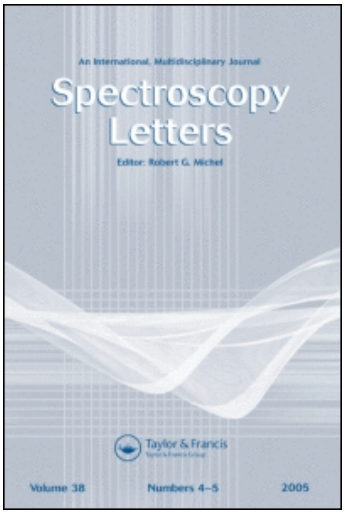

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Quantification of the Number of Silanol Groups in Silicalite and Mesoporous MCM-41: Use of Ft-Raman Spectroscopy

Sunil Ashtekar[a]; Jeremy J. Hastings[b]; Patrick J. Barrie[a]; Lynn F. Gladden[a]
[a] Department of Chemical Engineering, University of Cambridge, Cambridge, U.K. [b] BNFL Research & Technology, Springfields Works, Preston, Lancashire, U.K.

To cite this Article Ashtekar, Sunil , Hastings, Jeremy J. , Barrie, Patrick J. and Gladden, Lynn F.(2000) 'Quantification of the Number of Silanol Groups in Silicalite and Mesoporous MCM-41: Use of Ft-Raman Spectroscopy', Spectroscopy Letters, 33: 4, 569 — 584
To link to this Article: DOI: 10.1080/00387010009350140
URL: http://dx.doi.org/10.1080/00387010009350140

SPECTROSCOPY LETTERS, 33(4), 569–584 (2000)

QUANTIFICATION OF THE NUMBER OF SILANOL GROUPS IN SILICALITE AND MESOPOROUS MCM-41: USE OF FT-RAMAN SPECTROSCOPY

Key words: silica; silanol; silicalite; MCM-41; FT-Raman; pyridine adsorption

Sunil Ashtekar[1], Jeremy J. Hastings[2], Patrick J. Barrie[1] and Lynn F. Gladden[1]

1. Department of Chemical Engineering, University of Cambridge, Pembroke Street, Cambridge CB2 3RA, U.K.

2. BNFL Research & Technology, Springfields Works, Preston, Lancashire PR4 0XJ, U.K.

ABSTRACT

Infrared and FT-Raman spectra have been obtained on pyridine adsorbed within two siliceous materials, silicalite and MCM-41. Both spectroscopic techniques detect the presence of weak physisorbed pyridine and stronger hydrogen-bonded pyridine. In particular, the FT-Raman spectra are well resolved and can be used to measure the number of pyridine molecules that interact with hydroxyl groups. For silicalite, it is found that an average of one pyridine molecule per unit cell interacts with hydroxyl groups. The number of hydroxyl groups present at the surface of porous silica materials can also be obtained using this approach. For siliceous MCM-41, it is found that the hydroxyl group concentration is about 3 mmol/g of dry solid.

INTRODUCTION

There is considerable commercial interest in developing porous silicas for applications in adsorption and catalysis, and a variety of materials have now been prepared with different pore structures. These include microporous materials, such as the siliceous zeolite silicalite,[1] materials with mesopores in the range 30-100 Å typified by MCM-41,[2] and those with mesopores in the range 100-500 Å prepared by sol-gel methods. The chemistry of silica is strongly affected by the concentration and nature of the hydroxyl groups on the surface because the surface properties are largely determined by these characteristics.[3] It is also possible to functionalise the hydroxyl groups, thus changing the adsorption properties or allowing catalytically active groups to be tethered to the surface.[4-6] There is thus a strong motivation to determine the number of silanol groups present on the surface of siliceous materials. One of the major techniques used to characterise hydroxyl groups on the surface of silica is infrared spectroscopy, which may be employed in either transmission or diffuse reflectance mode. This can measure hydroxyl stretching frequencies directly, or alternatively study probe molecules such as carbon monoxide or pyridine adsorbed at hydroxyl groups.[7-13] Other techniques that have been usefully employed include ^{1}H and ^{29}Si solid-state NMR spectroscopy,[14-16] analysis of deuterated silicas,[17-19] and chemical treatment methods such as chlorosilylation.[20,21]

