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A Microwave-Heated Infrared Reaction Cell for the *in-situ* Study of Heterogeneous Catalysts

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Abstract

A transmission infrared microreactor cell which holds a catalyst pressed disc in a controlled atmosphere and allows microwave and conventional heating up to 423K is demonstrated using the oxidation of carbon monoxide over the standard catalyst, EUROPT-1. Optical characteristics are determined by the choice of CaF_2 as the window material, allowing transmission from 77000-1000cm^{-1}. An oscillating microwave power heating regime with a peak height of 200W is used and time-resolved infrared spectra and mass spectrometry show oscillations in the reaction which correspond to the microwave heating.

Key words: EUROPT-1 catalyt; infrared spectroscopy; microreactor; microwave heating.

Estudio *in situ* de catalizadores heterogéneos usando una celda de reacción infrarroja calentada por microondas

Resumen

En este trabajo se demuestra el uso una celda como microreactor de transmisión infrarroja la cual soporta un catalizador de disco prensado en atmósfera controlada y que permite el calentamiento convencional y con microondas hasta 423 K para evaluar la reacción de oxidación de monóxido de carbono sobre el catalizador EUROPT-1. Las características ópticas se determinaron usando ventanas de CaF_2 que permiten observar la transmisión desde 77000-1000 cm^{-1}. Se utilizó un régimen de calentamiento con fuente de microonda oscilante con una altura de pico de 200W. Los espectros infrarrojos y de espectrometría de masa mostraron oscilaciones en la reacción las cuales corresponden al calentamiento por microondas.

Palabras clave: Calentamiento con micro-ondas, catalizador EUROPT-1; espectroscopía infrarroja; micro reactor.

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Introduction

In the late 1930's the magnetron was designed by Randall and Booth and used for RADAR (Radio Detection And Ranging). It was soon recognised that microwaves could heat water in a very effective manner, and domestic microwave-heating appliances became available in the 1950's. These devices were widespread by the 1980's and it was around this time that the application of microwave heating for laboratory scale chemical reactions began to develop (1).

Although microwaves are best known for their use in the domestic microwave oven, they are used in a wide array of heating applications; from industrial-scale processing (2), through medical use (3), to synthesis in the research laboratory (4). This is due to the fundamental difference in the way a material is heated by microwaves when compared with conventional methods (5), and the high efficiency that can result from heating only the target rather than maintaining an oven or vessel at an elevated temperature.

While the greatest interest has been in the application of microwave heating to organic syntheses in solution (1, 5), a number of reactions involving solids have been performed, including the synthesis of ceramics (6), metal chalcogenides (7), superconductors (8), sulfides and selenides (9) . Reports of heterogeneous catalysts being heated using microwaves have also been published. These generally show reactions occurring at apparently lower temperature than the conventionally heated reaction system, however, there are reports of changes in selectivity (10, 11). Explanations offered for these effects are electrical discharge (12) and uneven heating (13). Reports have also been published which suggest that catalysts synthesised using microwaves (14,15). Heated or with microwaves (10, 16) have different reactivities/selectivities even when subsequently heated by conventional means.

To date, there has been little progress in elucidating the origins of these results. Infrared spectroscopy is a well established and powerful technique for following the course of a reaction. In many cases it has been possible to devise microreactor cells which allow investigation of the reacting species through *in-situ* infrared techniques (17-19). As the study of microwave enhanced chemistry is a relatively young field, there are no previous reports of microwave-heated reaction cells for infrared spectroscopy. The manufacture of a cell that allows investigation of a solid sample under microwave heating in catalytic reaction conditions with infrared spectroscopy was therefore undertaken and is detailed in this work.

Cell design

The basic elements of the transmission cell are a ceramic sample holder located between parallel metal applicator plates. An exploded view of the cell is shown in Figure 1.

