surfaces has been widely employed to quantify the surface acidity of metal oxides and zeolites. In these experiments, the probe molecule, P, interacts with a catalytic site, S, given by the following equilibrium:

$$P + S \leftrightarrow P\text{–}S. \tag{1}$$

In this equilibrium, P–S may be a coordination surface compound, a surface complex ion, or a charge transfer complex. This method, known as specific poisoning, requires that the probe molecule only interacts with the specific active sites being investigated [12–14]. Because metal oxides have several catalytic sites, including Brønsted acid, Lewis acid, and Lewis base sites, the complete characterization of surface acidity requires the use of several probe molecules with various properties [12–14].

In a previous manuscript, we showed that vibrational spectroscopy coupled with pyridine adsorption could distinguish between surface hydroxyl groups to which it associates, by hydrogen bond formation [1]. The OH-stretching frequency of these two types of OH groups is sufficiently similar so that we do not resolve the OH stretches of the uncomplexed OH groups. Pyridine interacts with the surface hydroxyl groups on ultrathin films of hydroxylated γ-Al_2O_3 to form two OH–pyridine complexes. The OH-stretching frequencies of the two OH–pyridine complexes are easily resolved by the HREELS experiment. These results indicated that there are two types of surface OH groups that differ in surface OH acidity on the ultrathin films of hydroxylated γ-Al_2O_3 grown under our experimental conditions.

There are a number of reports in the literature that provide structural assignments associated with the OH-stretching frequencies that have been observed for Al_2O_3 surfaces [6, 26–28]. The most recent assignments provided by Digne et al. rely on DFT calculations and models of the alumina surface generated by the dehydration of boehmite [28]. Based on these DFT calculations the surface OH structures that should exist within the linewidth of our OH-stretching mode include OH groups bridge bonded to two Al ions and OH terminally bonded to Al sites in a bonding geometry characteristic of the alumina (110) surface. However, it should be recognized that since the calculations of Digne et al. model a surface prepared in a much different manner than the oxidation of NiAl(100) done here, it is possible that the specific geometries suggested by their calculations may not be applicable to our experiments. Based on the most recent literature, however, we can surmise that the OH groups that exist on our ultrathin films on NiAl(100) involve isolated OH groups (not hydrogen bonded) and most likely in a bridge-bonded geometry to two Al ions or terminally bonded to one Al ion.

The formation of the OH–base complexes can be extended to include other bases, in addition to pyridine. In general, the interaction of electron pair donors (probe molecules), B, with surface hydroxyl groups, OH, on metal oxides results in the formation of an OH–B complex:

$$OH + B \rightarrow OH\text{–}B. \tag{2}$$

The formation of the OH–B complex shifts the frequency of the “free” O–H stretch to lower wavenumbers [2,29–36]. The perturbation is due to charge transfer and/or electrostatic interactions between the probe molecule and the surface hydroxyl group [29,32].

The magnitude of the frequency shift for the O–H stretch has been correlated, with varying degrees of success, to several parameters such as band half-width, integrated intensity, H–B bond length, heat of formation of the hydrogen bond, ionization energy of the probe molecule, and heat of adsorption of the hydroxyl groups [31,32,35,37]. However, the most successful correlations are between the observed OH frequency shifts and the pK_a of the surface OH group and/or the pK_b of the probe molecules. Specifically, there is a linear dependence between the observed OH frequency shift and the pK_b of the probe molecule [2,29–36].

The strength of the OH–B interaction depends on both the acid strength of the surface hydroxyl group and the Lewis base strength of the probe molecule. Since the observed OH frequency shift is an indication of the OH–B interaction strength, this shift also depends on the surface OH acidity and probe molecule basicity. In general, the magnitude of the OH frequency shift increases with the basic strength of the probe molecule and/or acid strength of the surface hydroxyl group [2,29–36]. Thus, the OH shifts for surface hydroxyls of differing acidity interacting with the same probe molecules can be used to determine the relative acidity of surface hydroxyl groups on various metal oxides.

In the work described in this paper we have used the dependence of the frequency shift on probe molecule basicity to determine the pK_a of the two distinct surface hydroxyl groups on our hydroxylated thin films of γ-Al_2O_3. We specifically chose basic probe molecules that have previously been reported to interact with the surface hydroxyl groups and form OH–B complexes on other metal oxides.

