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Manifestations of the acidity of adsorbed molecules in H-bonded complexes with silanol groups: Lewis acidity of ozone

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Abstract

Adsorption of binary mixtures of gases with acidic and basic properties on silica surface has been studied by FTIR spectroscopy at low temperatures. After introducing acidic molecules to silica sample with preadsorbed base, additional shifts of the band of silanol groups already perturbed by bases occur that are interpreted as caused by interaction of the acid with the oxygen atom of silanol group, leading to the H-bond strengthening. Comparison of the effects produced by different acidic molecules enables an estimate of their relative electron-accepting (acidic) properties to be made, including the acidity of ozone that is not easy to estimate by other methods. For strong bases, such as ammonia, pyridine or 2,6-dimethylpyridine, addition of SO_2 or NO_2 enhances the acidity of silanol groups to such extent that proton transfer occurs, indicating the appearance of Brønsted acidity induced by coadsorbed acids. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Hydrogen bond of adsorbed molecules with surface OH groups of various oxides is known to result in a downward frequency shift with respect to the band position of the isolated hydroxyls [1,2]. The shift value, besides the sample temperature, for the chosen adsorbent–adsorbate system strongly depends at least on two factors — on the pretreatment conditions that influence the surface OH concentration and on the surface coverage by adsorbed molecules.

When the surface coverage by adsorbed molecules increases, the band of perturbed OH groups could move in different directions. High-frequency displacement of the maximum is often observed for various metal oxides [3,4] and could be due to the heterogeneity of the adsorption sites. The most acidic OH groups are the first to be perturbed, then the additional absorption on the less acidic groups will result in a smaller shift and, hence, in the intensity increase at the high-frequency side of the initial band of the perturbed OH groups. As a result, the observed average shift will diminish with the increasing coverage. Increase of the shift with growing coverage is more typical of silica, where the surface silanol groups are more homogeneous in their acidic properties. The additional shift is obviously considered to be a result of non-specific interaction of the H-bonded complex with the surrounding molecules [2] or physisorption with the solvation of already existing H-bonded complex [5,6].

The effect of this interaction, however, could be rather strong and depends on the nature of molecules that form the environment. Our preliminary results have shown that surrounding of the complex by the same molecules that act as the base in the hydrogen bond does not affect too much the position of the perturbed OH band. However, for certain molecules the additional coverage-induced shift is comparatively

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large. For H_2S it increases from 210 up to $240\,cm^{-1}$ [7], for ozone adsorbed at 77 K, from 90 up to $120\,cm^{-1}$ [8]. This effect is too strong to be accounted for by physisorption, and an alternative explanation could be put forward, that another molecule interacts with the H-bonded complex specifically as an acid, forming weak coordinate or H-bond with the oxygen atom of silanol group. The ability of silica hydroxyls to display with some molecules simultaneously proton-donating and -accepting properties was discussed by Garrone and Ugliengo [9].

Two interesting consequences follow from that. First, the additional frequency shift observed on introducing of acidic molecules for a system with certain chosen base could be used as a measure of its acidity. This will enable us to range the molecules according to their acidic properties and to estimate the acidic properties of such molecules as ozone that due to its extremely high reactivity does not enable us to measure its acidity by conventional chemical methods.

Second, taking different acidic molecules, we are able to control the acidity of silanol groups and to create protonic acid sites of desirable strength. If the acidity increase is great enough, we could hope to provoke a proton transfer to base molecules, those, which are usually used as tests for surface Brønsted acid sites. Then, the fact of protonation of certain base induced by an acidic molecule could be considered as an evidence that the acidity of the latter is above some level, the height of which depends on the choice of the base. The set of such data obtained with different bases could also be used to range the molecules according to their acidity.

In this work, we have tried the first task using H_2S, acetone and ammonia molecules as bases and CO_2, SO_2 and ozone as acids. To choose the base, we had to meet several serious requirements. For our purpose, the base should have sufficiently low reactivity with respect to ozone, at least at 77 K, when ozone can be adsorbed at the surface. The base should not be too weak, otherwise there will be a simple competition of it with the acidic molecules, which normally display weak basic properties as well and can form H-bonds with surface silanols themselves. Too strong bases could be anticipated to react with strong Lewis acids directly, giving the binary coordinate acid–base complexes or new compounds.

Hydrogen sulphide was found to be a comparatively weak base that meets most of these requirements. It shifts the OH band to ca. $3540\,cm^{-1}$, the shift increases with coverage [7], that could be regarded as an evidence for certain acidity of SH groups of this molecule that reveal itself in the formation of weak H-bonds in the condensed phase.

Frequency shift of silanol groups after acetone adsorption on silica is close to that caused by H_2S. This molecule, however, has a certain advantage for our study, because the strength of H-bond between the silanol group with this molecule is reflected not only in the displacement of the OH-stretching vibration, but also in the frequency value of the carbonyl group, that decreases on H-bond formation. Unfortunately, however, both the shifts of OH groups perturbed by acetone and the C=O frequency value varies greatly with coverage [10,11].

Ammonia is a strong base that shifts the silanol band by $800\,cm^{-1}$ or more. Due to its ability to form H-bond not only as a base, but also as a donor of protons, it displays a tendency to form polymer chains that involve surface OH groups. This property manifests itself in a strong coverage dependence of the OH frequency shift [12].

The band shape of Si–OH groups perturbed by pyridine is complicated due to the interaction with the overtone of OH bending mode, that results in the so-called “Evans’ well” [13]. The same phenomenon could be observed in the spectra of adsorbed 2,6-dimethylpyridine (lutidine, DMP). This makes these basic molecules not convenient for frequency shift measurements, but both could be used as a test for Brønsted acidity. DMP molecule is excellent for that, since its two ν_8 vibrations are very sensitive to protonation [14]. Thus, to study Brønsted acidity, besides ammonia, we tried pyridine and DMP as bases. As one more acid, NO_2 was also used.