In this paper we report studies on pyridine adsorption within two siliceous materials using diffuse reflectance infrared spectroscopy and FT-Raman spectroscopy. In particular, it will be shown that FT-Raman spectroscopy is readily capable of determining the number of silanol groups accessible to pyridine within siliceous materials. The first material studied is silicalite, which is the siliceous form of the zeolite with the MFI structure. Silicalite has a microporous channel structure where the only hydroxyl groups expected to be present are silanol groups on the external surface and at defects within the

structure.[22] The second material studied is mesoporous MCM-41, which possesses a hexagonal array of one-dimensional channels of approximately 35 Å in diameter.[2,23] Both the internal and external surfaces of MCM-41 are terminated by a layer of silanol groups.[2,6,23]

While infrared spectroscopy has been extensively used for the characterisation of silica surfaces, Raman spectroscopy has been comparatively neglected. One disadvantage of conventional infrared spectroscopy when investigating surface adsorbates is that the solid itself strongly absorbs infrared radiation and so absorption bands from probe molecules at the surface are not easily detected if they overlap with bands from the adsorbent. On the other hand, Raman spectroscopy does not suffer significantly from overlapping bands between sorbate and adsorbent as the Raman intensity of the adsorbent is in general low and the observed spectrum is predominantly due to the adsorbed molecules.[24,25] Raman bands due to pyridine adsorbed on different types of hydroxyl groups have been assigned previously based on experimental results on zeolites.[26-28] Band assignments are in agreement with an earlier Raman study of a silica containing pyridine adsorbed from the liquid phase using a flow-through sample cell.[29]

Another important practical advantage of Raman spectroscopy is that no special sample preparation is normally required. In contrast to infrared spectroscopy, where window materials that transmit infrared radiation have to be used, it is possible to use glass sample cells for Raman experiments because glass is a weak Raman scatterer and transparent to both the excitation radiation and the Raman scattered light. For the study of adsorbates in porous solids, this allows Raman spectra to be recorded under conditions where the amount of adsorbate present is exactly known. It is this practical advantage that is used in this work to quantify the number of silanol groups present on silica surfaces. Diffuse reflectance infrared spectroscopy results are also presented to provide complementary information.

EXPERIMENTAL

The silicalite sample (Si/Al ratio > 800) was obtained from Chemie Uetikon AG. The MCM-41 sample used in the present work has a pore diameter of about 35 Å and was synthesised in the siliceous form using the procedure reported by Luan *et al.*[30] Both samples were calcined overnight at 500°C in air to remove organic material. Infrared and Raman spectra were acquired on a Nicolet-Magna-IR 750 spectrometer equipped with a controlled environment diffuse reflectance cell (Spectra Tech, model 0030-102), a Raman module and an InGaAs detector.

The samples for FT-Raman spectroscopy were prepared using the following procedure. A known mass of sample was dehydrated at 200°C for 12 hours under vacuum in a specially prepared glass tube. Above a constriction in the tube was a glass capillary containing a known amount of pyridine liquid. The tube was sealed and cooled, and the capillary was then broken allowing adsorption of the pyridine into the porous solid. The portion of the tube containing solid was then immersed in liquid nitrogen to prevent pyridine desorption, and the tube flame-sealed at the constriction. The resulting sealed glass tube was then heated to 60°C for 12 hours to ensure a homogeneous distribution of sorbate within the sample prior to recording the Raman spectra. This preparation method allows silica samples to be prepared containing known amounts of pyridine (to an accuracy within 5%). The activation temperature of 200°C was chosen because this avoided background fluorescence in the FT-Raman measurements arising from organic impurities associated with vacuum grease that can form at higher temperatures. The FT-Raman spectra were all acquired at room temperature using an Nd:YAG laser operating at a power of 200 mW, at an excitation wavelength of 1064 nm. The resolution was 4 cm^{-1}. For each spectrum, 4000 scans were co-added giving a data acquisition time of approximately two hours.