2. Experimental

The experiments were carried out in an ion-pumped UHV chamber that has a base pressure of $\sim 1 \times 10^{-10}$ Torr. The chamber is equipped with a single-pass cylindrical mirror analyzer (Physical Electronics 10-155) with a coaxial electron gun for Auger electron spectroscopy (AES) analysis, a UTI-100C quadrupole mass spectrometer for residual gas analysis, Varian low-energy electron diffraction (LEED) optics, an LK-2000 high-resolution electron energy-loss spectrometer (HREELS), and an ion gun for ion bombardment.

Typical HREELS conditions were incident electron beam with kinetic energy in the range of 5–7 eV, resolution of ~ 5–8 meV, and count rates ~ 100 kHz in the elastic, and 1–10 kHz in inelastic channels. All HREEL spectra presented here were recorded at a substrate temperature $\leqslant 170$ K. The period of signal averaging was kept at ~ 2 h per spectrum in order to maximize the signal-to-noise ratio. Each HREELS spectrum, unless otherwise noted, was normalized with respect to its own elastic peak and the corresponding number of scans.

NiAl(100) samples were prepared from a 1-cm-diameter single crystal rod of NiAl, obtained from GE Research Labs (Schnectady, NY). After cutting 2-mm-thick slices from the rod using an electric discharge machine (California Wire EDM), both sides of the crystal were polished using standard procedures. Angular alignment of the NiAl(100) surface was determined by Laue X-ray diffraction. The sample was mounted on a liquid nitrogen-cooled manipulator, equipped with resistive heating. A chromel/alumel thermocouple was spot welded to the side of the crystal. Initially, the sample was subjected to room temperature Ar^+ sputtering for 5 min, followed by annealing to 1300–1400 K, to regain the crystalline structure. Thereafter, it was cleaned by cycles of O_2 thermal treatment at $p(O_2) = 1.0$–2.0×10^{-7} Torr and ~ 1000 K for 2 min, followed by flashing the surface to ~ 1500 K. The cleanliness of the substrate was monitored by AES. Carbon and oxygen, the primary surface contaminants, are readily removed by several cleaning cycles.

All liquid (and solid) reagents used in these experiments, including 18 MΩ H_2O, D_2O (Cambridge Isotopes, 99.996 at.% D), pyridine (Fisher, certified ACS, 99.9%), perdeuterated pyridine (Aldrich, 99.96+at.% D), toluene (Aldrich, 99.8%, anhydrous), benzene (Fisher, certified ACS, thiophene free), perdeuterated benzene (Cambridge Isotopes, 99.6 at.% D), perdeuterated acetonitrile (Aldrich, 100 at.% D), pyrazine (Aldrich, 99+%), and perdeuterated pyrazine (CDN Isotopes, 99.6 at.% D), were degassed by freeze, pump, and thaw cycles. The cleanliness of all gases introduced into the chamber was checked in situ by mass spectrometry.

Ultrathin films of hydroxylated γ-Al_2O_3, used throughout the experiments, and characterized by AES and HREELS, were prepared by exposing the NiAl(100) substrate to H_2O at 1000 K. In previous experiments, we have shown that Al_2O_3 films grown at 1000 K with an AES O(505)/Ni(848) ratio in the range of 2.5–3.0 show intense, narrow, phonon structures indicative of high-quality ordered films, that are 10–15 Å in thickness [16]. The HREELS spectra and LEED pattern (streaked 2×1) are identical to those obtained by Gassman et al. and assigned to a γ-Al_2O_3 ultrathin film on the NiAl(100) substrate [16,24]. The AES ratio consistent with the previous work by Gassman et al. [24] was obtainable by a 100 L H_2O exposure ($1\ L = 1 \times 10^{-6}$ Torr $\times$ s). During preparation of γ-Al_2O_3 films for HREELS experiments, the background pressure in the chamber during the film growth did not exceed $p(H_2O) = 1.0 \times 10^{-8}$ Torr. The H_2O exposures were only corrected for the doser flux enhancement of $\times 50$.