2. Experimental

For IR studies, thin aerosil pellets were prepared and activated first in oxygen, then in vacuum ($<10^{-4}$ Torr) for 1 h at about 1000 K inside an IR cell, that allowed high-temperature activation, adsorption, and IR spectra measurements at 60–300 K to be carried out. Details on the design and performance of the cell are given elsewhere [15]. Liquid nitrogen was used as a coolant, and after its removal, if necessary, temperature was measured by means of a thermocouple inserted in the coolant volume. For better thermal contact between the sample and the cooled environment, about 0.5 Torr of helium was admitted into the sample compartment. Acetone, ammonia, DMP were dosed at 300–250 K after recording the background spectrum of pure silica at room temperature. Then the cell was cooled and IR spectrum was registered at 77 K in the presence of gaseous helium. H_2S was introduced into the cooled cell and condensed on the walls. The cell was then heated until pressure increase and OH perturbation reveal H_2S evaporation and adsorption on the sample. Then the cell was finally cooled to register the spectrum of adsorbed H_2S.

After described the above adsorption of basic molecules, the partner acid was either let into the cooled cell that was then gradually heated, or added directly at such temperatures, when the vapour pressure was high enough for adsorption (about 90 K for ozone, 130 K for CO_2, 140 K for SO_2 and 160 K for NO_2). The cell was then cooled again and IR spectra were registered at liquid nitrogen temperature. Spectra were recorded at 4 cm^{-1} resolution, by means of NICOLET 510 or NICOLET 710 FTIR spectrometers.

3. Results

3.1. Hydrogen sulphide

Changes in the spectra of silanol groups perturbed by H_2S only or H_2S coadsorbed with ozone are illustrated in Fig. 1. Ozone adsorption on silica was studied earlier [8], some of that results, showing the coverage dependence in the OH region, are presented for the comparison in Fig. 2. Addition of small quantity of H_2S to silica results in the shift of the maximum of free silanol band from 3750 to 3540 cm^{-1}. Increase of the amount of adsorbed H_2S sifts the band further to 3510 cm^{-1}. In the presence of ozone adsorbed alone the shift of the OH group frequency increases with coverage, but, as seen from Fig. 2, it does not exceed 120 cm^{-1}. If, however, ozone is admitted to the sample with preadsorbed small quantity of H_2S (Fig. 1, curve 4), band maximum occurs at 3480 cm^{-1}, i.e. at the position as low, as never could be observed for any surface coverage by the same compounds adsorbed separately. This means that in addition to the above OH band displacement by 210 cm^{-1} caused by H_2S only, supplementary shift by ca. 60 cm^{-1} takes place.

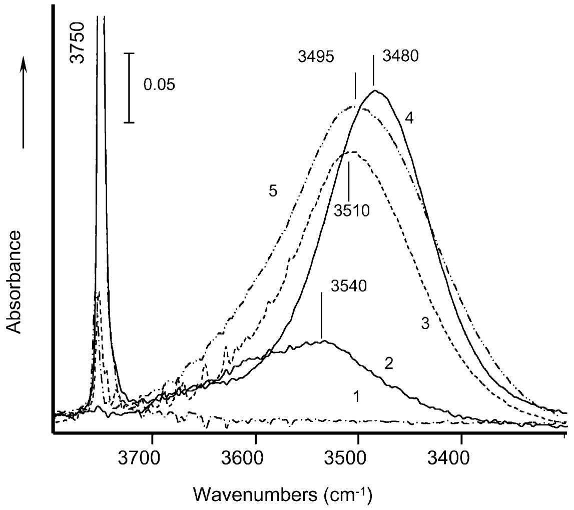


Fig. 1. IR spectrum of silica after pretreatment at 973 K (1); after addition of H_2S in a small dose (2); H_2S in excess (3); after coadsorption of H_2S and ozone (4); after coadsorption of H_2S and SO_2 (5). Spectra 1–4 are registered at 77 K and spectrum 5 at 120 K.

Similar "synergistic effect" when coadsorption of two substances produces a shift of the surface silanol

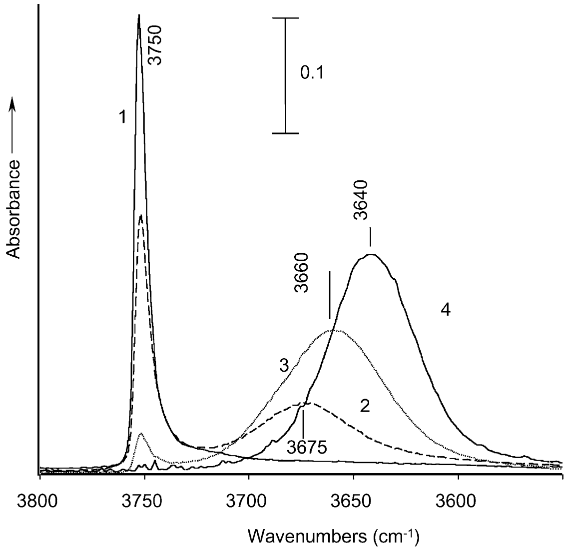


Fig. 2. IR spectrum of silica pretreated at 873 K and cooled up to 77 K (1), after adsorption of increasing amounts of ozone (2–4).

groups which exceeded those on adsorption of each compound solely, was detected for SO_2. When adsorbed alone, this molecule does not perturb the silanol groups too much, resulting in the band of perturbed OH groups that moves from 3662 to 3640 cm^{-1} with the increasing coverage. If the excess of SO_2 is added after preadsorption of H_2S, the band of perturbed hydroxyls is shifted from 3540 cm^{-1} (curve 2) to 3495 cm^{-1} (curve 5), and the overall shift value from 210 cm^{-1} becomes as high as 255 cm^{-1}, again more than for the excess of adsorbed H_2S alone (curve 3).