The samples for infrared spectroscopy were activated *in situ* in a diffuse reflectance cell at 500°C in a flow of dry helium for two hours. Background

spectra were recorded at both elevated and room temperature while maintaining the helium flow. Pyridine vapour was then introduced at room temperature into the helium stream for a period of five minutes. The sample was then equilibrated at room temperature for 30 minutes in a stream of pure flowing helium to remove all traces of pyridine vapour. A spectrum was then recorded at room temperature. The sample was then heated to 100°C under flowing helium and maintained at this temperature for 30 minutes, cooled back to room temperature and a spectrum again recorded. The spectra of pyridine-containing samples were corrected by background subtraction of the sample spectrum before pyridine adsorption. For the infrared spectra, 256 scans were co-added at a resolution of 2 cm^{-1}. The diffuse reflectance spectra are plotted assuming the model of Kubelka and Munk for diffuse reflectance,[31] with the Kubelka-Munk function being analogous to absorbance.[31,32]

RESULTS AND DISCUSSION

Silanol Groups in Silicalite

Both infrared and NMR spectroscopy have previously detected far more hydroxyl groups in silicalite than those that can occur at the external surface of the crystallites; thus it is known that hydroxyl groups must also exist at internal defects within the structure.[22,33] Various workers have speculated that these may be in the form of silanol "nests" at locations where a silicon atom is missing from the ideal framework structure. Evidence for this comes from the fact that the defects may be healed by thermal treatment.[34,35] It is also possible to insert aluminium atoms into silanol nest sites.[36] Figure 1 shows diffuse reflectance infrared spectra of silicalite at room temperature and at 500°C. At the high temperature, a single asymmetric band at about 3740 cm^{-1} is observed corresponding to terminal silanol groups; these will be on both the internal and external surfaces. At room temperature, additional broad bands at 3680 and 3600 cm^{-1} are present. The fact that these are not detected at 500°C indicates that they do not arise from acidic hydroxyl groups associated with aluminium

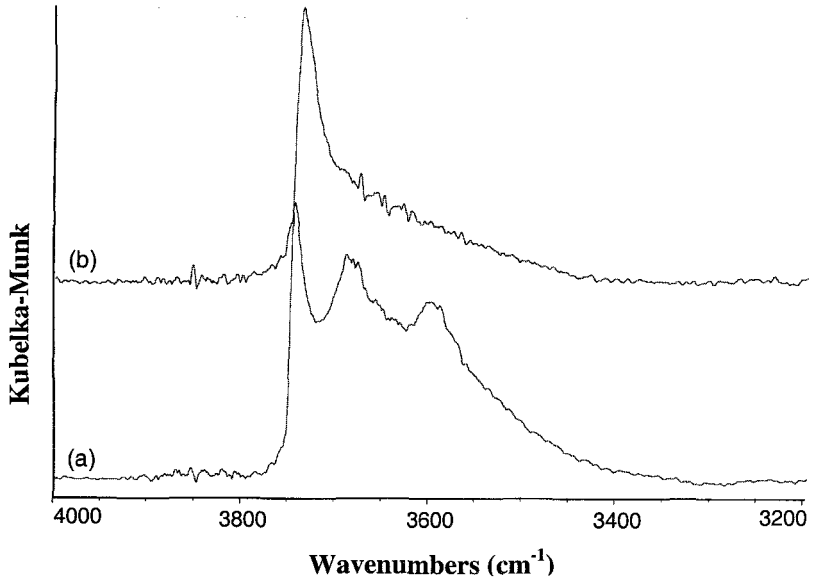

FIG 1 Infrared spectra of the hydroxyl region of silicalite at (a) room temperature, and (b) 500°C.

impurities in the framework. They are therefore assigned to internal silanol groups at defect sites that are perturbed to different extents by hydrogen bonding interactions.[22,37]

After pyridine adsorption and equilibration, new IR bands are observed corresponding to adsorbed pyridine species. Both weak physisorbed species and stronger hydrogen-bonded pyridine species are detected after equilibration at room temperature.[38] After heating to 100°C, only the hydrogen-bonded pyridine species are observed. In the pyridine ring-stretching region, bands arising from physisorbed pyridine occur at 1605, 1558, 1575, 1482 and 1440 cm^{-1}, while those due to hydrogen-bonded pyridine occur at 1597, 1581, 1486 and 1446 cm^{-1} (Figure 2).

Small changes are also observed in the C–H and hydroxyl stretching regions depending on which adsorbed pyridine species are present. However, it is

