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Heatable-Evacuable Cell and Optical System for Diffuse Reflectance FT–IR Spectrometry of Adsorbed Species

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A cell and optical configuration for measuring diffuse reflectance Fourier transform infrared spectra of adsorbed species at high sensitivity are described. The cell may be heated to 600°C and evacuated to 10^{-6} torr, permitting activation and treatment of catalysts and adsorbents in situ. It is shown that it is important to prevent radiation emitted from the material surrounding the sample from reaching the mercury cadmium telluride detector, or else the detector will be saturated at relatively low sample temperatures. Gases can be drawn through the samples to reduce the time taken for equilibrium to be reached. Spectra of carbon monoxide adsorbed at about 0.1% coverage on supported metal catalysts can be measured with high signal-to-noise ratio.

1. INTRODUCTION

The vast majority of infrared spectrometry of surface species is currently performed using the type of sampling technique originally described by Eischens *et al.* in 1956 (*1*), in which the transmittance of a very thin disk of the adsorbent is measured. Although a wealth of data on surface species has been obtained in this way, the transmittance of the samples is quite low, especially at very high wavenumber (where scattering is greatest) and at low wavenumber (where most adsorbents exhibit strong adsorption bands). Other techniques which have been studied include reflection–absorption (R–A) spectrometry, for which only very weak bands of adsorbed species at monolayer or partial monolayer coverage can be observed and is unsuitable for studying supported metal catalysts, and infrared emission spectrometry, which is plagued by severe emission from the adsorbent and the effect of temperature gradients.

Diffuse reflectance (DR) spectrometry was first used to study surface species by Kortüm and Delfs in 1964 (*2*); they showed rather low resolution spectra of HCN and C_2H_4 adsorbed on metal oxides measured using a grating spectrometer. In 1979, Niwa *et al.* (*3*) reported DR spectra of adsorbed species at high temperature, again measured using a grating spectrometer. The previous year, Fuller and Griffiths described a simple optical arrangement for the measurement of DR spectra using a commercial rapid-scanning interferometer (*4*). The signal-to-noise ratio (SNR) of spectra measured with this instrument was much higher than that of DR spectra measured using a grating spectrometer. The excellent sensitivity of DR spectrometry for infrared microsampling (*5*) was subsequently demonstrated; the DR spectra of submicrogram quantities of materials deposited from solution onto the surface of powdered KCl were

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reported, and the sensitivity of DR spectrometry was observed to be greater for species on the surface of a nonabsorbing support, such as KCl, than if bulk samples of the two components were mixed.

The microsampling capability of DR spectrometry led us to suspect its potential for studying surface species and the feasibility of this technique was demonstrated in our laboratory (*6*). In this work, the optical system originally described by Fuller and Griffiths (*4*) was used in conjunction with a small heated cell in which gas could be passed *through* the powdered adsorbent (*7*). In spite of the low optical efficiency of that system spectra of CO on several alumina-supported metal catalysts were measured with adequate SNR, provided that long scan times (at least 1000 scans at 4 cm^{-1} resolution) were used. Several serious drawbacks with the cell were noted: (i) the seal at the NaCl window was not good, so that only measurements at ambient pressure could be made; (ii) temperature calibration for the cell was done in a separate experiment, and temperatures were probably only accurate to about ±30°C, and (iii) each time the sample was changed, a time-consuming optical realignment was required.

It is the purpose of this paper to describe a new heatable-evacuable cell and optical system, and to show some of the high quality spectra of adsorbed species measured using the new DR/FT–IR system.

