Catalysis Letters 70 (2000) 159–163

Brønsted acidity of silica silanol groups induced by adsorption of acids

A.A. Tsyganenko [a], E.N. Storozheva [a], O.V. Manoilova [a], T. Lesage [b], M. Daturi [b] and J.-C. Lavalley [b]

[a] *Institute of Physics, St. Petersburg University, St. Petersburg 198904, Russia*
[b] *UMR 6506, ISMRa, Université de Caen, 14050 Caen Cedex, France*

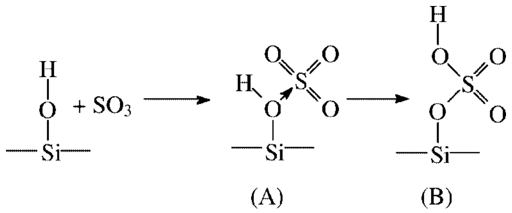
Received 15 May 2000; accepted 3 October 2000

Surface silanol groups of silica, which never revealed any Brønsted acidity, are shown to donate protons to adsorbed basic molecules, such as ammonia, pyridine or 2,6-dimethylpyridine, after addition of acids such as SO_2 or NO_2. The latter, when coadsorbed with bases, interact with the oxygen atoms of silanols leading to OH acidity increase and to protonation. Bases, in turn, enhance chemisorption of SO_2 or NO_2, and strongly held coadsorption products are formed as a result. The proposed mechanism of induced Brønsted acidity could account for the promoting effect of acidic gases in reactions catalysed by metal oxides.

Keywords: coadsorption, acidity, FTIR, silica, protonation

1. Introduction

Acid properties of surface hydroxyl groups on metal oxides are generally characterized by adsorption of basic molecules such as pyridine, ammonia, and carbon monoxide, followed by IR spectroscopy [1–3]. On silica, only H-bond formation occurs indicating a rather weak acidity of the silanol groups, quantitatively characterized by $pK_a = 7$ [4]. On metal oxides, adsorption of acid molecules such as CO_2 or SO_2 reveals, through the formation of hydrogen carbonate or hydrogen sulphite species, the basicity of some OH groups. On silica, only the strongest Lewis acids interact directly with the oxygen atoms of silanol groups [5]. For instance, SO_3 adsorption leads to the formation of new S–OH groups, as shown below in the scheme 1. Only species B, with the proton transferred to the oxygen atom of SO_3, was observed. However, on methoxylated silica, species corresponding to both A and B have been detected, species B being in such a case Si–O–SO_2–OCH_3 [5].



Scheme 1.

Recently some of us have observed that the frequency shift $\Delta\nu$(OH) of silanol groups interacting with weak bases such as O_3 or H_2S increases with growing amount of adsorbate [6,7]. The additional shift was supposed to be due to the interaction of one more adsorbate molecule (now acting as an acid) with the oxygen atom of a silanol group, already involved in a H bond. The increase of the OH frequency shift infers the increase of silanol acidity induced by interaction with the molecule of acid. This suggests that by adding certain gaseous Lewis acids, we can control the acidity of surface OH groups. For instance, it seems possible to create Brønsted acidity on pure silica, which was never observed if the surface was not modified by other compounds. To verify this hypothesis, we have tried CO_2, H_2S, SO_2 and NO_2 addition to silica with preadsorbed bases, such as ammonia, pyridine and 2,6-dimethylpyridine (DMP).

2. Experimental

For IR studies, thin aerosil pellets were prepared and activated first in oxygen, then in vacuum ($<10^{-2}$ Pa) for 1 h at 970 K or 2 h at 670 K. The IR cell allowed us to perform sample treatment at temperatures up to 1000 K and IR spectra measurements in the range 60–300 K. Details on the design and performance of the cell are given elsewhere [8]. For the low-temperature measurements, liquid nitrogen was used as a coolant and after its removal 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 50 Pa of helium was admitted into the sample compartment.

Normally ammonia, pyridine or DMP were dosed at 250–300 K after recording the background spectrum of pure silica at room temperature. Then the cell was cooled and IR spectra were registered at 77 K in the presence of gaseous He. Next the acid probe was added and condensed in the cooled cell, which was then heated until pressure increase and OH perturbation reveal its evaporation and adsorption. Finally, the cell was cooled to register the resulting spectrum.