Each 3x5cm applicator plate (a,b) is constructed from two pieces which are held together by countersunk screws and hold a 13mm diameter, 2mm thick, CaF_2 window (c). The window has a gas tight seal which is a circular gasket (d) of rectangular cross-subsection, cut from a 0.75mm thick sheet of Kalrez® compound 4079. The inner surface of the window is faced with a nickel 40 x 40 mesh wire cloth (e) with 0.13mm wire diameter to prevent microwave leakage and which attenuates the infrared signal by about 40%. This is held in place by a metal washer (f) that is pressed into the plate.

The thicker half of each applicator plate has a hole drilled to accept a 1/8 inch Firerod® cartridge heater (g), supplied by Watlow, for conventional heating. The ground applicator plate (a) has a 1mm diameter shielded K-type thermocouple (h) from Thermocoax running through the plate at angle of 45 degrees. This protrudes from the inner face by about 1.5mm to rest in contact

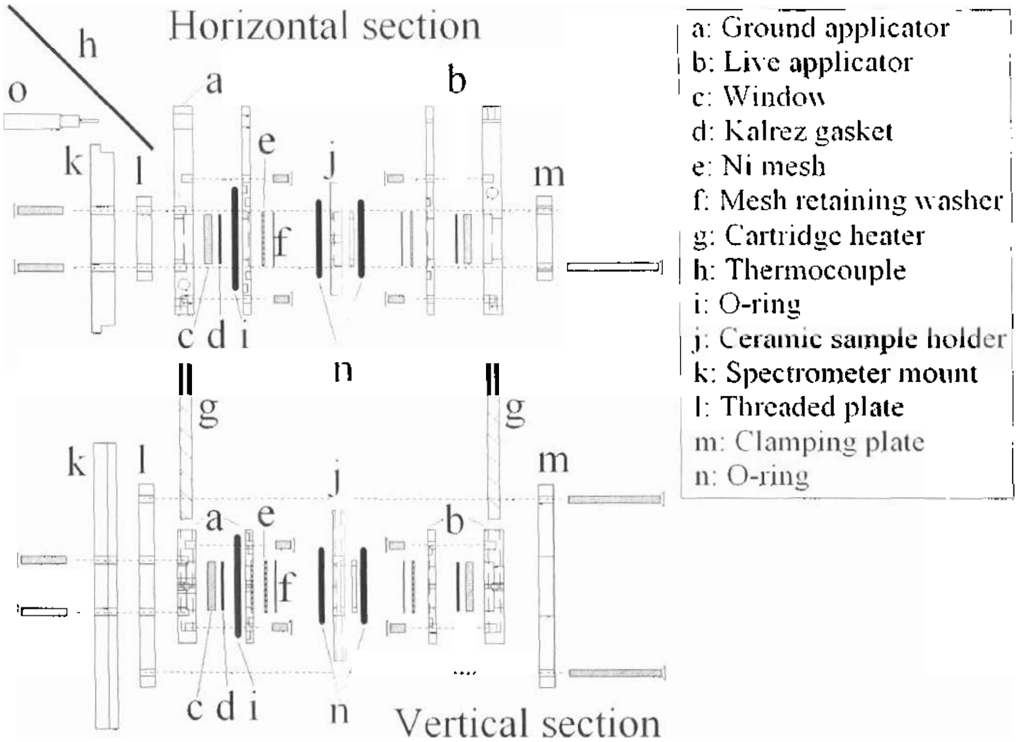

Figure 1. Exploded view of transmission cell.

with the pressed disc catalyst sample and is silver-soldered onto the outer face. An extra Kalrez® 4079 o-ring (i) between the two pieces of this applicator plate is used to ensure the cell is gas-tight.

The sample holder (j) is manufactured from a 3mm thick Macor® plate with a central hole for the passage of the infrared beam. Manufacture of this piece from Shapal-m®, a boron nitride ceramic, would have been preferred for its lower interaction with the microwave field, but proved too fragile. The Macor® component has acceptable microwave absorbance but was more mechanically robust in routine use. A step in the plate supports the catalyst disc, with a notch cut out to accept the thermocouple. 1/16 inch holes were drilled from the edges to the centre cavity to guide the flow of reactant gases in and out of the cell across the surface of the sample. Stainless steel pipes of 1/16 inch external diameter were inserted into these outside the microwave field and secured using high temperature silicone sealant.