It should be noted that the spectrum depends greatly on surface coverage. For low pressures of H_2S–SO_2 mixture at any temperature weak broad absorption could be seen, which is, evidently, due to superimposed 3662 and 3540 cm^{-1} bands of silanols perturbed, respectively, by SO_2 or H_2S alone. The maximum absorption intensity of perturbed OH groups with the lowest position of maximum, shown in Fig. 1, was achieved at saturating pressures of both gases at ca. 120 K. If surface coverage could be kept on cooling up to 77 K, we anticipated further downward displacement of the 3495 cm^{-1} band. However, we have not succeeded to cool the system with the fixed coverage up to 77 K, because pressure decrease on temperature lowering results first in the desorption of gases towards the cell walls and shifts the band of perturbed OH groups to higher wavenumbers.

Addition of CO_2 to silica sample at about 150 K results in the appearance of the band of adsorbed molecules at 2347 cm^{-1} and in the displacement of the band of free OH groups from 3750 cm^{-1} to about 3700 cm^{-1}. Determination of the exact position of the shifted band was complicated because of the superimposed band of CO_2 combination mode. CO_2 addition to the sample with small portion of preadsorbed H_2S shifts the maximum of the perturbed OH band from 3540 to 3520 cm^{-1}.

CO adsorption on the sample without H_2S, in accordance with earlier studies [16,17], besides the bands of adsorbed CO at 2158 and 2141 cm^{-1} results in the shift of the free silanol band to 3675–3655 cm^{-1}, depending on temperature and on the pretreatment conditions, but no dependence was reported so far or detected here on the amount of the adsorbed CO. If CO is added at 77 K after adsorption of different quantities of H_2S, the 2158 cm^{-1} band decreases in intensity, together with the decreasing amount of the remaining free silanols capable of hydrogen bonding. However, no additional shift of the OH groups perturbed by H_2S was detected after CO addition.

3.2. Acetone

The position of band due to silanol groups perturbed by acetone in the spectra registered at 77 K is even more sensitive to surface coverage than as it was observed before [10] at 300 K. After small doses of acetone, a band at 3420 cm^{-1} with a low-frequency shoulder appears, accompanied by C=O band at 1715 cm^{-1}. Coverage increase up to saturation results in the only intense OH band at 3240 cm^{-1}, while the maximum of C=O band, also greatly increased in intensity, occurs now at about 1720 cm^{-1}. To fix the conditions of measurements, the results presented below were obtained with small preadsorbed doses of acetone.

Acetone was found not to react with ozone in a sufficiently wide temperature interval. Fig. 3 shows the effect of ozone on the spectrum of silica with preadsorbed acetone that accounts for the band at 1715 cm^{-1} (curve 2) and the corresponding band of perturbed OH groups at 3420 cm^{-1}. Ozone addition (curve 3) results not only in the shift of the latter to 3370 cm^{-1}, but also in the displacement of the 1715 cm^{-1} band to 1692 cm^{-1}, that unequivocally testify for serious strengthening of the H-bond. The simultaneously appeared band at 3650 cm^{-1} corresponds to the remaining OH groups perturbed by ozone as a base.

Similar results with additional shift of perturbed OH groups to 3390 and 3235 cm^{-1} and downward shift of acetone carbonyl vibration up to 1696 and 1693 cm^{-1}, respectively, were obtained with introduced CO_2 and SO_2.

3.3. Ammonia

NH_3 adsorption on silica results in a broad band spreading down to 2600 cm^{-1}, accompanied by intensity decrease of the free silanol band at 3750 cm^{-1} and appearance of bands of adsorbed ammonia at about 3410 and 1635 cm^{-1}. With temperature lowering the bands of ammonia grow and sharpen, while the maximum of the perturbed OH band moves to lower wavenumbers. The exact position of the latter band

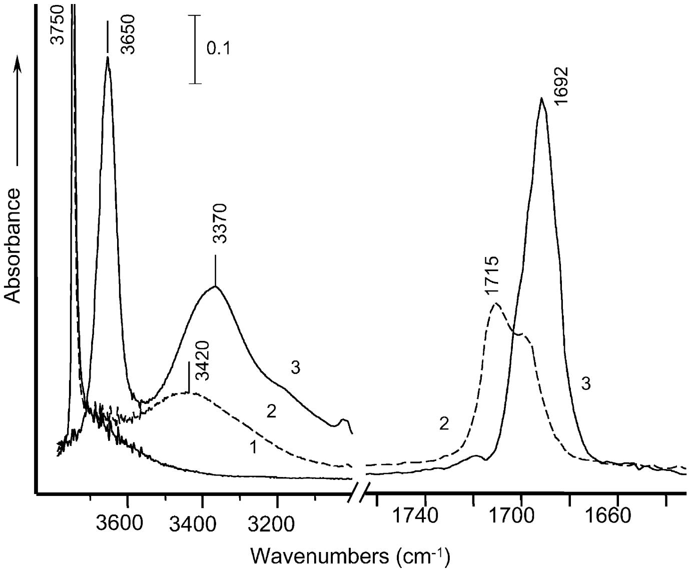


Fig. 3. IR spectrum of silica pretreated at 873 K and cooled up to 77 K before (1) and after (2) adsorption of acetone, and after addition of ozone at 77 K (3).

registered at 77 K depends on the pretreatment conditions and on surface coverage by adsorbed molecules [12]. That is why, to fix the observation conditions in our experiments, the additional OH frequency shifts caused by acid were measured with respect to the band position obtained at the same temperature and with the same amount of preadsorbed ammonia before introducing the acid.

