Fourier transform infrared cell for surface studies at controlled temperatures and in controlled atmospheres with time resolution and spatial resolution

V. A. Self and P. A. Sermon[a)]

Fractal Solids and Surfaces Research Group, Department of Chemistry, Brunel University, Uxbridge, Middx UB8 3PH, United Kingdom

A new micro-Fourier transform infrared cell has been constructed and evaluated using (i) the transformation of aurichalcite crystals at 298–475 K, (ii) the adsorption/desorption of pyridine on a Cu_2O/ZnO junction, and (iii) the adsorption of CO on Pt/alumina pellets; it enables spatial and time resolution of processes in such diverse samples held at known thermal and baric conditions. The potential of this cell in catalytic and analytical science is considered. © *1996 American Institute of Physics.* [S0034-6748(96)00306-1]

I. INTRODUCTION

Fourier transform infrared (FTIR) microscopy[1] has found a broad range of applications including forensic science and for polymers,[2] catalysts, crystals, and minerals,[3] and in biology, medicine, and pharmacy.[4] Typically, the area which may be analyzed depends on the sample but may be 10×10 μm to 795×795 μm.[5]

While high temperature and controlled-atmosphere infrared cells have been developed for spectrometers (e.g., used[6] in the study of polymers), those presently available for microscopy have not allowed specific *in situ* studies.

Here the value of a new cell for FTIR microscopy in controlled atmospheres and at controlled temperatures is investigated for the transformation of single crystals of a mineral, for analysis of acid/base sites at a junction and for CO adsorption on a pelleted catalyst: three samples of very different long-range order.

II. EXPERIMENTAL APPARATUS

The cell designed (63×38 mm in size and 14 mm in thickness; see Fig. 1) to allow microspectroscopic infrared studies to be performed on surfaces in a reflectance mode at 298–773 K has been constructed from 18/8 stainless steel. Its two halves were secured together forming a gas-tight seal with vacuum grease. The lower section of the cell is located above the condenser in the sample stage of an infrared microscope (IRPLAN; Spectra-Tech). Pairs of infrared (KCl or BaF_2) windows were selected for their high degree of optical clarity and their resistance to fogging under conditions of use. Water cooling through surrounding piping protected the windows from overheating.

The supported sample to be investigated was located in the lower section of the cell on the heater (Platfilm; E11340-A-P-G-2-NR-NR; Rosemount $3\times3\times0.6$ mm, consisting of a 10 Ω Pt heater array on a 96% alumina ceramic substrate). The heater array is shown in Fig. 2 schematically and by a scanning tunneling micrograph; sample heating was by conduction through to the upper surface of the alumina. Heater

leads entered the cell through gas-tight ports. The reproducibility with which temperatures could be achieved (measured in terms of resistance) is shown in Fig. 3. Gas inlet and outlet lines allowed a reactive or purge gas to pass over the sample at a controlled rate. The sample temperature was measured in the cell with a thermocouple. Reflectance FTIR spectra of the respective platinum and alumina band areas showed no distinct differences in the wave number range 4000–550 cm^{-1} in air or when heated in CO at up to 573 K (see Fig. 4) and this lack of heater/substrate reactivity was therefore likely to allow the use of the cell in reactive (as well as unreactive) atmospheres. Background subtractions for gaseous CO at all times were negligible but the lack of adsorbed CO could also be witnessed in the presence of gaseous CO by the well documented difference in wave number. Only on heating in $67\%CO/33\%H_2$ at 573 K were small bands for adsorbed CO at 2183 and 2115 cm^{-1} seen for the heater array and substrate. Hence this temperature might be the upper limit of cell use, without modification, e.g., Au plating.

III. EXPERIMENT

Aurichalcite $[(Cu_{5-x}Zn_x)(CO_3)_2(OH)_6]$ is a precursor phase in Cu/ZnO/alumina catalysts for methanol synthesis.[7] Here several single crystals [3 mm$\times$0.25 mm (Gregory, Bottley, and Lloyd)] were studied during heating in $6\%O_2/N_2$ at 298 K and higher temperatures. Calcination produced the oxides from the mineral crystals.