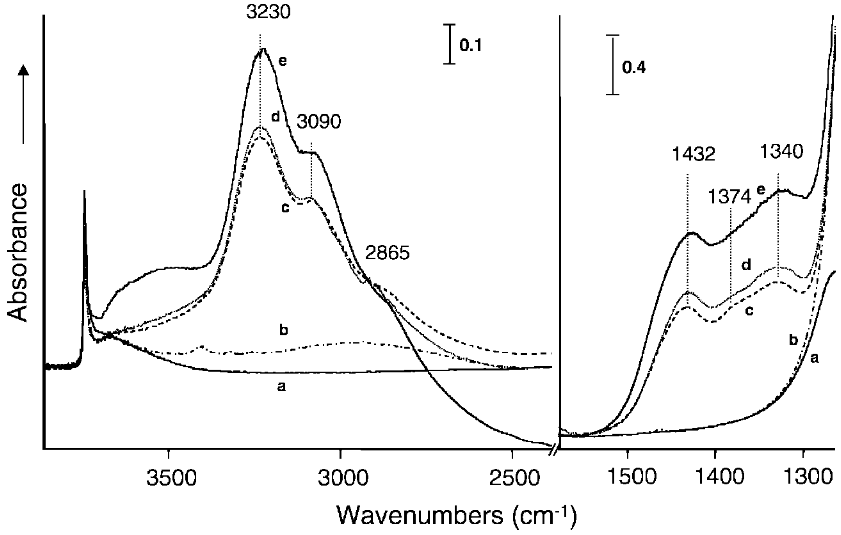


Figure 1. IR spectrum of SiO_2 after (a) pretreatment at 670 K, (b) adsorption of NH_3 at 300 K, (c) addition of 266 Pa of NO_2 and (d) subsequent heating to 325 K; (e) spectrum of a mechanical mixture of 15% NH_4NO_3 with silica. Spectra are registered at 300 K.

In the case of room temperature measurements the base (ammonia) was first added up to about 150 Pa in equilibrium. Then increasing pressures of NO_2 were introduced until surface saturation. Subsequently the sample was treated at increasing temperatures in the presence of the gas phase.

Transmission IR spectra were recorded, at 4 cm^{-1} resolution, by means of NICOLET 510 and 710 FTIR spectrometers.

3. Results

Ammonia adsorption on silica, as can be seen in figure 1, spectrum (b), results in a broad band centred at about 3000 cm^{-1}, accompanied by an intensity decrease of the free silanol band at 3750 cm^{-1} and the appearance of bands at about 3410 and 1635 cm^{-1} (not shown in the spectrum). These features are due to hydrogen bond formation between hydroxyl groups of silica and the lone electron pairs of nitrogen atoms in ammonia molecules. With temperature lowering, the bands of ammonia grow and sharpen, while the maximum of the perturbed OH band moves to lower wavenumbers [9].

Subsequent addition of CO_2 to the sample with preadsorbed ammonia 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 remaining free OH groups from 3750 to about 3700 cm^{-1}, but it does not affect the spectrum of adsorbed ammonia.

Addition of SO_2 at about 170 K causes serious changes in the spectrum. Besides the perturbation of residual OH groups, shifted to 3660 cm^{-1}, and the appearance of the band of adsorbed SO_2 molecules at 1343 cm^{-1}, which is in accordance with [10], SO_2 adsorption leads to the disappearance of the bands of adsorbed NH_3 at 3410 and 1635 cm^{-1} together with the "tail" of absorption of OH groups perturbed by ammonia. Instead of the latter, a strong absorption with maxima at 3320, 3170, 3025 and 2845 cm^{-1} arises together with a band at 1450 cm^{-1}, at the typical position for NH_4^+.

Even more dramatic is the effect of NO_2 addition at 300 K to the silica sample with preadsorbed ammonia, illustrated in figure 1. After the first introduction of 266 Pa of NO_2 (spectrum (c)) a massif constituted by three main components at 3230, 3090 and 2865 cm^{-1} appears. At the same time a strong absorption grows up below 1600 cm^{-1} with at least three components at 1432, 1374 and 1340 cm^{-1}, the first one being again in the region of the ammonium bending vibration. NH_4^+ species is stable enough up to 325 K (spectrum (d)), showing that the protonation process in these conditions is irreversible. For comparison, the spectrum of the mechanic mixture of 15% of NH_4NO_3 in silica is presented in the same figure (spectrum (e)), which turns to be almost identical to that obtained after NO_2–ammonia coadsorption. The only extra band at 3550 cm^{-1} in the spectrum of the mixture is due to molecular water which is always present in untreated silica.