The thin films of hydroxylated γ-Al_2O_3 were then exposed to the basic probe molecules (benzene, toluene, acetonitrile, pyrazine, and pyridine) via background dosing. The substrate temperature did not exceed 170 K during these experiments. HREELS spectra were collected as a function of exposure until a saturation coverage was reached. Saturation was determined when further exposure of the probe molecule to the surface did not result in a change in the C AES signal or the HREELS spectrum. The adsorption of all the probe molecules was mostly reversible. In the case of pyridine adsorption a very small amount of dehydrogenation of the pyridine was observed as we have discussed previously [1].

3. Results and discussion

3.1. Adsorption studies

The adsorption of pyridine on the hydroxylated thin films of γ-Al_2O_3 has been described in a previous paper [1]. At low coverages, perdeuterated pyridine interacts with the more acidic surface OH groups forming a pyridine(d_5)–HO complex. The O–H-stretching frequency for this complex is 2920 cm^{-1}. With increasing exposures of perdeuterated pyridine, a second pyridine(d_5)–OH complex is formed due to the interaction of pyridine with the less acidic surface OH groups. This complex has an O–H stretch at 3150 cm^{-1}. With increasing perdeuterated pyridine coverage, the intensity for the free O–H stretch at 3711 cm^{-1} decreases, confirming that pyridine(d_5) is interacting with the surface OH groups (see Fig. 1) (note that in this paper we use the term “free O–H” to refer to the hydroxyl group bonded to the surface but not complexed to an adsorbed base).

The amount that the free O–H stretch is red-shifted on complexation with a probe base (e.g., pyridine) depends on the strength of the interaction; the stronger the interaction, the more the O–H bond is weakened. The weakening of this O–H bond is responsible for the observed frequency shift for the O–H stretch of the complex. Since we observe two vibrations for the pyridine–HO complex, we conclude that we have two distinct surface OH groups differing in surface acidity [1]. The linewidth that we observe for the free OH species prior to exposure to pyridine is 80 cm^{-1} (Fig. 1a). This is limited by the experimental resolution of our HREELS instrument. Based on the Digne et al. assignments of OH-stretching frequencies for specific structures a number of potential bonding structures fall within this window of frequencies [28].

Table 1
Observed OH-stretch frequencies for surface OH groups interacting with various probe molecules on the hydroxylated γ-like Al_2O_3 thin films

Probe molecule	Gas basicity (kJ/mol)[a]	OH stretch for OH Complex 1 (cm^{-1})	OH stretch for OH Complex 2 (cm^{-1})	Free OH stretch (cm^{-1})
Benzene	725.4	3527	3703	3711
Acetonitrile	748.0	3500	3689	3711
Toluene	756.3	3484	3677	3711
Pyrazine	847.0	3061	3343	3711
Pyridine	898.1	2920	3150	3711

[a] Ref. [38].

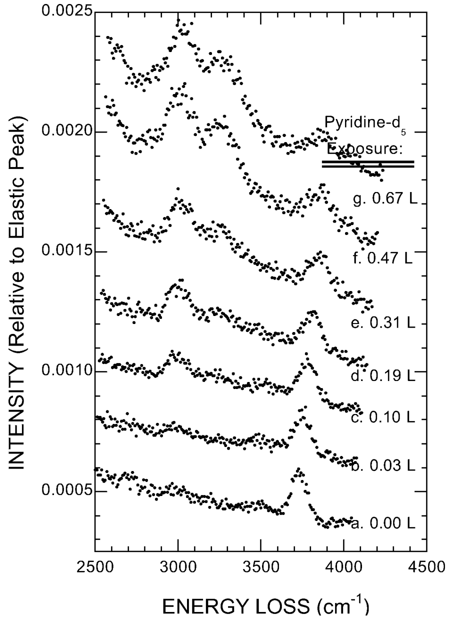


Fig. 1. HREELS spectra depicting the coverage dependence for C_5D_5N–HO complex formation on the hydroxylated γ-Al_2O_3 thin film at 170 K. Only the OH-stretch frequency regions of the spectra are shown for clarity. Perdeuterated pyridine (C_5D_5N) exposures are as indicated for each spectrum.