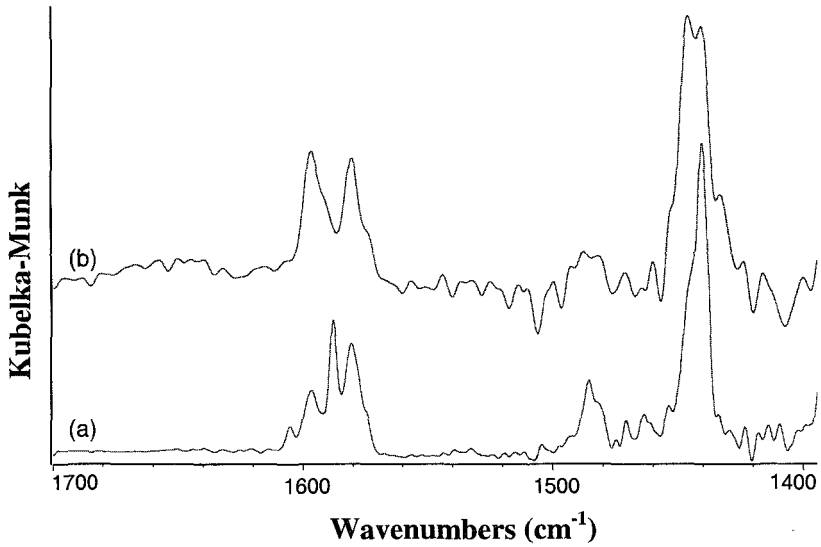

FIG 2 Infrared spectra of pyridine adsorbed within silicalite after equilibration at (a) room temperature, and (b) 100°C.

difficult to quantify the amount of pyridine present in each environment using infrared methods. While molar extinction coefficients for adsorbed pyridine on Brønsted and Lewis acid sites of some solid acid catalysts have been obtained,[39] literature values for them vary sufficiently widely that it is difficult to make reliable measurements using this method. Further the amount of band overlap in the infrared spectra between the physisorbed and hydrogen-bonded pyridine species probably precludes the use of such an approach. For this reason, FT-Raman spectra were obtained on samples of silicalite containing known amounts of pyridine.

In Raman spectra of adsorbed pyridine, bands corresponding to the ν_1 and ν_{12} ring-breathing modes have been found to be sensitive to the state of bonding between the adsorbed pyridine and the solid surface.[26-29] The ν_1 mode of liquid-like pyridine is observed at 991-992 cm^{-1}, of hydrogen-bonded pyridine at 996-

1005 cm^{-1}, and it occurs at higher frequencies when bonded to Brønsted or Lewis acid sites. The ν_{12} mode of liquid-like pyridine is observed at 1031-1033 cm^{-1}, of hydrogen-bonded pyridine at 1032-1040 cm^{-1}, and it also occurs at higher frequencies when bonded to Brønsted or Lewis acid sites. [26]

FT-Raman spectra of pyridine adsorbed in silicalite at various loadings are shown in Figure 3. The spectrum of the pure liquid is also shown, and gives ν_1 and ν_{12} bands at 992 and 1031 cm^{-1} as expected. In contrast to this, the spectrum obtained at a loading of one pyridine molecule per unit cell of silicalite gives bands shifted to 1005 and 1037 cm^{-1}, corresponding to a hydrogen-bonded species. This shift in frequency is expected for adsorption onto an electron pair acceptor site, such as a hydroxyl group.[27] No spectral peaks are observed at frequencies associated with adsorption onto stronger electron pair acceptors such as Brønsted or Lewis acid sites; this is expected to be the case as the aluminium content of the sample is very low (Si/Al ratio > 800). The lack of strong acid sites also means that there is no overlap between the ν_1 and ν_{12} band regions in the spectrum.

On increasing the pyridine loading above one molecule per unit cell, two resolved peaks are observed for the ν_1 mode. One corresponds to hydrogen-bonded pyridine at hydroxyl sites (1005 cm^{-1}), while the other corresponds to physisorbed pyridine, with only weak interactions with the channel walls, and this gives a peak at the same frequency as that of the pure liquid (992 cm^{-1}). Similar changes are also observed for the ν_{12} mode, though these are less well resolved. While the relative intensities of different vibrational modes in Raman spectra can vary widely with environment, there is not normally a large change in Raman cross-section for the same vibrational mode. Assuming that the Raman cross-section is similar for the two ν_1 modes, the number of pyridine molecules that are chemisorbed at hydroxyl groups and physisorbed at different loadings can be quantified by deconvolution of the ν_1 mode peaks using Lorentzian band shapes to obtain the relative areas under each peak (see Figure 4).