2. CELL DESIGN

The new cell is capable of being heated up to 600°C and pumped down to a pressure of 10^{-6} torr (and possibly lower with a better vacuum pump than the oil diffusion pump being used in this work). The gas pressure in the cell has been taken up to 2 atm, but the cell was not designed to function at significantly higher pressures. The cell is made of an upper and lower stainless-steel section (Figs. 1 and 2). The upper section (29 cm thick and 70 cm in diameter) comprises the main body, top cover (3-mm thick, with a 37.5-mm diam hole in the center), and a bottom plate (1.5-mm thick, with 12.7-mm hole in the center). A 6-mm thick and 49.5-mm diam KCl window (Harshaw Chemical Co., Solon, Oh.) is held between the main body and the top cover, 8 mm above the sample. The window is spaced by a 0.5-mm-Teflon gasket from the cover plate, and by a Viton O-ring from the main body to ensure vacuum tightness and avoid damaging the window. The cover is screwed down to the main body by four screws. The bottom plate is also screwed to the main body by six screws, with two Viton O-rings between them to avoid any water leakage from the cavity where the water flows.

The main body of the upper section accommodates the heating sleeve and five $\frac{1}{16}$-in. ports; one for the two wires of a 0.010-in. Chromel–Alumel thermocouple (Omega Engineering, Stamford, Conn.), one for a 10-torr range transducer-type manometer (MKS Instruments, Burlington, Mass.), another one for the gas inlet line, and the last two for the two leads to the heating sleeve. The vacuum tightness around the five ports was ensured by using $\frac{1}{16}$-in. Swagelock tube fittings, the stainless-steel ferrules of which were replaced by locally made Teflon ones. The cell has a provision for cooling water to flow through its body so that the O-ring seal does not break down when the sample is at high temperature, and also to allow the body of the cell to cool down rapidly. The heating sleeve was made of a machinable glass ceramic (Astro Met Associates, Cincinnati, Oh.) that was locally threaded and a nichrome wire was coiled around it. A high-temperature cement (Omega Engineering) was used to coat the wire and the 6-mm-high and 12-mm-wide heating sleeve was placed around the sample cup. It was cemented to the body of the cell after the 4-mm spacing around it was packed with a shredded mica insulator.

The lower section of the cell was made of a stainless-steel tube (10.7-mm i.d. and 77

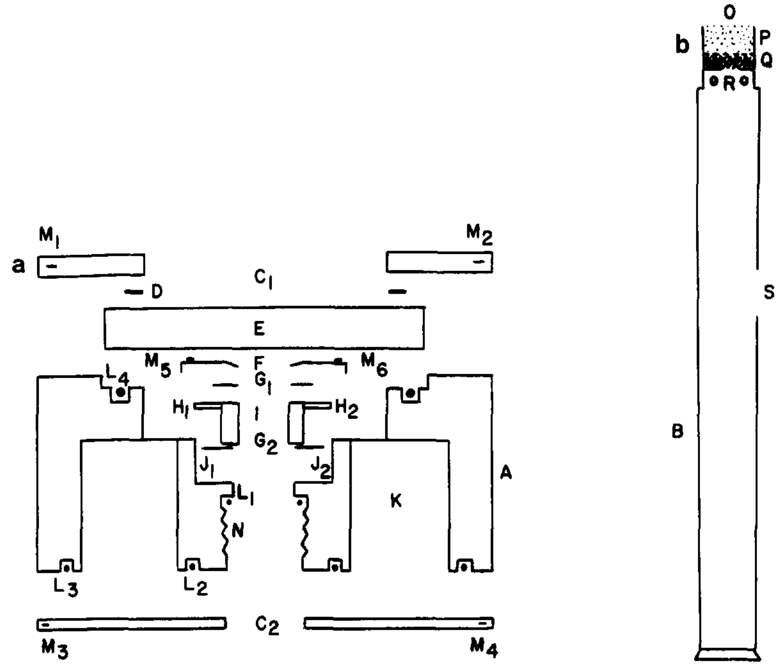

FIG. 1. (a) Side view of the components of the DR/FT–IR cell: (A) main body; (C_1) cover plate for sample compartment; (C_2) cover plate for cooling water cavity; (D) Teflon washer; (E) KCl window; (F) aperture to screen radiation emitted from sample heater; (G) mica washers; (H) high-temperature cement; (I) sample heater; (J) space between heater and cell wall; (K) cavity in cell body for cooling water; (L) Viton O-rings; (M) screws; (N) threads where the sample holder housing is screwed to the main body of the cell. (b) Sample holder assembly (B): (O) sample; (P) sample cup; (R) holes in wall of sample holder to prevent heat conduction down the sample holder; (S) gas-out orifice.