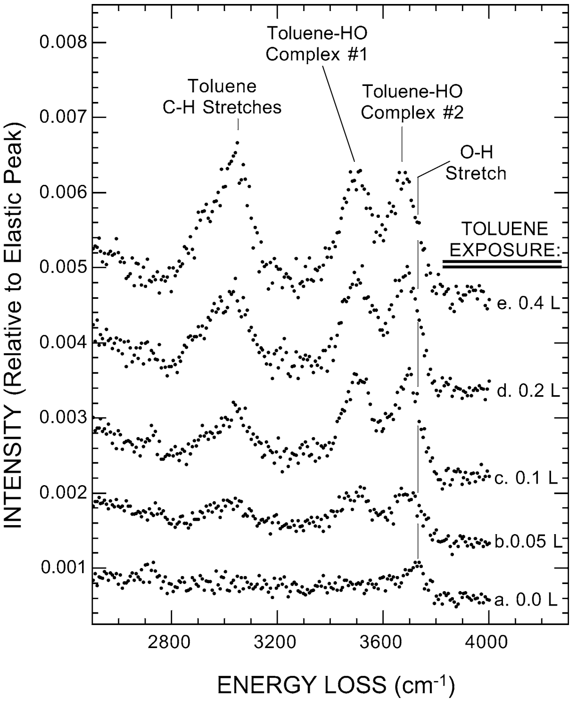


Fig. 2. HREELS spectra depicting the coverage dependence for toluene–HO complex formation on the hydroxylated γ-Al_2O_3 thin film at 140 K. Only the OH-stretch frequency regions of the spectra are shown for clarity. Toluene exposures are as indicated for each spectrum.

To confirm that the shifted O–H stretches that we observed for pyridine interacting with the surface OH groups are due to the formation of acid–base complexes, we studied the adsorption of toluene, benzene, pyrazine, and acetonitrile on our thin films of γ-Al_2O_3. Table 1 summarizes the observed shifted O–H stretches as a result of pyridine, pyrazine, acetonitrile, toluene, and benzene interacting with the surface OH groups on our thin films of γ-Al_2O_3. These molecules interacted with the surface hydroxyl groups, forming two acid–base complexes. These data confirm that there are two distinct types of surface hydroxyl groups, which differ in acidity, on our thin films of hydroxylated γ-Al_2O_3. The gas basicities for each probe molecule are also given in Table 1; where the gas basicity of a species (molecule, radical, or atom), M, at a temperature T is defined as the negative Gibbs free energy ($\mathrm{GB}(M,T) = -\Delta G(T)$) of the hypothetical gas-phase reaction shown below [38]:

$$M_{(\mathrm{g})} + H^{+}_{(\mathrm{g})} \rightarrow MH^{+}_{(\mathrm{g})}. \qquad (3)$$

We use gas basicity to describe the basicity of our probe molecules since a probe molecule's basicity depends on the environment [38]. The gas basicity is the more appropriate measure for the basicity of an isolated base than solution basicity that depends substantially on solvent effects.

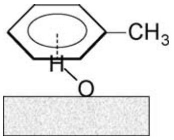
The data in Table 1 verify that the magnitude of the red shift in the free O–H stretch (3711 cm^{-1}) depends on the gas basicity of the probe molecule. The adsorption of pyridine on these surfaces has been described in detail previously in the literature [1], and the details of the adsorption of pyrazine and acetonitrile on the ultrathin films of hydroxylated γ-Al_2O_3 will be the subject of a future paper. We discuss here the adsorption of benzene and toluene on our hydroxylated thin films of γ-Al_2O_3 in some detail.

Since the adsorption of benzene is very similar to the adsorption of toluene, we only present the HREELS spectra collected for the adsorption of toluene, a very weak base, on the hydroxylated γ-Al_2O_3 thin films at 140 K (Fig. 2).

Fig. 2a is the spectrum for a freshly grown hydroxylated γ-Al_2O_3 film prior to toluene exposure. For clarity, only the O–H-stretching region is shown. After exposing the hydroxylated thin film of γ-Al_2O_3 to toluene (Fig. 2b–e), two shifted O–H stretches are observed at 3484 and 3677 cm^{-1}. The shifts in the free O–H-stretching frequency (3711 cm^{-1}) after the formation of OH-toluene complexes are much smaller than the observed shifts in the free O–H-stretching frequency (3711 cm^{-1}) after the formation of OH–pyridine complexes. This result is in agreement with the fact that pyridine is a significantly stronger base than toluene.