A Cu_2O/ZnO junction (prepared by vapor deposition) was also studied via pyridine adsorption. Adsorption was performed *ex situ* and the desorption of pyridine was studied *in situ* at 298–455 K in order to determine the presence of acidic sites.

Prereduced 0.5%Pt/alumina pellets (Englehard; DeOxo-M; 3.2 mm diameter and 3.5 mm length) were also studied. These had an ''eggshell'' Pt distribution in that this metal was predominantly located on the external surface, where microprobe analysis found the Pt/Al ratio ($\times10^{-3}$) to be 5–279. These pellets were studied after reduction *in situ* at 473 K in flowing $6\%H_2/N_2$ for 30 min, flushing in N_2 at the same temperature. Areas (250 μm$\times$250 μm) of its external surface were analyzed in reflectance 0, 30, 90, and 150 min

---

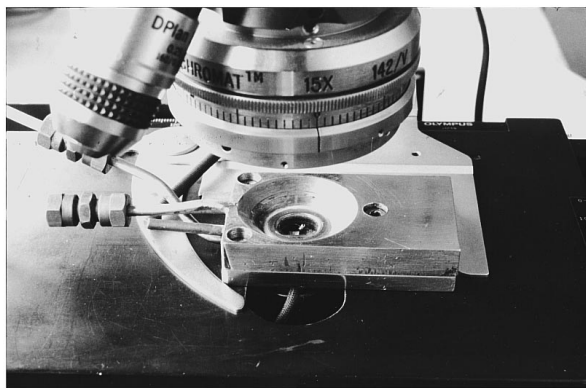[a)]Author to whom all correspondence should be addressed.

FIG. 1. Cell enabling control of the temperature and atmosphere of a solid sample during *in situ* micro-FTIR spectroscopy.

after introducing 6%CO/N_2 flowing at 40 cm^3/min at the same temperature. $CO_{(g)}$ is seen at 2360 cm^{-1}.

IV. RESULTS

Figure 5 shows infrared spectra of aurichalcite crystals in the micro-FTIR cell at one spatial position (a) in air at room temperature, (b) at 423 K in flowing 6%O_2/N_2, and (c) at 475 K in flowing 6%O_2/N_2. Aurichalcite bands attributable to the carbonate groups were present initially at 1556, 1350, 1201, and 971 cm^{-1}, but were diminished in intensity as the crystals are treated thermally on calcination at 423 K and then 475 K (i.e., a→b→c in Fig. 5) while at the same time the crystal color changed from pale green to black on oxide formation. Bands at 1425 and 1510 cm^{-1}, due to CO_2 symmetric stretching or OH deformation vibrations of carboxylic acid species (1425 cm^{-1}) or CO_2 antisymmetric vibrations (1510 cm^{-1}) were also seen to decrease in intensity on calcination as would be expected since CO_2 would be lost on decomposition to the oxide.

Synchrotron radiation[8] has been used to probe the short and long range structure in aurichalcite during heating at 2 K min^{-1} in dry air at 298–723 K when cupric oxide and zinc oxide are produced. By these techniques no loss of crystallographic order was seen at 583 K, which would accompany loss of carbonate and hydroxyl groups. However there was still no perceptible change in the Cu^{2+} environment even on full decomposition to CuO and zinc oxide at 423 K. Hence that assessment of local order is not particularly sensitive to any thermally induced phase changes in the aurichalcite. X-ray diffraction *does* show changes in long range order on heating to 723 K after the formation of an almost amorphous phase at 573 K, but at the critical stage of transformation to a highly dispersed or amorphous phase at 573 K, x-ray diffraction is of no value. The infrared approach therefore shows aurichalcite decomposition via loss of interlayer carbonate groups in O_2/N_2 atmospheres at 150–300 K *lower* than the temperatures deduced from these synchrotron structural studies. Often structural studies are restricted to ordered structures but here it may simply be that carbonate groups and hydroxyl groups are lost relatively easily, afterwhich the migration of Cu^{2+}, Zn^{2+}, O^{2-} ions produce separate phases (and solute ions within these) which may be a rather slow process. It is this which the structural studies are monitoring