mm long) with 100-mm-long stainless-steel side-tube as a gas outlet line. This lower section housing tube was threaded on each end so that it could be screwed into the main body of the upper section and to allow the nut around the bottom of the sample holder to be screwed to the housing tube. Vacuum tightness around the housing tube was achieved by using a Teflon O-ring, and a Viton O-ring was used to seal the bottom of the sample holder to the housing tube. The sample holder, which was 82.5 mm long and 10.7-mm o.d., had a sample cup (4 mm deep and 7.5-mm diam) fixed at its top. A frit was installed at the base of the cup to permit gas to be passed through the powdered sample. The nut around the sample holder screws around the lower threaded end of the housing tube so that when it is finger tight, the sample cup is held in the heating zone.

3. OPTICAL DESIGN

A completely new optical system, designed to be compatible with the cell described above, was constructed. The design allowed for collection of over 50% of the diffusely reflected radiation from the sample, in contrast to other designs that have been reported previously which are much less efficient with a cell in place. This optical configuration is based on the use of two complementary halves of a 31.7-mm focal-length paraboloidal mirror (Special Optics, Little Falls, N.J.) constructed from solid bar stock and cut to an angle of 107.5° which allows the beam emerging diffusely from the samples to be collected by one half of the mirror and refocused onto a downward-looking mercury cadmium telluride (MCT) high sensitivity detector (Infrared Associates, New Brunswick, N.J.) by the

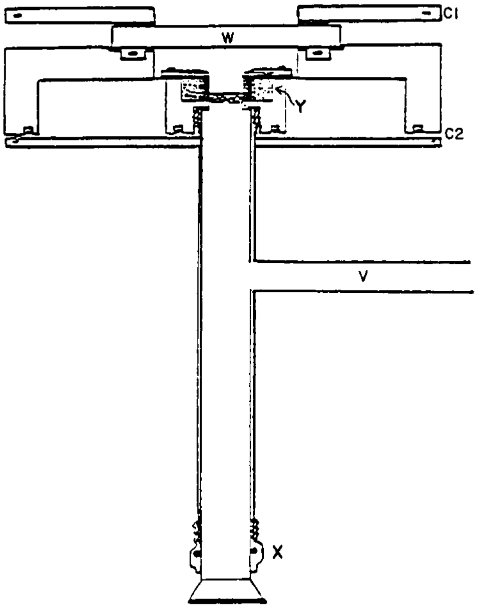

FIG. 2. A side-view diagram of the complete cell; (W) KCl window; (C1) cover plate for the sample compartment; (C2) cover plate for the cooling water cavity; (V) gas-out line; (X) nut to vacuum-tighten the sample holder to the housing tube; (Y) shredded mica used to fill the space between the heater and the wall of the cell.

other half. The two halves are positioned 20 cm apart, with the level of the collector 7 cm above the level of the focusing mirror. The sample is held 2 cm below the level of the collecting mirror and the MCT detector is mounted at 2 cm above the focusing mirror. An off-axis section of a 76.2-mm focal-length paraboloidal mirror (Special Optics) is used to focus the modulated beam from a Model 496 interferometer (Digilab Division of Bio-Rad, Cambridge, Mass.) onto the sample after raising its level by two beam-steering plane mirrors. As shown in Fig. 3, the whole cell is mounted underneath the collecting paraboloidal mirror by firmly clamping it to an aluminum mount on which the two halves of the paraboloidal mirror are held.