A mounting bracket (k) designed for a conventional infrared cell mount is attached to the ground plate, as is a second plate (l) with threaded holes to allow a clamping plate (m) to compress the assembly.

The ceramic sample holder seals against the metal applicator plates through o-rings (n) held in grooves in the applicator plates. Standard Kalrez® 4079 contains carbon black as a filler which causes heating in a microwave field. Selection of a high purity variant (Kalrez® compound 6221), designed for food and pharmaceutical use, for these o-rings avoided this problem.

The clamping plate is insulated from the signal applicator by a mica sheet. Power is supplied to the cell by a RG402/U semi-rigid coaxial cable with an SMA type connector (o) which is soldered to the ground plate, with the central pin fixed in the other plate through a grub screw.

A T-piece (not shown) is situated $3/4\lambda$ (approx. 9cm) along the cable from its central point between the applicator plates with an adjustable electrical short between the inner and outer conductors of the coaxial cable on the side branch. This can travel over a $\lambda/2$ range and allows tuning of the cells impedance for optimal power transfer to the sample. The excess energy is dumped to a resistor bank which is connected to the applicator plates by grub screws.

Experimental

The infrared spectrometer used for all data collection was a Bio-Rad FTS-6000 instrument fitted with an MCT detector. Gas flow was controlled using four MKS Mass Flow Controllers (model numbers 1159, 1259 and two model 1179), attached to a 247-C four channel readout. This system allows complete control of the atmosphere surrounding the catalyst for *in-situ* pre-treatment and analysis. Carbon monoxide was supplied by Argo, all other gases were supplied by BOC. The EUROPT-1 catalyst was provided by Johnson Matthey.

Mass spectrometry of the exhaust gases was conducted with a mobile mass spectrometer, model MMS-070 from Spectra. This system is based around a Microvision Plus quadrupole analyser, with associated vacuum and sample admission systems. The gas inlet was *via* a fused silica capillary inserted through an 1/8 inch Swagelok® T-piece into the outlet gas connection from the cell so that the sampling point was within 5cm of the catalyst sample. The instrument allows recording of analogue signals through an expansion port, and the data from the thermocouple in the cell was recorded using this method.

The microwave source used was an ASTeX AX-2100 microwave generator, which is a variable power 2.45GHz source that allows remote control and can generate up to 1kW. The source was connected to a Thurlby Thandar TG215 function generator for power control and the power was varied sinusoidally between 0 and 200W at a frequency of 0.1Hz.

To determine the effect of microwave heating on the cell containing and a purely gaseous sample, 5sccm CO and 15sccm air was first passed through the cell. The cell was raised to the experimental temperature by conventional heating and allowed to equilibrate at 300K before data collection was started. Time-resolved spectra were collected at 1s intervals at 4cm^{-1} resolution for a period of 120s. Data collection for the infrared and mass spectrometers was initiated simultaneously and after a short period of *circa* 20s, the varying microwave power was enabled. The collection of data in this manner allowed the stability of the system at the experimental temperature under conventional heating to be confirmed.

For the experiments with a catalyst sample, *circa* 30mg of a finely ground EUROPT-1 was pressed under 10 tonnes for 10s in a 13mm die with a hydraulic press. This was carefully transferred to the ceramic disc holder and the reaction cell assembled. The sample was then pretreated by oxidation in 15sccm air above 423K for an hour, followed by reduction under 15sccm hydrogen at the same temperature. The catalyst was allowed to cool to room temperature under hydrogen, before the reaction mixture of 5sccm CO and 15sccm air was passed over the catalyst disc. The sample was then again heated to 300K by conventional means and allowed to equilibrate. Data collection was the same as for the purely gaseous sample.