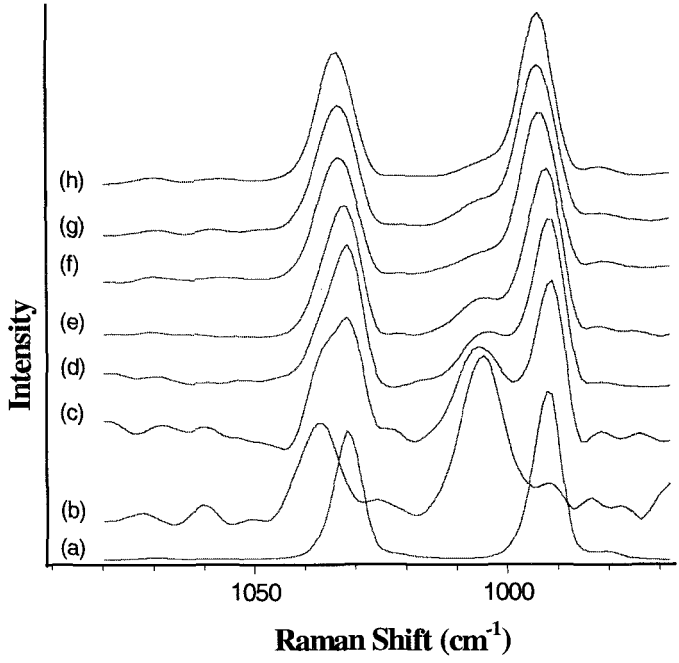

FIG 3 FT-Raman spectra of (a) liquid pyridine, and (b)-(h) pyridine in silicalite. The loadings are (b) 1, (c) 2, (d) 4, (e) 6, (f) 8, (g) 9 and (h) 10 molecules per unit cell.

It can be seen that the number of pyridine molecules hydrogen bonded to hydroxyl groups remains constant at about one molecule per unit cell throughout the range of loadings. Note that some unit cells may contain no defects and no adsorbed pyridine, while others may contain more than one hydrogen-bonded pyridine molecule. It should be pointed out that even if the assumption of similar Raman cross-section was false, the fact that physisorbed pyridine is only detected at a loading greater than one pyridine molecule per unit cell confirms that, averaged over the sample, one molecule of pyridine per unit cell can be in a hydrogen-bonding environment. Thus, the Raman spectra have provided an indication of the number of hydroxyl groups that are present. If one pyridine

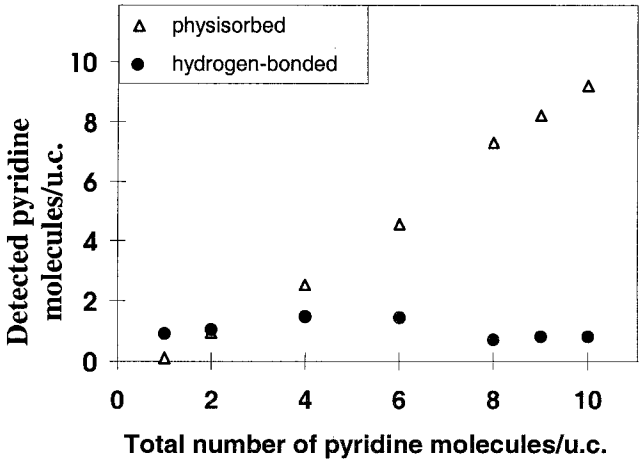

FIG 4 Plot of the number of pyridine molecules in different sites per unit cell of silicalite (obtained by deconvolution of the spectra in Figure 3) versus the total number of pyridine molecules present per unit cell.

molecule binds to one hydroxyl group, then this corresponds to 1% of the silicon atoms being present as silanol groups. However, the number of silanol groups present will be greater than this if a significant number of the defects present exist as silanol pairs or nests, as it may be the case that only one pyridine molecule can access each defect because of steric factors. Previous work using NMR methods has estimated that up to 8% of the framework silicon atoms in silicalite are present as silanol groups,[22,33] but this number depends critically on sample preparation method and thermal history.[33-35,40]

It is worth pointing out that the influence of defect sites within silicalite on adsorbed hydrocarbons has previously been used to explain adsorption behaviour in the literature. The presence of hydroxyl groups has been used to account for an initial fall in the differential heat of sorption of pyridine, consistent with initial adsorption onto a limited number of strong adsorption sites.[41] The presence of defects has also been used to account for higher heats of

adsorption and lower intracrystalline diffusivities at low concentrations for hydrocarbons within silicalite.[42]

Another feature of the Raman spectra shown in Figure 3 is that there is no increase in linewidth of the ν_1 peaks as the loading increases. This may be contrasted to the case observed for adsorbed benzene in silicalite, in which a significant linewidth increase occurs for loadings above four benzene molecules per unit cell.[25] This was rationalised by the presence of significant sorbate-sorbate interactions due to benzene molecules stacking only in the straight channels of silicalite.[25] In contrast to this, no sorbate-sorbate interactions are detected in the Raman spectra of adsorbed pyridine even at a loading of 10 molecules per unit cell, suggesting that the preferential adsorption of pyridine at hydroxyl defect sites causes pyridine to be located in both the straight and sinusoidal channels of the silicalite structure.