The new system shown in Fig. 3 is more than an order of magnitude more efficient than the original one, but this increased efficiency was not without a cost. It was found that the infrared radiation emitted by the heating sleeve around the sample cup is also collected and much of this radiation passes to the detector element. Even though this radiation is unmodulated, it still has the effect of raising electrons into the conduction band of the photoconductive MCT element. As the temperature of the cell is increased, the intensity of unmodulated radiation from the cell can exceed the intensity of the (modulated) diffusely reflected beam. The result is an effective saturation of the detector response to modulated radiation, and a severe reduction in the amplitude of the measured interferogram. In our original configuration, the interferogram completely disappeared when the sample temperature was greater than 300°C. This problem was, however, partially alleviated by installing an aluminum aperture of the same diameter as the inside diameter of the sample cup. The aperture, which is screwed to the body of the cell, is located 0.5 mm above the heating sleeve. An insulating mica washer was placed in between the aluminum plate and the cell. The aperture is somewhat water-cooled through its feet which are in contact with the main body of the upper section of the cell. This arrangement has enabled 50% of the original signal to be measured at 300°C, while 15% of the original signal could be still measured with the sample at 600°C, as shown in Fig. 4.

Although the particular MCT detector being used in this work had a wavelength cutoff (λ_{max}) of 15 μm, it should be noted that MCT detectors are commercially available which respond to longer wavelengths, albeit at reduced sensitivity. MCT detectors may be readily purchased with a λ_{max} down to 23 μm (440 cm^{-1}). For studies at longer wavelengths, a deuterated triglycine sulfate (DTGS) pyroelectric bolometer with a polyethylene window could be used, but very long data acquisition times will be needed to obtain spectra with an adequate SNR. For very high sensitivity studies below 500 cm^{-1}, a helium-cooled germanium

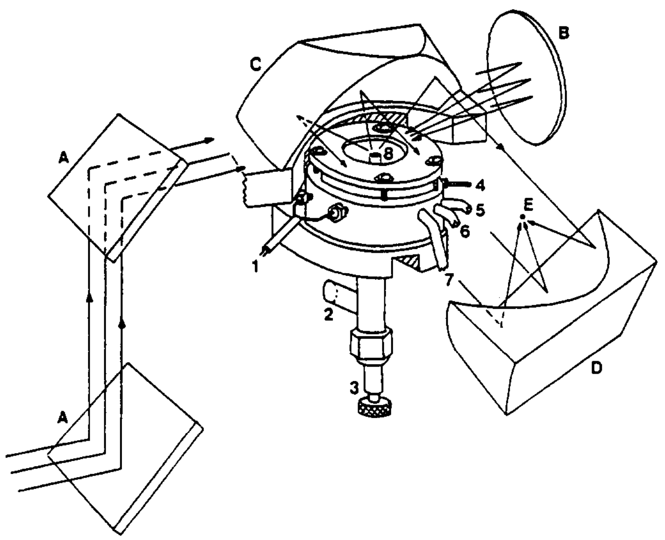

FIG. 3. Schematic of the DR/FT–IR system, with (A) plane mirrors; (B) 45° off-axis paraboloidal mirror; (C) collecting paraboloidal mirror; (D) focusing paraboloidal mirror; (E) focus of mirror D at which downward-looking MCT detector is held. (1) leads of the heating element; (2) gas-out line; (3) sample holder; (4) gas-in line; (5) and (6) cooling-water lines; (7) line to manometers; (8) sample cup.

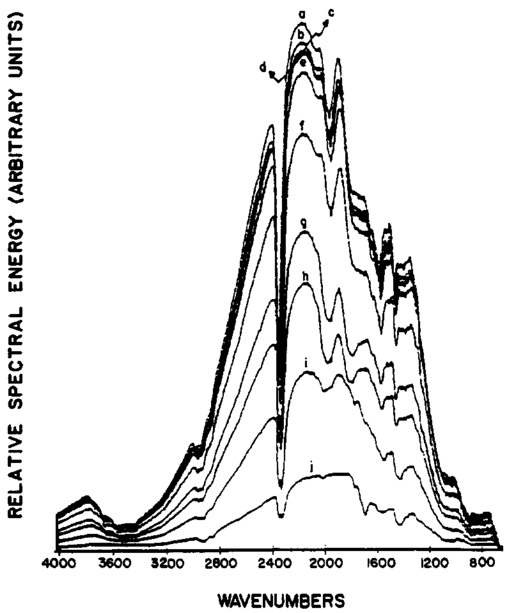

FIG. 4. Single-beam DR spectra of 5% Rh/Al_2O_3 measured under vacuum at different temperatures: (a) RT; (b) 50°C; (c) 65°C; (d) 75°C; (e) 115°C; (f) 185°C; (g) 250°C; (h) 290°C; (i) 400°C; (j) 600°C. Same number of scans were collected for all the spectra, after allowing 5 min for temperature equilibration.

bolometer could be used. The sensitivity of this detector is three orders of magnitude greater than that of DTGS.