With increasing toluene coverages (Fig. 2c–e), the intensity for the O–H stretches for the OH–toluene complexes continue to increase, while the intensity for the free O–H stretch continues to decrease. The intensity for the C–H stretches also increases. However, the ratio for relative intensity for the C–H stretches to the relative intensity of the O–H stretches of the OH–toluene complexes is approximately constant.

The shifted O–H stretches are evidence of toluene (and benzene) interacting with the surface hydroxyl groups. Because two different OH–toluene complexes are formed, the presence of two different types of surface OH groups, which differ in surface acidity, is confirmed. The very weak intensities for the C–H-stretching modes indicate that the toluene (benzene) molecular plane is lying parallel to the hydroxylated γ-Al_2O_3 thin film. Steric hindrance from the methyl groups on toluene may cause a slight tilt, however. This is indicated by a larger intensity for the C–H-stretching vibrations than observed in the HREELS spectra for benzene adsorbed on the hydroxylated thin films of γ-Al_2O_3. While one expects to observe the C–H-stretching modes for the methyl groups at ~2950 cm^{-1}, the C–H-stretch vibration is broad, thus also indicating the presence of the ring C–H stretches. The OH–toluene complexes are due to an interaction between the surface OH groups and the π-system of the toluene aromatic ring, as shown schematically below [13,39,40].



The above interaction would cause a change in the distribution of the electron density of the toluene aromatic ring. Changes in the electron density of the toluene aromatic ring are confirmed by the frequency for toluene ring vibration at ~1492 cm^{-1}. The ring vibration is slightly lower than expected for gas-phase toluene (1499 cm^{-1}). Benzene interacts with the surface OH groups in a similar manner as the above depicted toluene interaction. A similar shift in the ring-stretching vibration was observed; however, the shift is greater than that observed for toluene [41]. This result is not surprising since it has been observed that the frequency shift for the ring vibrations due to the perturbation of the π-electron system of the aromatic ring decreases as the number of substituent methyl groups attached to the benzene ring increases [39].

3.2. Development of acidity calibration plot

The magnitude of the OH shift can indicate the relative acidity of the surface hydroxyl groups on our films when compared to the shift observed for the same probe molecule interacting with surface hydroxyl groups on other metal oxides. In order to quantify the acidity of the surface hydroxyl groups on our thin films of γ-Al_2O_3, we developed a calibration plot using the published data for the observed frequency shifts for a series of probe molecules interacting with various metal oxides with known surface OH acidity, specifically, silica ($pK_a = 7.6$), silica–alumina ($pK_a = 7.1$), magnesia ($pK_a = 15.5$), and phosphate on silica ($pK_a = -0.4$) [2]. For each of these metal oxides, the observed frequency shifts for the surface hydroxyl groups interacting with various probe molecules were plotted as a function of probe molecule gas basicity [2,38]. Such a plot for probe molecules interacting with the surface OH groups on silica is depicted in Fig. 3. In this plot, which we define as an interaction plot, we observe a linear dependence between the magnitude that the free O–H stretch is red-shifted and the gas basicity of the probe molecule.

For each of the metal oxides, the observed frequency shift is linearly dependent on the gas basicity. However, the slope