Results

Heating of CO and Air

The time resolved data for the microwave heating of CO and air in the absence of a catalyst sample is detailed in Figure 2 with

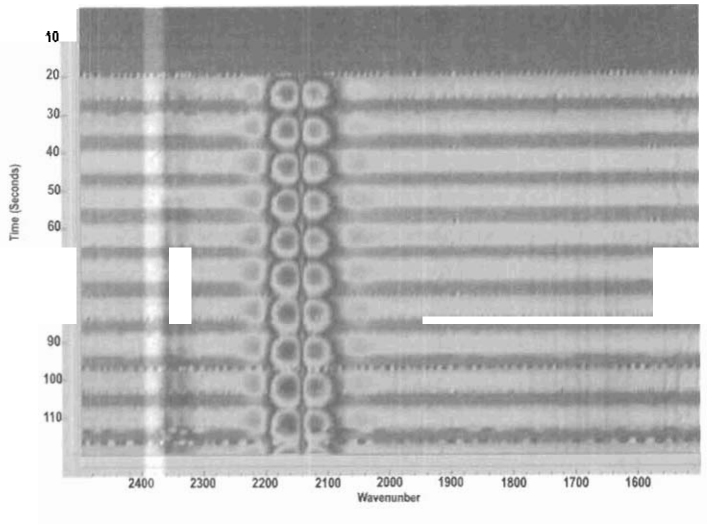

Figure 2. Infrared spectrum for CO and air under oscillating microwave power.

black denoting negative absorbance and white positive.

No features are evident in the spectrum before 20s indicating stable flow/temperture through the cell. The dominant feature in the spectra immediately the microwave power is applied is the appearance of periodic banding across the entire spectral range. Each microwave cycle heats the cell contents and thereby the cell components and so there is a periodic shift of the temperature at which the spectra are collected from that of the original background spectrum for the dataset. Similar effects also occur under conventional heating where there are differences between sample and background spectra temperatures and are associated with differences in the level of infrared emission.

In a transmission infrared experiment, emission in proportion to the sample temperature is not sampled directly as the radiation is not modulated by the spectrometer interferometer, however, a proportion of the emission can be 'back sampled' through the optics and none the less contribute to the observed spectrum. The modulation over the broad spectral range in this instance suggests emission from the window materials or Ni gause in the optical path. This effect is stronger at lower wavenumber and in proportion to the intensity/wavenumber profile associated with a blackbody emitter at the appropriate temperature.

Other than the the effects of emission, the spectra show a series of negative features at 2123 and 2166 cm^{-1} oscillating with 0.1Hz frequency corresponding to the maxima in the P and R branches of the gas phase CO spectrum. A representative cross-section spectrum through the time resolved data during microwave heating, together with a normal absorbance spectrum of CO at the same spectral resolution for comparison, is shown in Figure 3. Positive features outside these negative bands at 2235 and 2027cm^{-1} indicate heating of the gas phase CO, as higher rotational states become more populated at elevated temperature. Depopulation of the low rotational states causes a loss of signal closer to the position of the Q-branch, while an increase is seen at the fringes of the peaks due to an increased population of higher rotational states. In addition to the above features associated with CO there are peaks from CO_2 and water vapour. The CO_2 peaks are centred at 2345cm^{-1} and the water vapour rotational fine structure can be seen from 1870 to 1500cm^{-1}. These features are due to miscalculation