4. PERFORMANCE

As would be expected, when adsorbate gases are first admitted to the cell, the intensities of bands assignable to adsorbed species increase rapidly, but are then observed to decrease over a period of approx 5 min to an equilibrium value (see Fig. 5). The probable reason for the behavior seen in Fig. 5 is as follows. When CO is first admitted into the cell, the pressure of CO over the upper layers of the sample is greater than it is at greater depth, so that the coverage of adsorbed CO will also be greater near the top of the sample. It is known that the majority of the signal in a diffuse reflectance infrared spectrum is caused by the top millimeter of the powdered sample (*7*, *8*), so that the intensity of bands due to adsorbed CO will be high immediately after the gas is admitted. Undoubtedly the pressure of gas above and below the sample equalizes very quickly, but the rate at which the coverage of adsorbed

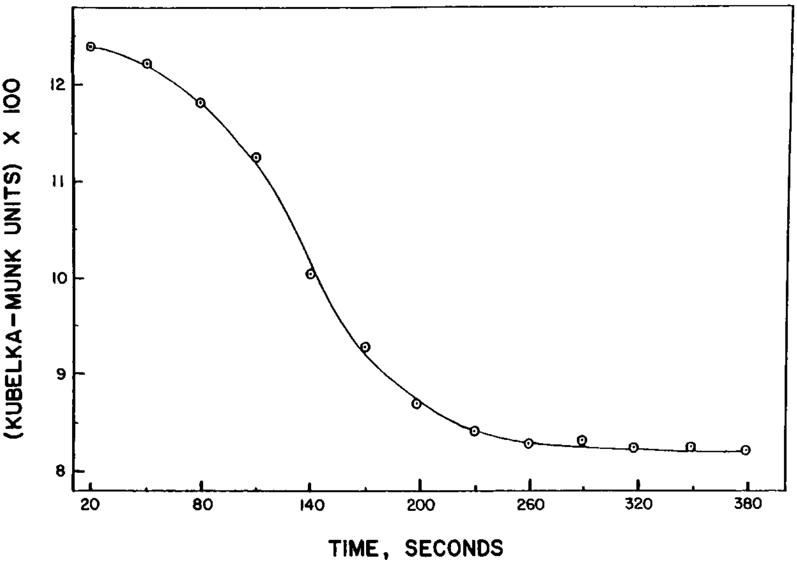

FIG. 5. Intensity of the band at 1853 cm^{-1} due to bridge-bonded CO on 1% Rh/Al_2O_3 plotted against time after CO was admitted to the cell. The cell was at ambient pressure and the equilibrium pressure of CO was 0.010 Torr.

CO becomes uniform throughout the sample appears to be much slower unless a very high pressure of gas (corresponding to more than the amount required for monomolecular coverage) is admitted.

Although other heatable cells for DR infrared spectrometry have been developed and have even become commercially available (*9*), the particular cell design described above has two definite advantages. The first is sensitivity: if a powdered alkali halide such as KCl is placed in the sample cup and interferograms are measured using a medium range mercury cadmium telluride detector ($\lambda_{max} = 15\ \mu m$) the SNR with a scan speed of about 6-mm retardation/sec can be so great that a 16-bit analog-to-digital converter (ADC) is needed to avoid digitization noise. This greatly increased sensitivity is in part due to the large window of the cell, which allows the majority of the radiation that has been diffusely reflected from the sample to emerge from the cell (in marked contrast to earlier designs), and in part because of the very efficient collection optics. With metal catalysts supported on silica or alumina, the signal is attenuated by more than a factor of 2, so that spectra can still be measured at high SNR without being limited by the dynamic range of most 15-bit ADCs.