When ozone is admitted, the bands of adsorbed NH_3 are not affected and an additional shift of the

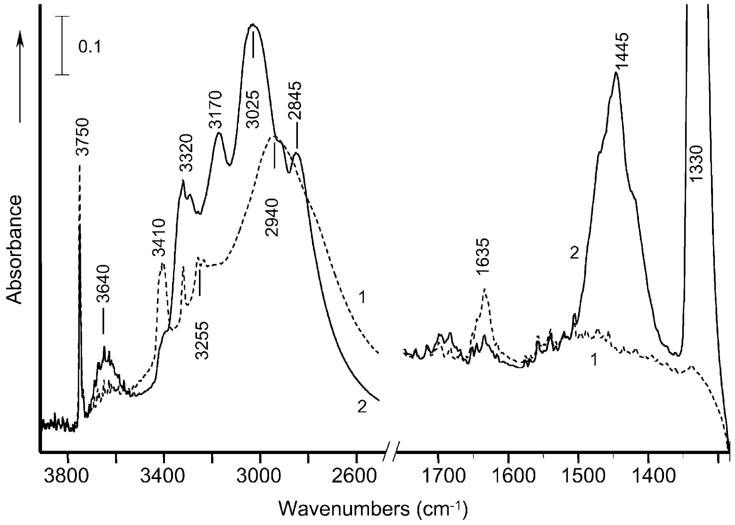


Fig. 4. IR spectra of SiO_2 pretreated at 873 K after adsorption of ammonia at 293 K (1) and subsequent addition of SO_2 at 140 K (2). Spectra are recorded at 77 K. In the low-frequency region, absorption of pure sample is subtracted.

band of perturbed OH groups by about 230 cm^{-1} was observed. The resulting position of the band maximum becomes 2720 cm^{-1}, that is much lower than for ammonia adsorbed alone at any condition.

Additional shift of the OH band after CO_2 admitting to the sample with preadsorbed ammonia at about 130 K does not exceed 50 cm^{-1}. On raising the temperature in the presence of coadsorbed CO_2 and NH_3, new bands arise at 1555 and 1400 cm^{-1} with, perhaps, one more broad component between them.

Fig. 4 shows changes in the spectrum of silica with preadsorbed ammonia after addition of SO_2 at about 170 K. Besides the perturbation of residual OH groups by SO_2, that shifts the OH band to 3640 cm^{-1}, and the appearance of the band of adsorbed SO_2 molecules at 1330 cm^{-1}, one could see the disappearance of the bands of adsorbed ammonia at 3410 and 1635 cm^{-1} together with the “tail” of the perturbed OH adsorption. Instead of the latter, a strong absorption with maxima at 3320, 3170, 3025 and 2845 cm^{-1} arises together with a band at 1445 cm^{-1} at the position very typical of ammonium NH_4^+ ion.

Similar changes in the spectrum of adsorbed ammonia were observed when H_2S was admitted at about 120 K. Instead of the $\delta_{as}(NH_3)$ vibration band at 1635 cm^{-1}, a strong band at 1450 cm^{-1} accompanied by a weaker one at 1670 cm^{-1} appear. On raising the temperature up to 300 K, these bands disappear and the recovered intensity of free silanol band indicates of almost complete desorption of all the observed surface species.

3.4. Pyridine and 2,6-dimethylpyridine

When SO_2 is added in excess to the sample with preadsorbed pyridine (Fig. 5), two strong bands of H-bonded molecules at 1600 and 1445 cm^{-1} disappear together with the broad band at 2845 cm^{-1}, due to OH groups perturbed by pyridine. Instead, together with the band of adsorbed SO_2 at 1330 cm^{-1} and two broad bands at 3390 and 2600 cm^{-1}, new bands of pyridinium ion appear at 1640, 1580, 1555, 1490, 1453 cm^{-1}. Not less pronounced are the changes observed using DMP molecule. Fig. 6 shows the effect of NO_2 addition on the spectrum of DMP adsorbed on silica. Only the bands of H-bonded molecules are observed at 1605 and 1585 cm^{-1} in the spectrum of preadsorbed DMP recorded at 77 K (curve 1), while the broad band of perturbed silanols has its maximum at 2670 cm^{-1}. Addition of NO_2 into the cooled cell and gradual heating results first (at about 130 K) in the appearance and growth of bands at 1300 and 1740 cm^{-1} with a shoulder at 1715 cm^{-1}. On raising the temperature, this group of bands soon

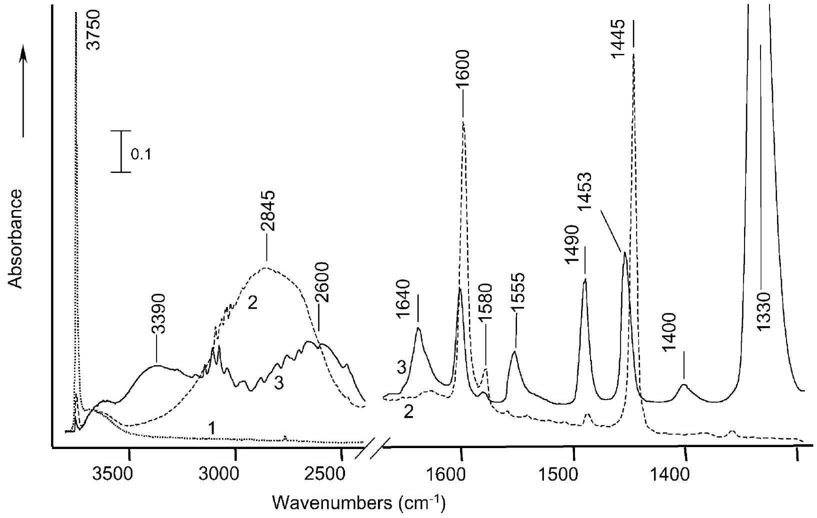


Fig. 5. IR spectrum of SiO_2 pretreated at 773 K (1), after adsorption of pyridine at 300 K (2), subsequent addition of SO_2 at about 180 K (3). Spectra are recorded at 77 K. In the 1700–1300 cm^{-1} region, absorption of pure sample (curve 1) is subtracted.