Silanol Groups in MCM-41

The diffuse reflectance infrared spectrum of dehydrated MCM-41 (not shown) is similar to that of Chen *et al.*[43] and shows a sharp peak at 3740 cm^{-1} due to terminal silanol groups, and a broad band covering 3450-3700 cm^{-1} arising from silanol groups in different hydrogen-bonding environments.[43] Given the large surface area of this material (1001 m^2/g), the majority of the silanol groups must be on the internal surface. For MCM-41 containing adsorbed pyridine after equilibration at 100°C, infrared peaks in the aromatic ring-stretching region are only observed at 1597, 1578 and 1447 cm^{-1} indicating that only hydrogen-bonded pyridine species are present (spectrum not shown). It should be noted that most infrared studies reported in the literature on MCM-41 materials are for samples containing significant amounts of framework aluminium, and so significant numbers of Brønsted and Lewis acid sites were present. This is not the case here, as the main purpose of this work is to use vibrational spectroscopy, and Raman spectroscopy in particular, to determine the number of silanol groups present for a purely siliceous material.

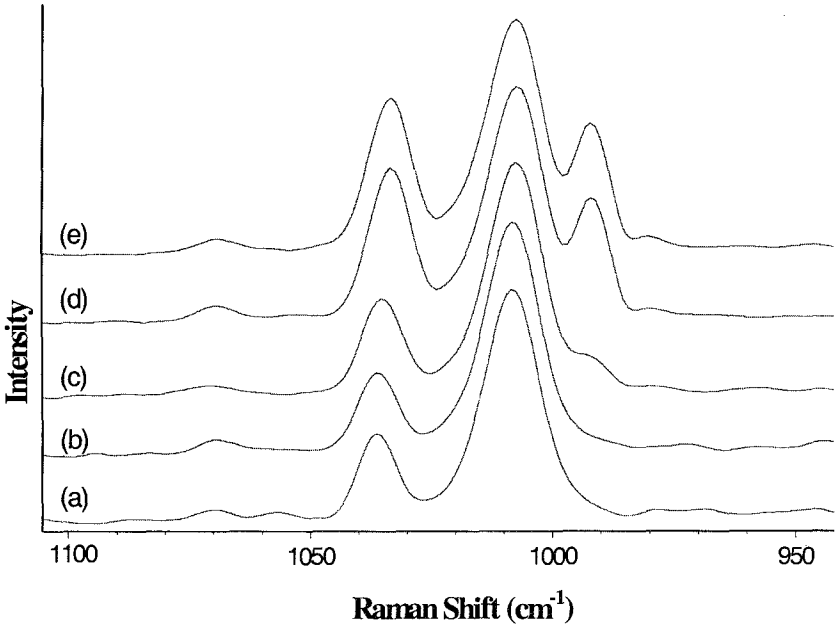

FIG 5 FT-Raman spectra of pyridine in siliceous MCM-41 at loadings of (a) 1.5, (b) 2.5, (c) 3.2, (d) 4.9 and (e) 6.4 mmol/g dry solid.

The FT-Raman spectra of pyridine adsorbed on siliceous MCM-41 are shown in Figure 5. At low loadings, the ν_1 and ν_{12} peaks observed correspond to hydrogen-bonded pyridine associated with the silanol groups present on the channel surface. At loadings of 3 mmol/g and higher, a ν_1 peak due to physisorbed pyridine with no significant interactions with the channel walls is observed. Assuming a constant stoichiometry of one pyridine molecule per hydroxyl site in MCM-41 for non-physisorbed pyridine, based on the results of Jentys *et al.*,[44] the Raman results imply that the number of hydroxyl groups in MCM-41 is about 3 mmol/g. This is in good agreement with a recent study that measured the concentration of hydroxyl groups in siliceous MCM-41 to be 2.7 mmol/g by ^{1}H NMR methods.[45] On the other hand, it may be contrasted with a recent study on pyridine adsorption using IR spectroscopy that had to employ a