The second advantage concerns the capability of drawing gases through the sample. Three benefits are in fact derived from this property. The first concerns the reproducibility of DR spectra. It has been shown that band intensities in DR infrared spectra can increase dramatically when powdered samples are compressed (*10*). When samples are loosely loaded into a cup and leveled with a straightedge, different parts of the powder are subjected to different pressures, so that band intensities vary microscopically across the sample, leading to irreproducible overall band intensities. If the samples are subjected to a certain pressure for a fixed duration the repeatability of band intensities is improved by an order of magnitude. Samples used in this cell should not be compressed, otherwise gases will not be readily drawn through them. Nevertheless, by drawing an inert gas through the samples for several minutes after loading them into the cup, the intensity of bands due to the adsorbent and absorbate becomes very constant, so that large ordinate expansion becomes possible for the observation of weak adsorbate bands after the adsorbent bands have been subtracted.

The second benefit concerns the activation of the catalyst. Usually supported metals are activated as pressed disks by evacuation and heating for at least 1 hr, followed by reduction by hydrogen. When we treated the powdered catalyst with hydrogen, even at very low pressure, the residual oxygen on the surface which had not been removed by evacuation reacted violently when hydrogen was admitted into the cell. Only when the catalyst is at ambient temperature and the pressure of hydrogen does not exceed 3 torr is a violent reaction averted. The temperature of the sample and pressure of H_2 could then be slowly increased to the desired values. This observation suggests that catalysts may be more efficiently activated in the powdered form than when pressed into translucent disks.

The third benefit is the capability of sweeping products from the cell for subsequent characterization, e.g., by trapping onto an adsorbent or on-line mass or FT–IR spectrometry. When relatively nonvolatile products are formed, they are swept away from the infrared window and are therefore prevented from condensing on the window and interfering with the measurement of adsorbed species.

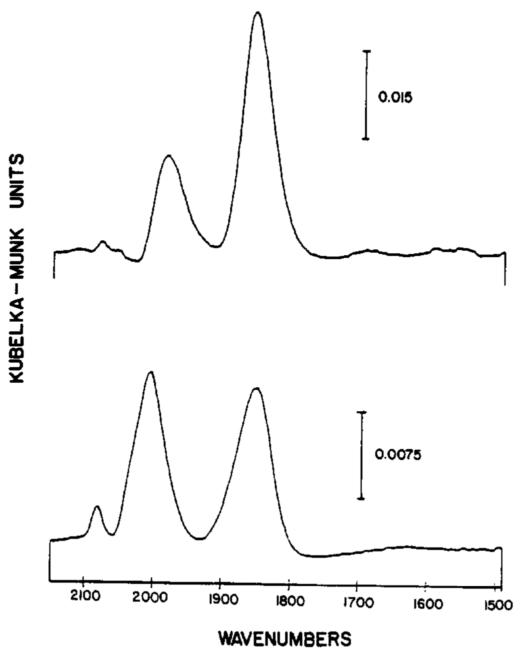

FIG. 6. DR/FT–IR spectra of CO on 1% Rh/Al_2O_3 (lower trace) and 5% Rh/Al_2O_3 (upper trace) at low CO coverage (0.015 torr).

The performance of this cell may be illustrated by the spectra shown in Fig. 6. These are spectra of CO adsorbed on a Rh/Al_2O_3 catalyst with metal loadings of 1% (lower trace) and 5% (upper trace). In each case the equilibrium pressure of CO above the samples was 0.015 torr. These spectra are quite different in appearance from spectra of CO on Rh/Al_2O_3 at higher surface coverage, as can be seen by comparing the spectra in Fig. 6 to those in Fig. 7, where the CO pressure was about 45 torr. The capability of measuring spectra of adsorbed CO at very low surface coverage should lead to an improved understanding of the infrared spectra of adsorbed CO. It is noteworthy that large shifts are observed as the pressure of CO above a Rh/Al_2O_3 adsorbent is increased from zero to 0.1 torr, and we believe that a detailed study of these shifts will lead to improved vibrational assignments for this already well-studied system (*11–14*).