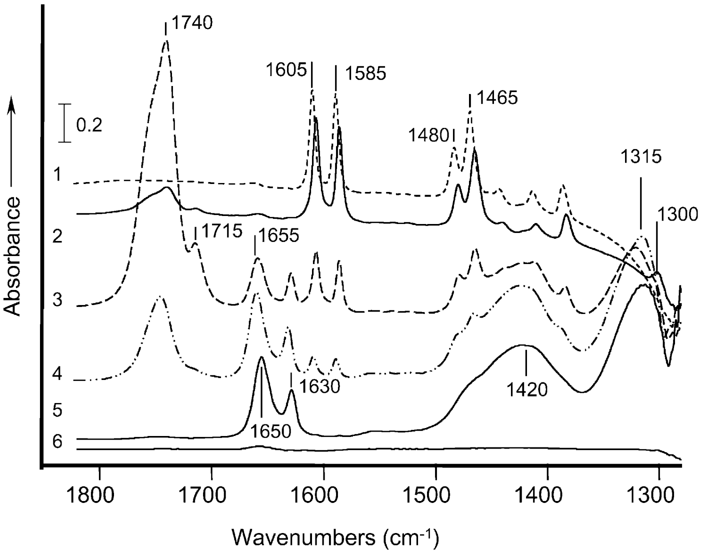


Fig. 6. IR spectrum of SiO_2 after adsorption of DMP at 300 K and cooling up to 77 K (1); after subsequent addition of NO_2 at 77 K and raising the temperature up to 130 K (2), 160 K (3), and 260 K (4); after evacuation for 20 min at 300 K (5) and 373 K (6).

reaches its maximum intensity at about 160 K, and then diminishes up to complete disappearance after pumping at 300 K. Meanwhile, the initial bands of adsorbed DMP diminish in intensity and broad bands at 1420 and 1315 cm^{-1} arise together with two sharp peaks at 1655 and 1630 cm^{-1}, typical of protonated $DMPH^+$ species [14]. Simultaneously, great changes occur in the stretching OH region. The maximum at 2670 cm^{-1} disappears, replaced by a new broad band with complicated contour centred at about 3000 cm^{-1}. The bands at 1655 and 1630 cm^{-1} resist pumping at 300 K, when the bands of DMP are gone, but could be removed by evacuation at 373 K, when the spectrum of initial sample is almost completely restored.

The same spectral manifestations of the transformation of H-bonded DMP into protonated form with the replacement of the band of perturbed silanols by broad absorption at higher wavenumbers was observed after addition of SO_2 at 140 K to the sample with preadsorbed DMP. The difference is that instead of the bands at 1740, 1715, 1420 and 1315 cm^{-1}, only the band of adsorbed SO_2 arises at 1330 cm^{-1}. At low temperatures, the changes are to certain extent reversible: pumping at 180 K results in the diminishing of $HDMP^+$ bands at 1655 and 1630 cm^{-1}, while the intensities of the bands due to H-bonded DMP (1605 and 1585 cm^{-1}) grow up. However, after keeping the sample at 300 K in the presence of SO_2, evacuation leads first to gradual decrease of the bands due to H-bonded DMP, while those of $HDMP^+$ species, shifted to 1650 and 1630 cm^{-1}, were found to be more stable, exactly like above in the case of NO_2 (Fig. 6, curve 5).

Insertion of CO_2 or O_3 does not produce any remarkable alterations in the spectrum of adsorbed DMP.

4. Discussion

4.1. Coverage dependence for single adsorbates

Before turning to binary system, let us consider the coverage dependence of H-bonded systems on silica, based on the earlier as well as new data presented here on the adsorption of single adsorbates.

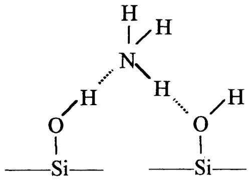
Coverage dependence of the OH band position is comparatively strong for systems where the interaction of silanol group with the first adsorbed molecule is weak and produces a shift close to that caused by non-specific interaction of the resulting surface complex with other physisorbed molecules (see [20] and references therein). In the early work by McDonald

[21], the ν(OH) shifts caused by adsorption of small amounts of oxygen and nitrogen increased with coverage becoming twice greater, from 12 and 24 cm^{-1} up to 25 and 47 cm^{-1}, respectively, when the sample was submerged into liquid O_2 and N_2.

For certain systems with stronger interaction with silanol groups, such as CO [17,18] or ethylene [19] adsorbed on aerosil, coverage dependence of the perturbed OH band position was not detected, although the amount of adsorbate monitored by the band intensity of physisorbed molecules varied in wide limits. Nevertheless, submerging of the sample with preadsorbed ethylene into liquid oxygen shifts the band of silanol groups perturbed by C_2H_4 from 3598 to 3582 cm^{-1}, that is by about 16 cm^{-1} [19]. Thus, the formed surface complexes with weak H-bond are still accessible for other molecules and their OH frequency could be affected by physisorbed oxygen, but not by the same molecules of CO or ethylene. Thus, higher basicity of these molecules in the H-bond does not lead to greater additional OH frequency shifts.

If we take a look at the spectra of adsorbed ozone (Fig. 2), which exhibit almost the same basicity as CO, but a comparatively large additional OH frequency shift, one could notice that the observed shift of the band position to 3640 cm^{-1} cannot be explained as additional absorption of new surface species. In fact, absorption increase near 3640 cm^{-1} is accompanied by decrease of absorption above 3660 cm^{-1}. Such behaviour, when adsorption of new molecules results in the modification of the spectrum of previously formed surface complexes, is typical of lateral interactions between the adsorbed species. For metal oxides, such interaction was studied for adsorbed CO, and was shown to be mediated by the surface and enhanced due to the ionic polarisability of solid by the mechanism of surface relaxation induced by adsorption [22]. In our case, adsorption of two molecules onto the same OH group could be regarded as a kind of lateral interaction that is mediated by the hydroxyl group and is enhanced as a result of its polarisation. Then the increased ν(OH) shift could be considered as an evidence for the OH acidity increase induced by coadsorption of acid.