modified molar extinction coefficient model to determine hydroxyl concentrations; this estimated a hydroxyl concentration of only 0.79-0.86 mmol/g for siliceous MCM-41.[44] The measured hydroxyl concentration of about 3 mmol/g corresponds to 18% of the silicon atoms present in MCM-41 being associated with a hydroxyl group. This result is in agreement with molecular dynamics simulations which predict 17-28% of the silicon atoms in MCM-41 materials being present as silanol groups.[46] Given that the BET surface area of the MCM-41 sample is 1001 m^2/g, the detected surface silanol group concentration corresponds to 1.8 groups/nm^2. This may be compared to values found using other techniques of 2.5-3.3 groups/nm^2 (for siliceous MCM-41),[47,48] and 1.2 groups/nm^2 (for an aluminosilicate MCM-41).[49]

CONCLUSIONS

Infrared and FT-Raman spectra have been obtained on pyridine adsorbed within two siliceous materials, silicalite and MCM-41. Both spectroscopic techniques detect the presence of weak physisorbed pyridine and stronger hydrogen-bonded species. The Raman spectra are well-resolved, easy to interpret, and measure the number of adsorbed pyridine molecules that interact with hydroxyl groups at the silica surface. This in turn can be used to determine the number of hydroxyl groups present on the silica surface. Analysis of hydroxyl group concentrations using Raman spectra does not depend on knowledge of molar extinction coefficients, which is a factor that limits quantification using conventional infrared spectroscopy. It should be pointed out that the FT-Raman technique described will not detect any hydroxyl groups that are inaccessible to pyridine. For silicalite, it is found that an average of one pyridine molecule per unit cell interacts with hydroxyl groups. For MCM-41, it is found that the hydroxyl group concentration is about 3 mmol/g of dry solid.

ACKNOWLEDGEMENT

Dr. S. Ashtekar wishes to thank BNFL, Research & Technology for financial support.

REFERENCES

1. E. M. Flanigen, J. M. Bennett, R. W. Grose, J. P. Choen, R. L. Patton, R M. Kirchner and J. V. Smith, Nature **271**, 512 (1978).
2. C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, Nature **359**, 710 (1992).
3. R. K. Iler, *The Chemistry of Silica* (John Wiley & Sons, New York, 1979).
4. K. C. Vrancken, L. de Coster, P. van der Voort, P. J. Grobet and E. F. Vansant, J. Colloid & Interface Sci. **171**, 71 (1995).
5. T. Sano, M. Hasegawa, S. Ejiri, Y. Kawakami and H. Yanagishita, Microporous Mater. **5**, 179 (1995).
6. D. S. Shephard, W. Zhou, T. Maschmeyer, J. M. Matters, C. L. Roper, S. Parsons, B. F. G. Johnson and M. J. Duer, Angew. Chemie Int. Ed. **37**, 2719 (1998).
7. L. H. Little, *Infrared Spectra of Adsorbed Species* (Academic Press, New York 1966).
8. M. I. Hair, *Infrared Spectroscopy in Surface Chemistry* (Marcel Dekker, New York, 1967).
9. A. V. Kiselev and V. I. Lygin, *Infrared Spectra of Surface Compounds* (John Wiley & Sons, New York, 1975).
10. J. W. Niemantsverdriet, *Spectroscopies in Catalysis* (VCH, Weinheim, 1993).
11. L. M. Kustov, Topics Catal. **4**, 131 (1997).
12. H. Knozinger and S. Huber, J. Chem. Soc. Faraday Trans. **94**, 2047 (1998).
13. J. A. Lercher, V. Veefkind and K. Fajerwerg, Vibrational Spectrosc. **19**, 107 (1999).
14. C. E. Bronnimann, R. C. Zeigler, G. E. Maciel, J. Am. Chem. Soc. **110**, 2023 (1988).
15. I. S. Chuang, D. R. Kinney, G. E. Maciel, J. Am. Chem. Soc. **115**, 8695 (1993).
16. M. Hunger, Catal. Rev. Sci. Eng. **39**, 345 (1997).
17. L. T. Zhuravlev, Langmuir **3**, 316 (1987).
18. L. T. Zhuravlev, Colloids Surfaces A **74**, 71 (1993).
19. B. A. Morrow and A. J. McFarlan, Langmuir **7**, 1695 (1991).
20. K. Yoshinaga, H. Yoshida, Y. Yamamoto, K. Takakura and M. Komatsu, J. Colloid Interf. Sci. **153**, 207 (1992).
21. P. van der Voort, S. Vercauteren, K. Peeters and E. F. Vansant, J. Colloid Interf. Sci. **157**, 518 (1993).
22. G. L. Woolery, L. B. Alemany, R. M. Dessau and A. W. Chester, Zeolites **6**, 14 (1986).