(a)

(b)
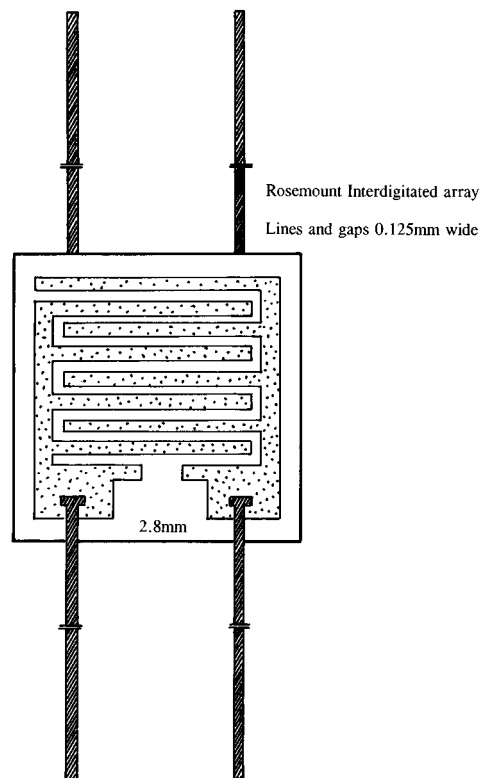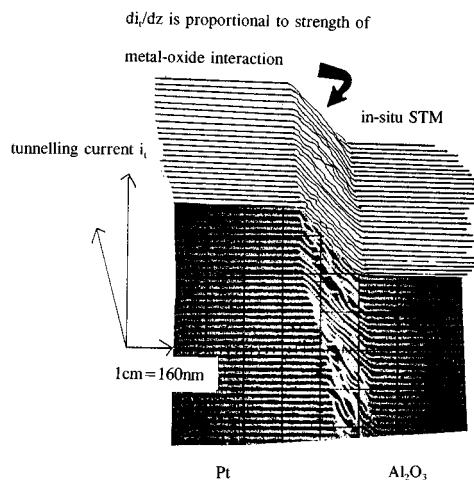
FIG. 2. Platfilm Pt resistance heater for the cell in Fig. 1 viewed (a) schematically and (b) by STM microscopy.

but only at higher temperatures; hence the structural and spectroscopic approaches are complementary.

Figure 6 shows micro-FTIR spectra of pyridine desorption after adsorption at room temperature on a Cu_2O/ZnO interface. Both Bronsted and Lewis sites are seen on the ZnO surface and at the interface, whereas there is no evidence of adsorption on the Cu_2O. With increasing temperature at 298–455 K bands due to Lewis sites disappear while those attributable to Bronsted sites (although small) are still detectable by *in situ* micro-FTIR.
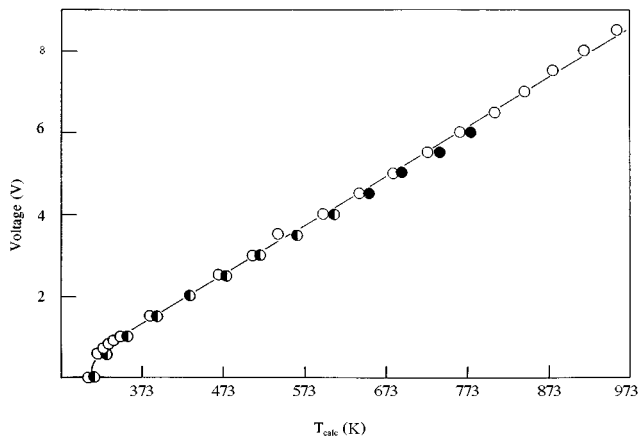
FIG. 3. Temperatures achieved in static air using the heater shown in Fig. 2. Filled and half-filled symbols denote repeated measurements.