Spectra resulting from SO_2 addition to pyridine adsorbed on silica are illustrated in figure 2. In the spectrum of pyridine adsorbed alone (spectrum (a)), in agreement with the earlier data [1], only H-bonded and physisorbed molecules reveal themselves by the bands at 1600 and 1445 cm^{-1}. After SO_2 addition (spectrum (b)) new bands at 1640, 1555, and 1490 cm^{-1} arise, that can be considered as the evidence for pyridinium ion formation.

The most pronounced are the changes observed using DMP which is an excellent test molecule for proton acidity, since its two ν_8 vibrations are very sensitive to protonation [11]. Figure 3 shows the effect of SO_2 addition on the spectrum of DMP adsorbed on silica. Only the ν_8 vibration bands of H-bonded molecules are observed at 1606 and 1585 cm^{-1} in the spectrum of preadsorbed DMP recorded at 77 K (spectrum (b)), while the wide band of perturbed

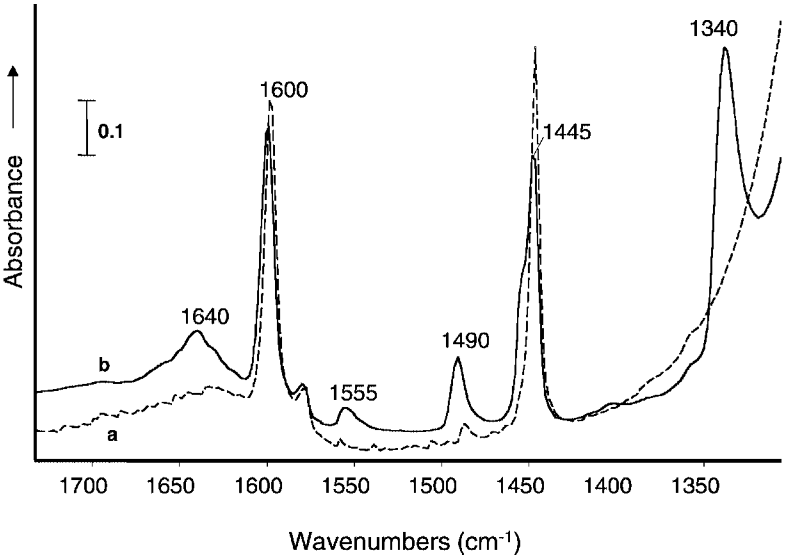


Figure 2. IR spectrum of SiO_2 after (a) adsorption of pyridine at 300 K and (b) subsequent addition of SO_2 at about 180 K. Spectra are registered at 77 K.

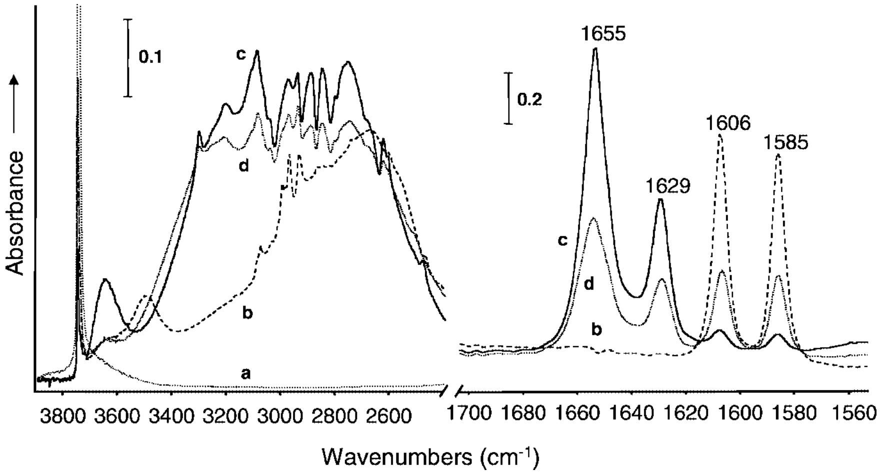


Figure 3. IR spectrum of SiO_2 after (a) pretreatment at 670 K, (b) adsorption of DMP at 300 K and cooling to 77 K, (c) addition of SO_2 and (d) evacuation for 1 min at 180 K. Curves (b–d) in the 1800–1300 cm^{-1} region are presented after subtraction of the background silica absorption (spectrum (a)).

silanols has its maximum at 2670 cm^{-1}. Addition of SO_2 at about 180 K (spectrum (c)) results in almost complete disappearance of these bands, while new bands arise at 1655 and 1629 cm^{-1} together with the band of adsorbed SO_2 at 1340 cm^{-1}. Simultaneously, instead of the broad band of perturbed OH groups, a new broad band centred at 2950 cm^{-1} appears.