Coverage dependence of the perturbed OH band position for systems with strong H-bond could be anticipated when a molecule is able to interact with two silanol groups simultaneously.



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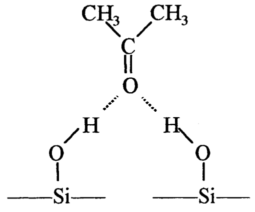


II

H-bonded ammonia molecule can act as a donor of proton in one more H-bond with the oxygen atom of adjacent silanol group as shown in Scheme I. Adsorption on such double sites is energetically favourable and results in greater OH frequency shift. After saturation of these double sites, H-bond with isolated silanol groups should occur that results in a smaller OH shift. The observed for ammonia $\Delta\nu$(OH) decrease with coverage [12] is thus, due to such heterogeneity of surface sites distribution. The same, but weaker effect of $\Delta\nu$(OH) diminution with increasing amount of adsorbate was observed for pyridine [13] that could interact with the next OH group forming one more H-bond with the π-electrons of the ring.

In the case of acetone, a stepwise increase of $\Delta\nu$(OH) with growing coverage is consistent with the explanation suggested by Griffiths et al. [10] that adsorption occurs first on two adjacent silanol groups (Scheme II). In fact, if the initial ν(OH) and ν(CO) bands at 3420 and 1715 cm^{-1} correspond to the structure II, then formation of H-bonded complexes of one acetone molecule with one silanol, that could be expected at higher surface coverages by acetone, will result in the strengthening of the H-bond and ν(OH) frequency lowering. This can account for the shift of the band of perturbed OH groups to 3240 cm^{-1} with the increasing amounts of adsorbed acetone. The band position of carbonyl group, however, will not be affected more by this one H-bond, than by two weaker bonds shown in Scheme II, and the band at 1720 cm^{-1}, observed at high coverages, could be attributed to the same 1:1 acetone–silanol complexes.

The alternative explanation of the observed spectral manifestations by strengthening of the only H-bond in 1:1 complex, caused by interaction of second acetone molecule with the same OH group, as in the above case of ozone, does not work, because then one could anticipate ν(CO) frequency decrease for those acetone molecules that play the role of proton acceptors in the new H-bond.

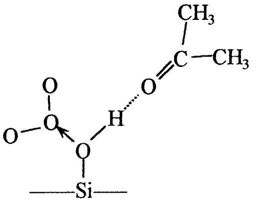
SO_2, and H_2S, like ozone, demonstrate well-pronounced downward frequency additional shifts of the band of perturbed OH groups on coverage increase. To find out, if these molecules, besides their basic properties, exhibit electron-accepting or proton-donating ability and interact with oxygen atoms of silanol groups as acids, let us now consider the data on coadsorption.

4.2. Binary mixtures of coadsorbed molecules

First of all, we would like to note that CO, SO_2 and ozone produce almost the same frequency shift of about 90 cm^{-1} when adsorbed in small amounts on the silanol groups, and, hence, have very close basicity in the H-bond. However, the effect of their addition on the spectrum of adsorbed H_2S is quite different. While CO does not affect the OH groups perturbed by H_2S at all, admitting of SO_2 or ozone results in additional shifts that exceed the shift by 30 cm^{-1}, observed after insertion of H_2S in excess to silica sample with preadsorbed small portion of H_2S. We can, thus, conclude that it is not the physisorption and not the basicity of molecules that accounts for additional ν(OH) lowering, but rather their acidity. Molecules that do not reveal notable coverage dependence of the perturbed OH band if adsorbed alone, do not affect the position of the band of silanol groups perturbed by other bases.

The results on the additional frequency shifts obtained for binary coadsorbed mixtures are summarised in Table 1. In the second column, the frequencies of OH groups perturbed by adsorption of the three bases, H_2S, acetone and NH_3, are presented. Third column gives the corresponding $\Delta\nu$(OH) values with respect to the frequency of free silanol groups (3750 cm^{-1}). Additional shifts $\Delta\nu_a$(OH) caused by admitting of coadsorbed molecules are presented in the next three columns.

We suppose that for all these molecules, the mechanism of the effect of coadsorbed molecules is the same. Then the additional shift values presented in the table can be used as a measure of weak Lewis acidity of molecules coadsorbed with the same bases, as illustrated below (Scheme III) for the case of ozone coadsorption with acetone as an example:



III

Additional shifts caused by CO_2 admitting are always smaller than those induced by O_3 or SO_2. The effect of two latter molecules is comparable. For H_2S as a base, the $\Delta\nu_a$(OH) caused by ozone is a little greater, but taking into account that for SO_2 band position was determined at higher temperature, we can only state that the values are close enough. The $\Delta\nu_a$(OH) obtained for SO_2 with acetone as a base is greater than that for ozone, but it seems to be overestimated because the shifted band overlaps with the low-frequency band of OH groups perturbed by acetone adsorbed alone. It is possible that the transition of structure II to acetone complex with single silanol group is somehow favoured in the presence of SO_2. Anyway, we can estimate the increase of H-bond strength from the carbonyl C=O frequency decrease. This effect is observed in both cases, and ν(CO) shift from 1715 to 1692 and 1693 cm^{-1} for ozone and SO_2, respectively, demonstrates practically equal increase of silanol acidity induced by these two molecules.