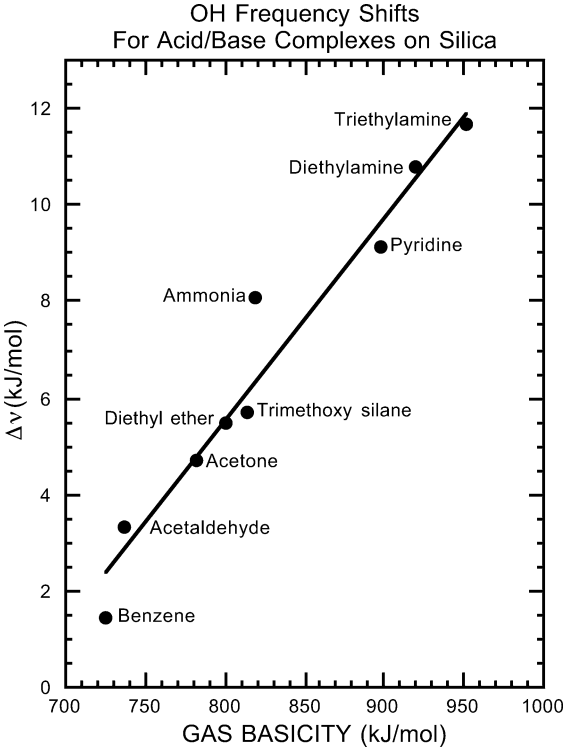


Fig. 3. $\Delta\nu$ for the O–H stretch for OH groups on silica, resulting from the formation of an OH–B complex, as a function of probe molecule gas basicity (Refs. [2,38]). The solid line is a linear least-squares fit to the data. The resulting slope is 0.042.

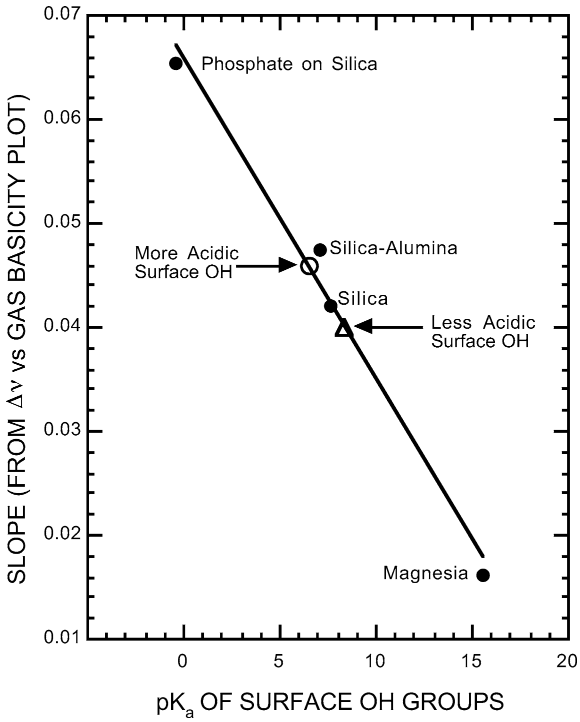


Fig. 4. Calibration plot: the slopes from the Δν versus gas basicity plots for various metal oxide surfaces are plotted as a function of the pK_a of their surface OH groups (closed circles). The slopes from the Δν versus gas basicity plots for probe molecules interacting with surface hydroxyls on the hydroxylated γ-Al_2O_3 thin film are shown as open symbols. Specifically, the open circle is the slope for the more acidic surface hydroxyl groups and the open triangle is the slope for the less acidic surface hydroxyl groups. The solid line is a linear least-squares fit to the solid points.

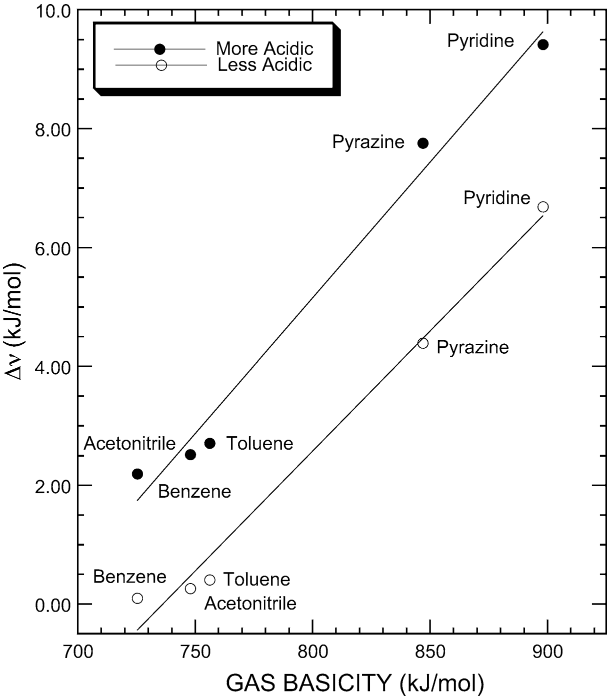


Fig. 5. Δν for the O–H stretch versus probe molecule gas basicity plot for the surface hydroxyl groups on the hydroxylated thin films of γ-Al_2O_3. The closed circles are the shifts observed for the more acidic surface hydroxyl groups (Complex 1 from Table 1), while the open circles represent the shifts observed for the less acidic surface hydroxyl groups (Complex 2 from Table 1). The solid lines are linear least-square fits to the data. The resulting slope from the data fit for Complex 1 (more acidic) is 0.046 ± 0.003. The slope resulting from the fit to the data for Complex 2 (less acidic) is 0.040 ± 0.003.