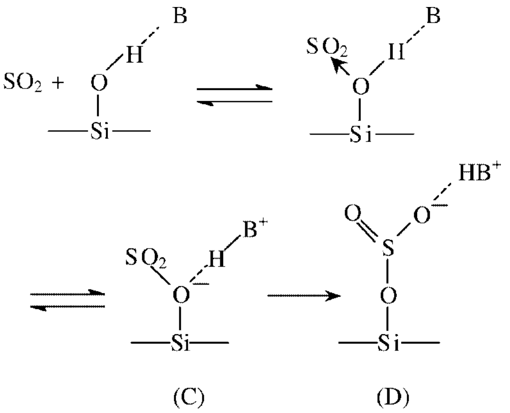
Spectrum (d) in figure 3, registered after removal of SO_2 gas at about 180 K, demonstrates certain reversibility of the observed changes when the $HDMP^+$ bands (1655 and 1629 cm^{-1}) diminish, and the intensity of the bands due to H-bonded DMP (1606 and 1585 cm^{-1}) is partially restored. However, when the sample is evacuated after keeping at 300 K in the presence of SO_2 (spectrum not shown), this leads to gradual decrease of the bands due to H-bonded DMP species. Those of $HDMP^+$ were found now to be more stable and still remain in the spectrum at slightly different wavenumbers of 1650 and 1629 cm^{-1} after outgassing at 300 K for 10 h.

The same bands at ca. 1655 and 1629 cm^{-1} arise after NO_2 addition to silica with preadsorbed DMP. Besides, a strong band at 1740 cm^{-1}, accompanied by another much less intense band at 1713 cm^{-1}, arises as soon as the gas appears in the cooled cell. These bands, but much less intense, could be observed at 300 K and disappear after short pumping. No remarkable changes in the spectrum of adsorbed DMP were detected after CO_2 or H_2S addition, neither at low (about 120 K) nor at room temperature.

4. Discussion

The presented results show that addition of a Lewis acid to silica with preadsorbed bases in certain cases results in protonation of the latter. Acidity of CO_2 or H_2S is not high enough to induce the proton transfer, at least to DMP molecules. SO_2 and NO_2 were found to provoke protonation of all the bases tried by us: ammonia, pyridine and DMP with SO_2, and NO_2 with NH_3 and DMP. In the absence of bases both SO_2 and NO_2 are known to interact with silica only reversibly, acting as a base in H bond with surface silanol groups.

The mechanism of base molecule protonation induced by SO_2 can be illustrated by scheme 2 below, where B stands for the base:



Scheme 2.

In the case of ammonia, disappearance of the bands of adsorbed NH_3 as well as those of perturbed OH groups after SO_2 addition means that the species with coordinately bound SO_2 is not stable and in the conditions of the reaction it leads to complete protonation of the H-bonded base. The bands of surface sulphite should occur at about 1100 cm^{-1} [12], in the region of total bulk absorption of silica.

Reaction of ammonia preadsorbed on silica with NO_2 should be similar. The fact that the spectrum of surface species formed as a result of reaction practically coincides with that of NH_4NO_3 mixed with silica means that NO_2 reacts with the OH group and that protonation has taken place.

The mechanisms of reactions observed when SO_2 or NO_2 are added to silica samples with preadsorbed pyridine and DMP are completely analogous to those of ammonia and could be described by the same scheme 2. Although the bands of pyridinium are close to those of adsorbed pyridine, appearance of the band at 1555 cm^{-1}, absent for pure pyridine, infers that after SO_2 addition pyridine is at least partly protonated.

In the case of DMP, bands at 1655 and 1629 cm^{-1}, that appear after SO_2 or NO_2 addition, should be unequivocally attributed to ν_8 vibrations of protonated DMP referred below as $HDMP^+$. The accompanying broad absorption centred at 2950 cm^{-1} is due to the N–H vibration perturbed by a H bond with the oxygen atom of the former silanol.