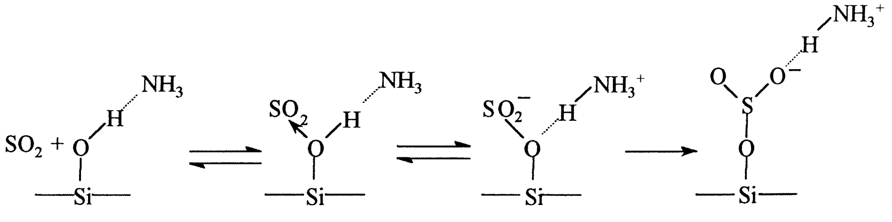
Table 1
Band positions of surface silanol groups ν(OH) and shift values $\Delta\nu_b$(OH) caused by adsorption of bases, and additional shifts $\Delta\nu_a$(OH) observed after admitting acid to the sample with preadsorbed base (cm^{-1})

Base	ν(OH)	$\Delta\nu_b$(OH)	$\Delta\nu_a$(OH) caused by acids		
			CO_2	O_3	SO_2
H_2S	3540	210	20	60	>43
Acetone	3420	330	30	60	185
NH_3	2780–2960	790–970	50	236	Protonation

Changes in the spectra of adsorbed ammonia after addition of CO_2, ozone and SO_2 also testify for greater effect of ozone as compared with that of CO_2, while SO_2 leads even to ammonia protonation, that could be regarded as an evidence for further OH acidity increase. Proton transfer induced by SO_2 addition was established as well for adsorbed pyridine and DMP [23], while ozone admitting to silica with preadsorbed DMP does not lead do its protonation, as in the case of ammonia. The mechanism of this reaction will be discussed in more detail below.

4.3. The induced Brønsted acidity

Spectra shown in Fig. 3 unambiguously testify for the formation of ammonium NH_4^+ ions after addition of SO_2. Bands at 3320, 3170, 3025 and 2845 cm^{-1} could be assigned to the NH-stretching vibrations, while that at 1445 cm^{-1} is due to the ν_4 bending mode of NH_4^+ [24]. For pure silica, ammonia protonation does not occur, with a possible exception of some early works, where small quantity of ammonium ions were detected on silica gel [25]. Here H-bonded ammonia becomes almost completely protonated, and we believe that this is a result of silanol acidity increase induced by SO_2, and the scheme of transformation could be as follows:

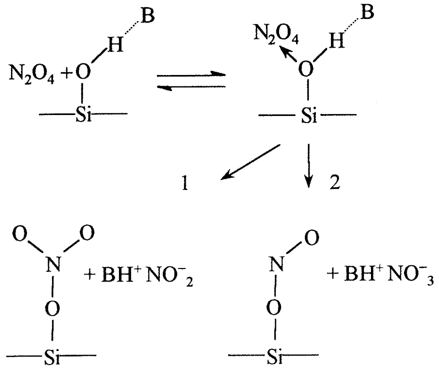


Surface sulphite formed in this process should absorb near 1100 cm^{-1} [24], in the region of very strong bulk absorption of silica and can scarcely be detected in IR spectra.

It is known, however, that ammonia can react directly with acids. In the presence of water, this leads to ammonium salts, while in the lack of water NH_2-substituted anions could be formed. So, NH_3–CO_2 interaction leads to $NH_4^+[CO_2NH_2]^-$ carbaminate compound [26]. Apparently, the bands at 1555 and 1400 cm^{-1} that arise after CO_2 and NH_3 coadsorption could be due to such species. With H_2S, ammonia can easily react at 300 K to form ammonium sulphide [26]. We have to adopt then that ammonium ions could be formed using protons of other ammonia molecules or of H_2S in some direct or initiated by silica surface processes. Fortunately, the above-presented results on pyridine or DMP protonation induced by SO_2 and NO_2 show that at least for these molecules, the proton originates from silanol groups, because neither these bases nor acids possess any hydrogen that could be used for proton donation.

Disappearance of broad bands of the perturbed OH groups together with the formation of protonated forms is in agreement with the proposed scheme. New bands that appear at 3390 and 2600 cm^{-1} after SO_2 addition to preadsorbed pyridine or at 3000 cm^{-1} in the case of DMP protonation should be, apparently, attributed to the NH group perturbed by H-bond. While the H-bond is with the oxygen of former silanol group, the proton transfer should be reversible, as it was found for DMP–SO_2 system at low temperatures. The loss of reversibility at 300 K, to our mind, is due to structural reorganisation when new H-bond links the nitrogen with the terminal oxygen atom bound to sulphur. We suppose that the same reorganisation shown in Scheme IV takes place in the case of ammonia as well.

Reaction of DMP preadsorbed on silica with nitrogen dioxide should be similar to that one shown in Scheme IV, although somewhat complicated. First, because NO_2 is mostly dimerised even at 300 K. The positions of the band at 1740 cm^{-1} and its weaker satellite at 1715 cm^{-1} are very close to frequencies reported for the symmetric N_2O_4 (1748 and 1712 cm^{-1} [24]) showing that in the adsorbed state we deal mainly with dimers. Second, NO_2 cannot produce surface nitrates only, because nitrogen formal valence state in dioxide is 4, and if some part is oxidised, some others should be reduced. On metal oxide surfaces, NO_2 forms equal quantities of nitrate and nitrite ions in the reaction of disproportionation: $2NO_2 + O^{2-} = NO_3^- + NO_2^-$. One NO_2 molecule takes the extra electron and is reduced to the nitrite ion, while another one is oxidised and forms nitrate ion with surface oxygen ion. In our case, after reaction of DMP as a base (B) with silanol group we shall have either dimethylpyridinium (BH^+) nitrite and nitrate bound to silicon as a result of process 1, or dimethylpyridinium nitrate and surface silicon nitrite formed in reaction 2.



The bands at 1420 and 1315 cm^{-1} that accompany the protonation and do not appear when the same $DMPH^+$ is formed after SO_2 addition, are, evidently, due to N–O-stretching vibrations of nitrate and nitrite ions, however these data are not sufficient for the final choice between the reactions 1 and 2.