23. J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T.-W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins and J. L. Schlenker, J. Am. Chem. Soc. **114**, 10933 (1992).
24. S. Ashtekar, P. J. Barrie, M. Hargreaves and L. F. Gladden, Angew. Chem. Int. Ed. **36**, 876 (1997).
25. S. Ashtekar, J. J. Hastings and L. F. Gladden, J. Chem. Soc. Faraday Trans. **94**, 1157 (1998).
26. P.-P. Knops-Gerrits, D. E. De Vos, E. J. P. Feijen and P. A. Jacobs, Microporous Mater. **8**, 3 (1997).
27. R. Ferwerda, J. H. van der Mass and P. J. Hendra, Vib. Spectrosc., **7**, 37 (1994).
28. R. Ferwerda and J. H. van der Maas, J. Phys. Chem. **99**, 14764 (1995).
29. S. F. Simpson and J. M. Harris, J. Phys. Chem. **94**, 4649 (1990).
30. Z. Luan, C. F. Cheng, W. Zhou and J. Klinowski, J. Phys. Chem., **99**, 1018 (1995).
31. P. Kubelka and K. Munk, Z. Tech. Phys. **12**, 593 (1931).
32. T. Burger, J. Kuhn, R. Caps and J. Fricke, Appl. Spectrosc. **51**, 309 (1997).
33. M. Hunger, J. Kärger, H. Pfeifer, J. Caro, B. Zibrowius, M. Bülow and R. Mostowicz, J. Chem. Soc. Faradays Trans 1 **83**, 3459 (1987).
34. R. M. Dessau, K. D. Schmitt, G. T. Kerr, G. L. Woolery and L. B. Alemany, J. Catal. **104**, 484 (1987).
35. R. M. Dessau, K. D. Schmitt, G. T. Kerr, G. L. Woolery and L. B. Alemany, J. Catal. **109**, 472 (1988).
36. K. Yamagishi, S. Namba and T. Yashima, J. Phys. Chem. **95**, 872 (1991).
37. A. Zecchina, S. Bordiga, G. Spoto, L. Marchese, G. Petrini, G. Leofanti and M. Padovan, J. Phys. Chem. **96**, 4991 (1992).
38. R. Buzzoni, S. Bordiga, G. Ricchiardi, C. Lamberti, A. Zecchina and G. Bellussi, Langmuir **12**, 930 (1996).
39. C. A. Emeis, J. Catal. **141**, 347 (1993).
40. M. Hunger, D. Freude, H. Pfeifer and W. Schweiger, Chem. Phys. Lett. **167**, 21 (1990).
41. H. Thamm, J. Phys. Chem. **92**, 193 (1988).
42. J. R. Hufton, D. M. Ruthven and R. P. Danner, Microporous Mater. **5**, 39 (1995).
43. S. Chen, Q. Li, R. Xu and F. Xiao, Angew. Chem. Int. Ed. **34**, 2694 (1995).
44. A. Jentys, K. Kleestorfer and H. Vinek, Microporous Mesoporous Mater. **27**, 321 (1999).
45. M. Hunger, U. Schenk, M. Breuninger, R. Gläser and J. Weitkamp, Microporous Mesoporous Mater. **27**, 261 (1999).
46. B. P. Feuston and J. B. Higgins, J. Phys. Chem. **98**, 4459 (1994).
47. T. Ishikawa, M. Matsuda, A. Yasukawa, K. Kanodori, S. Inagaki, T. Fukushima and S. Kondo, J. Chem. Soc. Faraday Trans. **92**, 1985 (1996).

48. X. S. Zhao, G. Q. Lu, A. K. Whittaker, G. J. Miller and H. Y. Zhu, J. Phys. Chem. B **101**, 6525 (1997).
49. P. L. Llewellyn, F. Schüth, Y. Grillet, F. Rouquerol, J. Rouquerol and K. K. Unger, Langmuir **11**, 574 (1995).

Date Received: December 31, 1999
Date Accepted: March 15, 2000