FIG. 5. Infrared spectra of several aurichalcite crystals obtained at one spatial position: (a) in air at room temperature; (b) at 423 K in flowing $6\%O_2/N_2$; (c) at 475 K in flowing $6\%O_2/N_2$. Initial aurichalcite bands (highlighted at 1556, 1350, 1201, and 971 cm^{-1}) diminished in intensity as the crystals are treated thermally, while their color changed from pale green to black as CuO (and ZnO) were formed.

Figure 7 shows micro-FTIR spectra of CO adsorbed on the external surface of a Pt/alumina pellet at different times. In each segment studied, the intensity of absorption for linearly bound CO at 2046 cm^{-1} increases as time progresses at 30–90 min. In other words the adsorption of CO is relatively slow even on this time scale on the prereduced surface of supported Pt crystallites. Second, the intensity of absorption in the segments at the *outer* edge is far stronger at any chosen time than those at the *center* of the external surface. In other words the surface is not homogeneous with respect to the extent of adsorption of linearly bound CO and hence also presumably the concentration or nature of the surface Pt varies with spatial position; Auger electron spectroscopy (AES) or microprobe analysis would detect changes in Pt concentration, but not so easily activity in CO adsorption, in the way seen here using *in situ* micro-FTIR.
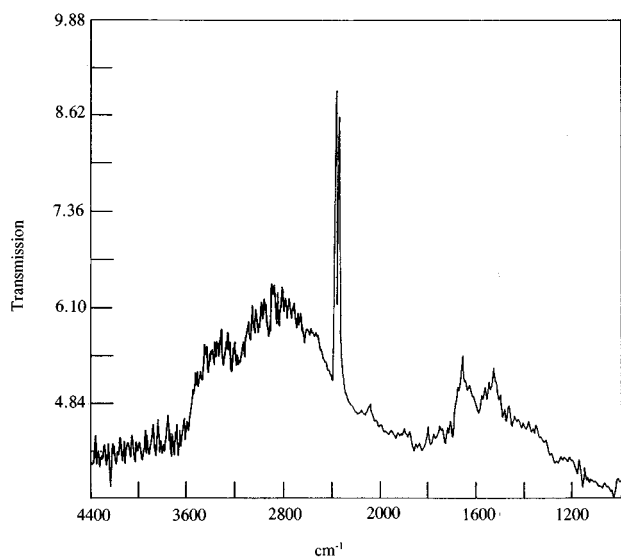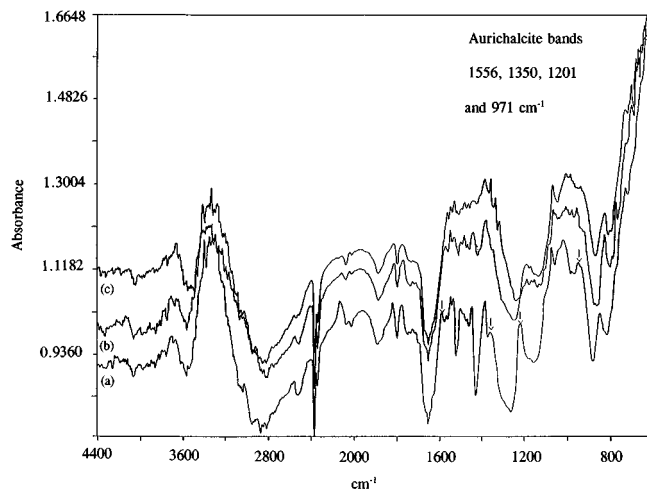
V. DISCUSSION