If the acidity of OH group could be affected by interaction of acid molecule with oxygen atom, the basicity of this oxygen atom should be enhanced as well on the formation of H-bond with the adsorbed bases. In the case of reactions with proton transfer this means a mutual enhancement of adsorption. While acid and base adsorbed separately could be removed from silica by pumping at 300 K, their silanol-mediated interaction leads to irreversible at 300 K adsorption of both compounds, as it was found for SO_2 and NO_2 coadsorbed with DMP or ammonia. The increased basicity of oxygen, evidently, leads first to the strengthening of its bond with acid molecule, and finally, to the formation of salt-like surface species that could be desorbed only at elevated temperatures.

If we try now to characterise the acidity of molecules starting from their ability to cause basic molecule protonation, the resulting sequence will almost coincide with that one obtained above from the perturbed OH frequency shifts. The difference is in mutual position of ozone with respect to H_2S. As far as the latter was found to induce ammonia protonation, while O_3 does not exhibit such properties with any of basic molecules used, the acidity should increase now in the following sequence: $CO_2 < O_3 < H_2S < SO_2, NO_2$. The reason of this small discrepancy is not quite clear yet. We suppose that it is the ability of H_2S and ammonia to form H-bonded polymer clusters, that accounts for the enhanced acidity of silanol groups and increased basicity of ammonia, and that, finally, results in the proton transfer. Then, reversibility of ammonia protonation induced by H_2S can be explained by ease of the proton back transfer in H-bonded polymer chain, as compared with the case of surface ammonium sulphide formation.

4.4. General outlook

Let us now consider some applications of the above-developed notion on the bifunctional character of silanol groups and their ability to interact with adsorbed molecules as an acid and a base simultaneously.

The phenomenon of silanol-mediated enhancement of interaction between acidic and basic molecules enables us to suggest a new explanation of the old problem of silica–alumina surface OH groups. It is known that despite a high concentration of aluminium at the surface that could be detected as Lewis site by adsorption of different test molecules, no bands of Al–OH vibrations could normally be seen, and the only OH band observed for this material is that of surface silanol groups at about 3750 cm^{-1}. Nevertheless, adsorption of bases reveals certain amount of very acidic hydroxyl groups with a great shift of OH frequency on adsorption [27].

Apparently, some of silanol groups have Al^{3+} ions in local environment, but only after H-bond formation the basicity of oxygen becomes high enough to form coordinate bond with aluminium. As a result, the group becomes bridged between silicon and aluminium atoms, and its acidity turns to be close to that of similar groups in zeolite framework. Desorption of base restores the initial geometry and frequency of silanol group.

In zeolites, existence of bridged acidic OH groups is stabilised by weak interaction of these hydroxyls with the field of adjacent oxygen atoms in the cavity that causes the OH frequency decrease to about 3650–3600 cm^{-1}. This is in coherence with the idea recently proposed by Busca [28] that in zeolites the bridged OH groups exist because their structure is stabilised by the lattice.

The mechanism of promoter action of gases like H_2S [7], SO_2, CO_2, NO_2, etc. in a great number of reactions catalysed by oxides and zeolites could be somewhat clarified as well. Weak reversible adsorption of these gases is known to increase the Brønsted acidity and activity of some zeolites in the reactions catalysed by proton sites [29]. As it was already shown by some of us [7], in the case of H_2S these are the OH groups, either formed as a result of dissociation, or already existing at the surface, that play the role of Brønsted acid sites. The above-presented data once again point to possible decisive role of OH groups and, in particular, of their induced acidity, caused by interaction with the promoter, in these catalytic processes.

5. Conclusions

Coverage dependence of the OH frequency shift, caused by some molecules adsorbed alone, and particularly shifts on coadsorption of binary mixtures demonstrate the bifunctional character of silanol group that could interact with two molecules, acting simultaneously as an acid and a base.

Addition of SO_2 or ozone to the sample with preadsorbed H_2S, acetone or ammonia results in shifts that are greater than those observed at any coverages by only one of coadsorbed molecules. The obtained data could be interpreted as a result of the increased proton-donating ability of silanol groups on interaction via the silanol oxygen atom with coadsorbed Lewis acids, leading to the strengthening of the hydrogen bond with the preadsorbed basic molecule. The additional shift values of the SiOH groups perturbed by certain bases, observed after addition of acidic molecules, could be used for semi-quantitative estimation of Lewis acidity of the latter molecules. This points to the Lewis acidity of ozone, that is stronger than that of CO_2, close, and slightly lower than the acidity of SO_2.

From the comparison of the values of the OH frequency perturbation, it follows that the acidity (Brønsted or protonic) increases in the sequence: $CO_2 < H_2S < O_3 < SO_2$. If we take into account that the basicity, determined from the silanol group frequency shifts upon H-bonding with the same molecules, decreases in other sequence: $H_2S > SO_2, O_3 > CO_2$, we have to state that there is no correlation between thus determined acidity and basicity.

For strong bases, such as ammonia, pyridine or 2,6-dimethylpyridine, addition of SO_2 or NO_2 enhances the acidity of silanol groups to such extent that proton transfer occurs, indicating the appearance of Brønsted acidity induced by coadsorbed acids. Even H_2S addition was found to induce ammonia protonation, while O_3 does not exhibit such properties with any of basic molecules used. Then, if the relative acidity of molecules could be characterised by their ability to induce basic molecule protonation, the sequence of acidity increase is slightly different: $CO_2 < O_3 < H_2S < SO_2, NO_2$. The origin of dissimilarity in the mutual positions of ozone with respect to hydrogen sulphide is believed to be due to the ability of H_2S and NH_3 molecules to form the H-bonded cluster chains with the participation of silanol groups.

The suggested mechanism of the induced OH acidity increase could account for the earlier established surface properties of some systems, such as the promoting effect of acidic gases in some reactions catalysed by oxides or zeolites.

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