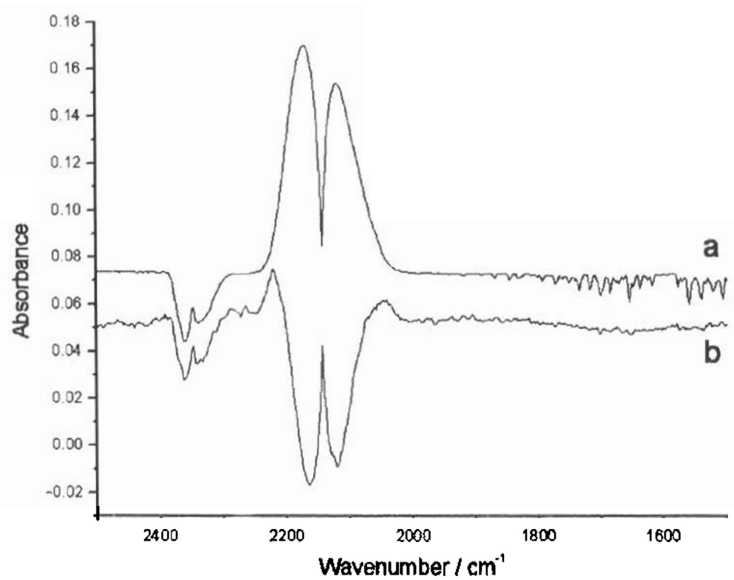

Figure 3. Typical gas phase absorbance spectrum of the reacting gases.

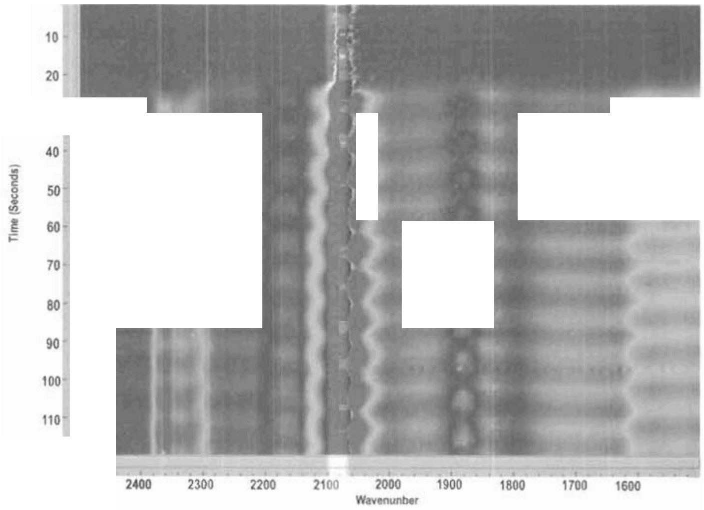

Figure 4. Oscillating microwave power infrared spectrum for CO and air over EUROPT-1 sample.

between the sample and background IR spectra caused by variations in the composition of the gas phase in the instrument beam path.

Oxidation of CO over EUROPT-1

In the time resolved spectra for the CO/air reactants over the catalysts, the peak due to linearly absorbed CO at 2083 cm^{-1} is so intense that small absolute changes in signal lead to large absorbance changes, resulting in a very poor signal to noise ratio around this feature, both before and after the application of microwaves. On introducing the microwave power, the linear CO peak shows clear oscillations at the applied frequency, and also exhibits an increase in intensity at lower wavenumber, and a corresponding decrease at high wavenumber over the course of the experiment. The peak position of linearly adsorbed CO species on Pt is coverage dependent, shifting to higher wavenumber as coverage increases (21) . The reaction conditions as well as the peak position suggest that the platinum surface is saturated before the microwave heating is applied. The shift to lower wavenumber under this heating regime indicates a lowering of the CO coverage due to the increased conversion to CO_2 associated with the temperature rise occurring with each microwave cycle.

The horizontal banding associated with emission is less marked at higher wavenumber compared to that from the CO/air reactant mix alone. The emission is, however, still pronounced at lower wavenumbers suggesting that the thermal emission is now mainly from the solid catalyst rather than cell components, in turn implying that less input microwave energy is absorbed by the reaction cell components as more is absorbed by the sample.

The bridged CO at *circa* 1840 cm^{-1} also oscillates at 0.1Hz and shows a decrease in intensity at 1890 cm^{-1} and 1800 cm^{-1}, with a slight increase at 1840 cm^{-1}. This would suggest that there are also changes in the surface coverage of the bridged CO species associated with the microwave sample heating. The signal due to gas phase CO is dwarfed by the adsorbed linear CO feature, but slight oscillations in the R-branch can be seen at 2166 cm^{-1}. The CO_2 doublet centred around 2343 cm^{-1} increases as time progresses, with oscillations at 0.1Hz again clearly visible. There are also changes at 1600 -1640 cm^{-1} associated with loss of water from the catalyst support. These changes are perhaps more evident in Figure 5 which compares an absorbance spectrum for the reacting mixture over EUROPT-1 at 300K, gained by the ratio of the single beam spectra of the catalyst under CO/air against that of the catalyst under He (Figure 5a), with a representative section through the time resolved data during microwave heating (Figure 5b).

