Infrared Spectra of Adsorbed Molecules on Thin Silica Films

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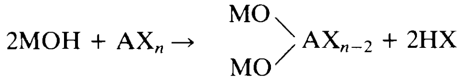
Using a thin film of silica deposited on a ZnSe window we have been able to observe, after spectral subtraction, the i.r. spectra due to the ≡SiOSi, ≡SiOTi, and ≡SiOGa stretching modes when surface hydroxy groups react with $(Me_3Si)_2NH$, $TiCl_4$, or $GaMe_3$ respectively; this versatile technique permits rapid acquisition of i.r. spectral data, over a wide range of temperature or pressure, in regions where an oxide is strongly absorbing.

Low-frequency i.r. spectra of species adsorbed on oxide surfaces can rarely be obtained using self-supporting discs owing to the opacity of the substrate in the region of the lattice vibrations.[1—3] With most oxides or zeolites it is generally necessary to use at least 4—10 mg/cm^2 in order to make a self-supporting disc and such samples are usually opaque below 1300—1000 cm^{-1}, depending on the material. Therefore, in the reaction of surface hydroxy groups, MOH, with a hydrogen sequestering agent AX_n, such as in the two representative cases (A) and (B), the new vibrational modes due to the MOA framework will generally lie in a spectral region where the transmission of the substrate is essentially zero.

$$MOH + AX_n \rightarrow MOAX_{n-1} + HX \quad (A)$$



$$2MOH + AX_n \rightarrow (MO)_2AX_{n-2} + 2HX$$

(B)

We report here the use of a thin film technique which, when applied to a silica adsorbent, has permitted us to observe the i.r. spectra of the SiOA or $(SiO)_2A$ modes which could arise from reactions as depicted above. The essential experimental feature involves the deposition of a thin film of silica (Cab-O-Sil HS5 was used here) on a suitable i.r.-transparent window such that the background absorption due to SiO_2 near 1100 cm^{-1} has a maximum optical density of about 1 (Figure 1A). For reasons of thermal and chemical stability we use ZnS or ZnSe as the window material and the film can be produced either by spreading the self-adhering powder on the window, or by spraying a dispersion of SiO_2 in a volatile solvent such as CH_2Cl_2 on to the window. The window is then placed in an i.r. cell which remains thereafter in a fixed position in the beam of an i.r. spectrometer. The latter is an important point since such films are usually not homogeneously distributed over the surface of the window and, since computer controlled spectral subtraction must be carried out, minute changes in sample position can drastically alter the spectra in regions of strong adsorbate absorption. With the quartz cell used in this work, samples can be heated to 1200 °C, although a limitation of about 800 °C is imposed by the properties of ZnS or ZnSe (higher temperature could be tolerated using a Si or Ge substrate).

We show in Figure 1C—E i.r. spectra, after background subtraction, of $TiCl_4$, $(Me_3Si)_2NH$, and $GaMe_3$ after reaction with isolated surface hydroxy groups on silica to yield $≡SiOTiCl_3$, $≡SiOSiMe_3$, and $≡SiOGaMe_2$ respectively. The reactions of the Ti and Si compounds with silica are well known and have been followed at frequencies above 1250 cm^{-1} using i.r. spectroscopy[4—7] and over the range 100—4000 cm^{-1} using Raman spectroscopy.[3] In the Raman study, we noted our inability to detect the high-frequency symmetric ≡SiOSi stretching mode of various silane agents on silica.[3] This is expected[8] to lie in the range 1150—1050 cm^{-1} and be intense in the i.r. spectrum; we can clearly assign the band at 1100 cm^{-1} to this mode for adsorbed $(Me_3Si)_2NH$. This band did not shift using deuteriated $(Me_3Si)_2NH$ whereas other bands did. Similarly, the equivalent ≡SiOGa and ≡SiOTi modes are at 1010 and 1045 cm^{-1} respectively. Most interestingly, the reaction of $TiCl_4$ with a surface which also contains H-bonded pairs of silanols shows (Figure 1F) a stronger band at 920 cm^{-1} which we assign to $(SiO)_2TiCl_2$ as depicted by reaction (B). This ability to distinguish between linear and bridged structures is the essential new feature of this technique.