of this linear dependence depends on the acidity of the surface hydroxyls on the metal oxide; the slope increases with increasing surface OH acidity. The **slopes** from the respective interaction plots for the various metal oxides were plotted as a function of surface OH acidity (pK_a), as shown in Fig. 4. From this plot, we conclude that there is a linear dependence between the **slope** of the interaction plot and the pK_a of the surface hydroxyl groups. We refer to Fig. 4 as our calibration plot since this plot enables one to determine the surface OH acidity (pK_a) from the slope of an interaction plot.

3.3. Determination of OH acidity

We have successfully used the calibration plot to determine the pK_a of the two types of surface hydroxyl groups on our thin films of hydroxylated γ-Al_2O_3. Specifically, the observed frequency shifts for the isolated O–H stretch (3711 cm^{-1}) were plotted as a function of gas basicity for the two distinct surface hydroxyl groups on our thin films of hydroxylated γ-Al_2O_3; this plot is shown in Fig. 5. As expected, the slope of this plot depends on the strength of interaction between the probe molecule and the surface hydroxyl groups. The different slopes observed in this plot for the two types of hydroxyl groups on our thin films of hydroxylated γ-Al_2O_3 confirm that these hydroxylated surfaces contain two types of hydroxyl groups that differ in their surface acidity. The slopes from the interaction plots were plotted on the calibration plot and are indicated by the open symbols in Fig. 4. Specifically, the open circle is the slope for the more acidic surface hydroxyl groups and the open triangle is the slope for the less acidic surface hydroxyl groups. Reading the pK_a from the calibration plot in Fig. 4, we have determined the pK_a for the more acidic OH groups to be 6.5 ± 1.1 and the pK_a for the less acidic surface OH groups to be 8.4 ± 1.1.

4. Conclusions

Benzene, toluene, acetonitrile, pyrazine, and pyridine interact with the surface hydroxyl groups on ultrathin films of γ-Al_2O_3 grown on NiAl(100). The basic probe molecules interact only with the more acidic surface OH groups at low coverage. Complex formation results in a shift of the frequency of the isolated O–H stretch (3711 cm^{-1}) to lower frequency. At higher coverage, a second acid–base complex is formed due to an interaction between the less acidic OH groups and the basic probe molecule. The red shift of the O–H-stretching frequency for this complex was less than the red shift of the O–H-stretching frequency observed for the more acidic surface O–H groups. The magnitude of this red shift depends on both the acidity of the surface OH groups and the gas basicity of the probe molecule. Since we observe two shifted O–H stretches, our data indicate that there are two distinct types of surface hydroxyl groups, which differ in surface acidity, on our thin films of hydroxylated γ-Al_2O_3. To determine the surface OH acidity for the surface hydroxyl groups on the hydroxylated γ-Al_2O_3 ultrathin film, we developed a calibration plot using existing data available in the literature for silica, silica–alumina, magnesia, and phosphate on silica. Using this calibration plot, and the vibrational spectra obtained in the work described here, we find that the pK_a for the more acidic surface OH groups is 6.5 ± 1.1 and that the pK_a for the less acidic surface OH groups is 8.4 ± 1.1. Our experiments quantify a potentially significant difference between the ultrathin films of Al_2O_3 grown on NiAl and powdered alumina, in that the highly ordered ultrathin films only have 2 types of OH groups as opposed to the 5–7 types of OH groups that have been identified on powdered alumina surfaces.

Currently, we are investigating the influence of growth conditions on the types and proportions of the surface OH observed via the formation of acid–base complexes. We plan to use hydroxylated thin films of γ-Al_2O_3 with well-defined surface OH acidity, concentration, and types to investigate the impact of OH groups with well-defined acidity on surface chemistry and metal dispersion.

Acknowledgments

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