Heterogeneous catalysts are extensively used[9] in chemical processing, petroleum refining, and pollution control. Nevertheless, there is insufficient information on the chemistry prevailing at their surfaces at a microscopic level[10] under reaction conditions[11] and how this changes with real time
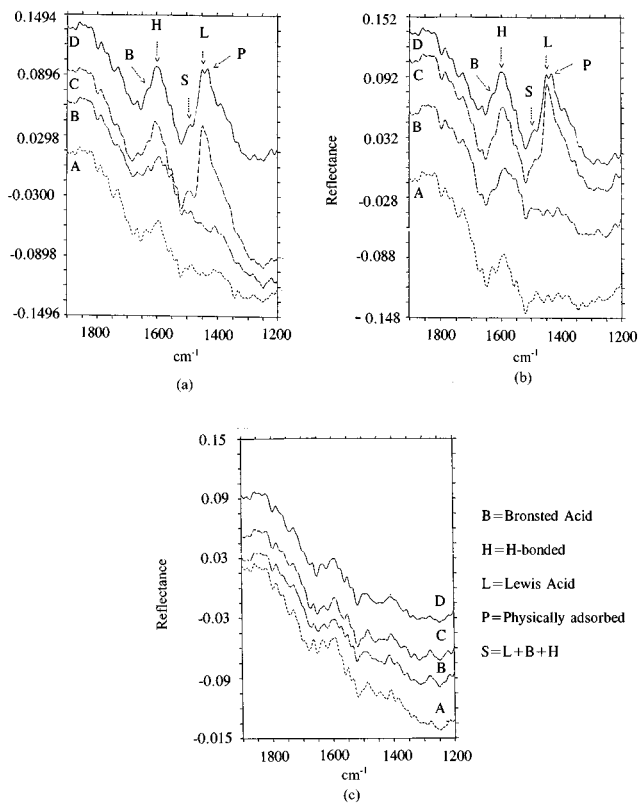

FIG. 4. Reflectance spectra of Platfilm Pt/alumina after 2.5 h in $67\%CO/33\%H_2$ at 473 K and flushing N_2 for 15 min. This shows the relative inertness of the cell heater in that no adsorbed CO was noted in the IR.

B = Bronsted Acid
H = H-bonded
L = Lewis Acid
P = Physically adsorbed
S = L + B + H

FIG. 6. Micro-FTIR of pyridine desorption in N_2 at the (a) Cu_2O/ZnO interface, (b) ZnO surface, and (c) Cu_2O surface as a function of temperature; room temperature (A), 313 K (B), 384 K (C), and 455 K (D).
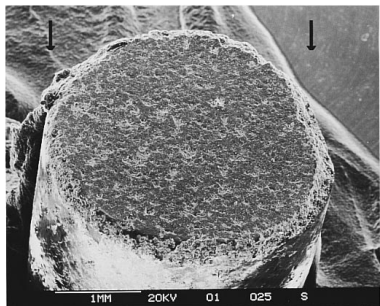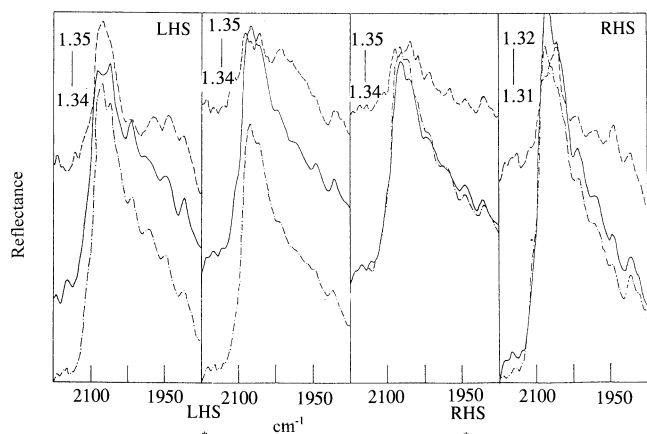
FIG. 7. Micro-FTIR spectra of CO adsorbed on the external surface of a Pt/alumina pellet at 473 K after - - - 30, — 90, and $-\cdot-\cdot-$ 150 min in 6 kPa CO in N_2. Spectra are shown of 400 μm sections from the left-hand to the right-hand side of the surface.

and how heterogeneous such a surface really is. Thus, ideally, *in situ* analysis requires the potential of time and spatial resolution. It is hoped that the present results (for the transformation of aurichalcite precursors to Cu/ZnO, the concentration of acidic sites at materials interfaces and CO adsorption on supported Pt/alumina pellets) at least illustrate the potential of micro-IR spectroscopy for spatial-, thermal-, and time-resolved analysis of interfacial processes. Such a cell may therefore have a useful role in catalyst characterization; certainly even higher resolution could be achieved with a higher flux source.