Typical data recorded by the thermocouple during irradiation is plotted in Figure 6a along with the CO_2 pressure (Figure 6b) and shows both signals oscillating at 0.1Hz allied with a general rise throughout the course of the experiment. The temperature rise over the approximately 100s under irradiation is *circa* 13K, with a rise of around 2.5K per cycle. The resultant increase in conversion of CO to CO_2 under microwave heating is consistent with that noted in for the

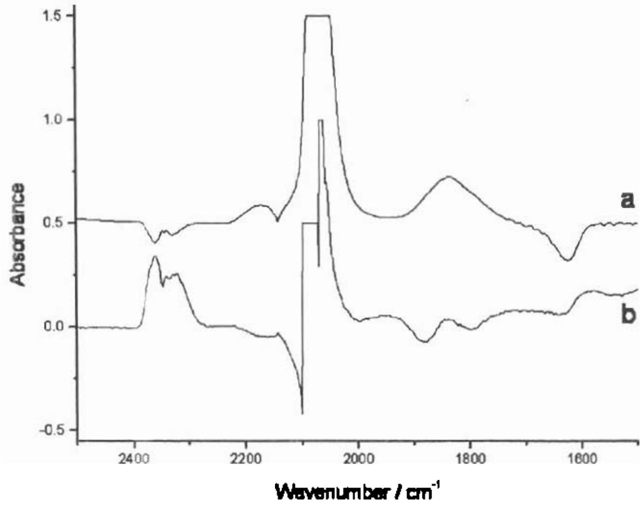

Figure 5. Typical absorbance spectrum for CO and air over EUROPT-1

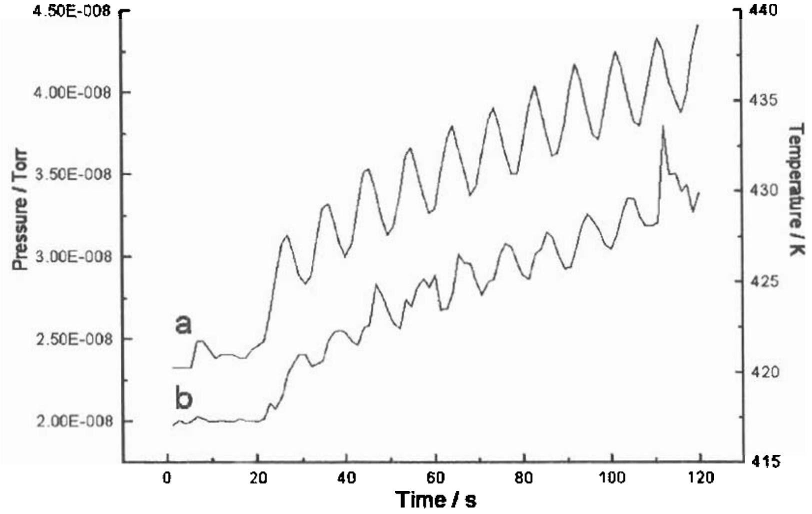

Figure 6. Temperature (a) and CO_2 pressure (b) recorded under microwave irradiation.

equivalent temperature rise in experiments carried out under conventional heating.

Conclusion

The cell has been shown to heat samples under microwave radiation, with evidence provided through the thermal peak broadening for the purely gaseous sample and the increased rate of CO oxidation in the presence of a catalyst. Infrared emission from the sample or cell components is evident in the spectra but is not problematic. It is possible to follow the course of microwave heating using this cell by both infrared spectroscopy and mass spectrometry. Some success has also been achieved in utilising this system in the analysis of liquid reactions, and small modifications to the design, such as a decrease in path length, should allow its further use in this field.

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