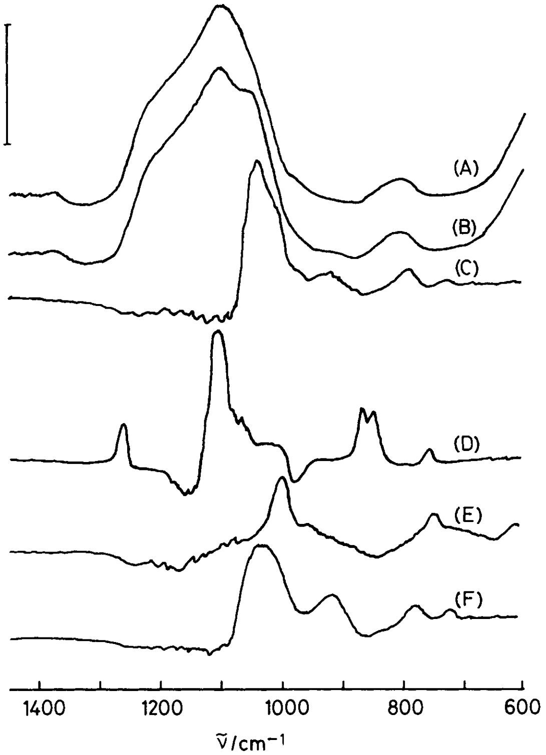


Figure 1. (A), Background thin-film i.r. spectra of silica which had been degassed *in vacuo* at 673 K; (B) after reaction of (A) with excess of $TiCl_4$ at 300 K and evacuation for 10 min; (C) spectrum after subtraction of (A) from (B); (D) and (E), as for (C) after reaction with $(Me_3Si)_2NH$ or $GaMe_3$ respectively; (F) spectrum after the reaction of $TiCl_4$ with silica which had been degassed at 400 K. The bar at the left corresponds to 0.4 absorbance for curves (A) and (B), or 0.1 absorbance for the others.

The band at 1265 cm^{-1} from adsorbed $(Me_3Si)_2NH$ is the symmetric methyl deformation mode whereas the bands between 900 and 700 cm^{-1} are due to methyl rocking modes in the case of adsorbed $(Me_3Si)_2NH$ and $GaMe_3$ and that at 605 cm^{-1} for $GaMe_3$ is due to a GaC_2 stretching mode. Most of these bands from $(Me_3Si)_2NH$ have also been observed using Raman spectroscopy.[3] The bands at 790 and 730 cm^{-1} for adsorbed $TiCl_4$ are possibly due to pseudosymmetric SiOTi stretching modes.[9]

Photoacoustic spectroscopy has recently been used to study the adsorption of $TiCl_4$ and $AlMe_3$ on silica.[9] Although in principle such spectra can be obtained without much sample preparation, it has been our experience that long data acquisition times are necessary before a suitable signal/noise ratio can be achieved. Furthermore, it is difficult to treat such samples under high-vacuum and high-temperature conditions. Similar spectra can also in principle be acquired using diffuse reflectance spectroscopy but again *in situ* treatment of the sample under widely varying conditions of pressure and temperature is difficult.

A feature of the present technique is that catalyst samples can be treated under the full range of conditions of temperature and pressure normally used in i.r. studies of adsorbed species on oxide surfaces. Above all, data acquisition times of the order of seconds to minutes are possible using Fourier transform techniques. Finally, it is essential to note that the entire experiment must be carried out *in situ*. Minute changes in the homogeneity of the sample can give rise to spectral artefacts in the region between 1250 and 1000 cm^{-1} in the case of silica. For this reason, we have found that one cannot in general simply use a compensating SiO_2 disc in, for example, the reference beam of a conventional dispersive spectrometer. Thus, a computer-controlled instrument is essential for this work.

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References

1 A. V. Kiselev and V. I. Lygin, 'Infrared Spectra of Surface Compounds,' Wiley, New York, 1972.
2 B. A. Morrow, A. C. S. Symposium Series, No. 137, 'Vibrational Spectroscopies for Adsorbed Species,' 1980, p. 119.
3 B. A. Morrow and A. H. Hardin, *J. Phys. Chem.*, 1979, **83**, 3135.
4 J. Kunawicz, P. Jones, and J. A. Hockey, *Trans. Faraday Soc.*, 1971, **67**, 848.
5 M. L. Hair and W. Hertl, *J. Phys. Chem.*, 1973, **77**, 2070.
6 W. Hertl and M. L. Hair, *J. Phys. Chem.*, 1971, **75**, 2181.
7 J. Chimielowiec and B. A. Morrow, *J. Colloid Interface Sci.*, 1983, **94**, 319.
8 N. B. Colthup, L. D. Daly, and S. E. Wiberley, 'Introduction to Infrared and Raman Spectroscopy,' Academic Press, New York, 1964.
9 J. B. Kinney and R. H. Staley, *J. Phys. Chem.*, 1983, **87**, 3735.