[1] J. E. Katon and A. J. Sommer, Anal. Chem. A **64**, 931 (1992); R. Houriet, Analysis **21**, M7 (1993); B. Foster and R. Mulligan, Am. Lab. **25**, 44 (1993).

[2] J. C. Shearer, D. C. Peters, and T. A. Kubic, Trends Anal. Chem. **4**, 246 (1985); S. R. Challa, S. Q. Wang, and J. L. Koenig, Appl. Spectrosc. **49**, 267 (1995); A. M. Mavrich, H. Ishida, and J. L. Koenig, *ibid*. **49**, 149 (1995); C. A. Mcfarland, J. L. Koenig, and J. L. West, *ibid*. **47**, 321 (1993); T. P. Abbot, F. C. Felker, and R. Kleiman, *ibid*. **47**, 180 (1993); T. Nishioka, T. Nakano, and N. Teramae, *ibid*. **46**, 1904 (1992); E. Sebillotte, S. Theoleyre, S. Said, B. Gosse, and J. P. Gosse, IEEE Trans. Electron. Insul. **27**, 557 (1992); S. C. Hsu, D. Linvien, and R. N. French, Appl. Spectrosc. **46**, 225 (1992); R. Schafer, J. Kressler, R. Neuber, and R. Mulhaupt, Macromolecules **28**, 5037 (1995); C. Spiteri, M. F. Vallant, F. Schultz, A. Belgrine, G. Evrard, and A. Compond, Vide-Couche Murices **272**, 470 (1994); J. A. J. Jansen, F. N. Paridaans, and E. J. Heynderickx, Polymer **35**, 2970 (1994).

[3] F. Marlow, D. Demuth, G. Stucky, and F. Schuth, J. Phys. Chem. **99**, 1306 (1995); R. Lin and G. P. Ritz, Org. Geochem. **20**, 695 (1993); H. Behrens and G. Muller, Minerol. Mag. **59**, 15 (1995); S. Stone, L. Sunmeta, U. Roland, K. Herzog, and R. Salzer, J. Mol. Struct. **349**, 93 (1995).

[4] J. A. Reffner and R. G. Ferrillo, J. Thermal Anal. **34**, 19 (1988); E. L. Varetti and C. R. Volponi, Appl. Spectrosc. **49**, 537 (1995); S. M. Levine and D. L. Wetzel, J. Am. Path. **145**, 1041 (1994).

[5] M. A. Harthcock and S. C. Atkin, *Infrared Microspectroscopy, Theory and Applications*, edited by R. G. Messerschmidt and M. A. Harthcock, Practical Spectroscopy Ser. A (Marcel Dekker, New York, 1988), Vol. 6, p. 21.

[6] R. J. Karpowicz, Rev. Sci. Instrum. **61**, 188 (1990); J. C. Chevin, B. Canny, J. M. Besson, and P. Pruzan, *ibid*. **66**, 2595 (1995).

[7] D. Waller, D. Stirling, and F. S. Stone, Faraday Discuss. Chem. Soc. **87**, 107 (1989).

[8] J. W. Couves, J. M. Thomas, D. Waller, R. H. Jones, A. J. Dent, G. E. Derbyshire, and G. N. Greaves, Nature **354**, 465 (1991).

[9] B. F. Greek, Chem. Eng. News **29** (29 May 1989).

[10] G. A. Somorjai and D. W. Blakely, Nature **258**, 580 (1975).

[11] R. P. H. Gasser and P. R. Vaight, Nature **221**, 166 (1969).