To explain the changes in the high-frequency region, we should take into account that the abrupt slope below 2600 cm^{-1} of the perturbed OH band in the spectrum registered before SO_2 addition is caused by "Evans' well" – Fermi resonance with the overtone of the OH bending vibration [13]. After proton transfer, such resonance is no longer possible, but now the NH stretching vibration of the newly formed NH group of $HDMP^+$ can interact with CH stretching modes of the same ion, which evidently accounts for the complex contour in the CH stretching region (3200–2600 cm^{-1}).

Somewhat unexpected is the partial reversibility of protonation at low temperatures, when the bands of newly formed $HDMP^+$, stable during pumping at 300 K, diminish on evacuation at about 180 K. In our opinion, this can be explained by structural rearrangement, analogous to that shown above in scheme 1. In fact, in structure C (scheme 2) the NH group still interacts with the O atom of the former silanol group, and a simple proton transfer recovers the system to the initial state. This stage could be reversible at low temperature. At 300 K irreversible transition to the more stable species D takes place with the H bond to the oxygen of the former SO_2 molecule. Desorption of such a product will need more serious rearrangement, and should, evidently, occur at elevated temperatures. Species C and D should have slightly different band positions, and could account for the observed ν_8 bands at 1655 and 1650 cm^{-1}, respectively.

5. Conclusions

The presented results show that the H-bond interaction between silica silanol groups and bases increases in the presence of molecules acting as acids such as NO_2 or SO_2, which when adsorbed alone do not interact strongly with the silanols in the same conditions. The presence of these acids enhances the acidity of silanol groups to such extent that it leads to proton transfer to probe molecules like ammonia, pyridine or DMP. On the other hand, interaction of the proton of a silanol group with the base leads to the increase of OH group basicity and favours the nucleophilic attack of its oxygen atom towards acidic molecules, leading to chemisorption of SO_2 or NO_2. The acidity of CO_2 or H_2S in the same conditions is not high enough to provoke protonation of DMP, the most basic of the studied test molecules. The silanol group demonstrates here its bifunctional character interacting simultaneously as an acid and a base.

The results suggest a possibility to control the processes catalysed by Brønsted acidic sites, where the promoting effect of acidic dopants could be previewed or explained. In particular, this enables us to explain the reversible increase of Brønsted acidity of several metal oxides in the presence of molecular H_2S, detected by DMP adsorption [7].

Finally, our results well demonstrate that acid and basic properties of a solid measured by probe molecules under inert atmosphere could be modified in working conditions. This points to the necessity to perform surface characterisations by *in situ* measurements, under the presence of reactants and products.

References

[1] L. Little, *Infrared Spectra of Adsorbed Species* (Academic Press, London, 1966).

[2] A.V. Kiselev and V.I. Lygin, *Infrared Spectra of Surface Compounds* (Wiley, New York, 1975).

[3] G. Busca, Catal. Today 41 (1998) 191.

[4] R.G. Rouxhet and R.E. Sempels, J. Chem. Soc. Faraday Trans. I 70 (1974) 2021.

[5] A.A. Tsyganenko and E.A. Trusov, Colloid J. USSR 40 (1978) 875 (English translation).

[6] K.M. Bulanin, A.V. Alexeev, D.S. Bystrov, J.C. Lavalley and A.A. Tsyganenko, J. Phys. Chem. 98 (1994) 5100.

[7] A. Travert, O.V. Manoilova, A.A. Tsyganenko, F. Maugé and J.C. Lavalley, to be published.

[8] M.A. Babaeva, D.S. Bystrov, A.Yu. Kovalgin and A.A. Tsyganenko, J. Catal. 123 (1990) 396.

[9] A.Yu. Pavlov and A.A. Tsyganenko, Opt. Spectrosk. 77 (1994) 21 (English translation).

[10] M.A. Babaeva, A.A. Tsyganenko and V.N. Filimonov, Kinet. Katal. 25 (1984) 787 (English translation).

[11] J.C. Lavalley, Trends Phys. Chem. 2 (1991) 305.

[12] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds* (Wiley, New York, 1986).

[13] A.Yu. Pavlov and A.A. Tsyganenko, Opt. Spectrosk. 82 (1997) 21 (English translation).