The spectra in Figs. 6 and 7 are plotted linearly in the Kubelka–Munk function $f(R_\infty)$ given by

$$f(R_\infty) = (1 - R_\infty)^2/2R_\infty,$$

where R_∞ is the diffuse reflectance of an "infinitely thick" sample relative to that of the untreated catalyst. $f(R_\infty)$ is linearly proportional to the concentration of the adsorbed species. Above a certain sample thickness, $f(R_\infty)$ does not change. For weakly absorbing samples, previous studies have indicated that samples of greater thickness than 3 mm may be considered "infinitely thick" (*5*). Supported metal catalysts are rather strong absorbers, and do

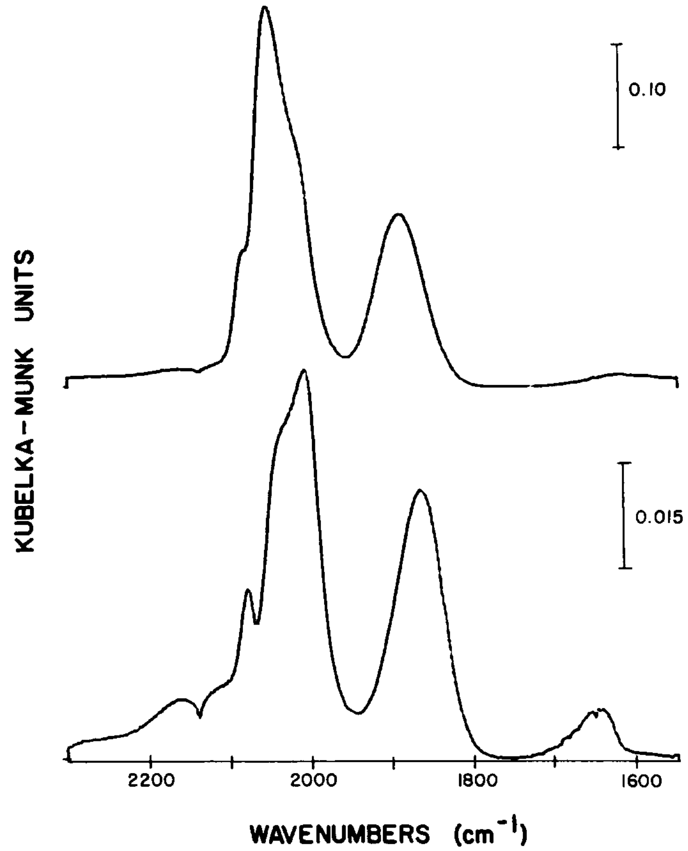

FIG. 7. DR/FT-IR spectra of CO on 1% Rh/Al_2O_3 (lower trace) and 5% Rh/Al_2O_3 (upper trace) at high CO coverage (45 torr). For the lower spectrum, it may be noted that the band intensity is only about twice that when the CO pressure was only 0.015 torr (Fig. 6).

not need to be of greater thickness than 1 mm to meet the infinite thickness criterion.

In spite of the low equilibrium pressure of CO, the bands seen in Fig. 6 cannot be considered to be weak. For example, the intensity of the 1853-cm^{-1} band due to bridged CO in the upper spectrum is 0.044, corresponding to above 26% absorption. Nevertheless, the CO coverage is considerably less than a monolayer. Based on these and other data, we believe that adsorbed CO present at about 10^{-4} monolayers may be observed using the cell and optics described in this paper.

We believe that a cell of this efficiency will therefore permit previously unobserved intermediates in several heterogeneous catalytic reactions of commercial significance to be observed under reaction conditions. This is in contrast with the use of many other surface characterization techniques for which a high vacuum is necessary. A diffuse reflectance cell capable of operating to 10^5 torr is currently being designed in the laboratory of one of the authors (PRG). Thus we believe that because of the high sensitivity and versatility of DR infrared spectrometry, the application of this technique to the study of heterogeneous catalysis will become increasingly important.

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