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Application of a cw quantum cascade laser CO₂ analyser to catalytic oxidation reaction monitoring

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Catalytic oxidation reaction monitoring has been performed for the first time with a trace gas carbon dioxide analyser based on a continuous wave (cw), thermoelectrically cooled (TEC), distributed feedback (DFB) quantum cascade laser (QCL) operating at around 2307 cm⁻¹. The reaction kinetics for carbon monoxide oxidation over a platinum catalyst supported on yttria-stabilised zirconia were followed by the QCL CO₂ analyser and showed that it is a powerful new tool for measuring low reaction rates associated with low surface area model catalysts operating at atmospheric pressures. A detection limit was determined of 40 ppb (1 standard deviation) for a 0.1 s average and a residual absorption standard deviation of 1.9 x 10⁻⁴.

Keywords: carbon dioxide, quantum cascade laser, optical sensor, gas sensor, direct absorption spectroscopy, catalytic oxidation

1. Introduction

Trace gas detection is an important requirement in many aspects of experimental scientific research. Recent advances in laser science and engineering have enabled very high sensitivity and specific trace gas detection techniques based on tunable infrared absorption spectroscopy with portable instruments to open up new areas of research and extend others. In the area of heterogeneous catalysis there is an on-going need for developing new catalysts for specific chemical reactions of industrial interest such as in the oil and gas sectors. Understanding the mechanism of catalysis can also lead to new advances being made. In order to gain a better understanding of the mechanism of catalysis at the gas-solid interface, model catalysts (of low surface area and well-defined structure) are required. The challenge lies in the ability to perform kinetic experiments on such model catalysts under real operating conditions (i.e. atmospheric pressure and above) as these systems are normally tested in ultra-high-vacuum (UHV). To achieve this, high performance gas analysis is required as only traces of the product gases may be present in the outlet stream. The main requirements for following the kinetics of small scale catalytic reactions are: high sensitivity to the analyte, species specificity (no interferences), low volume sampling, time resolution down to sub-second, and finally ease of use. Currently gas chromatography is often used for this type of measurements but it lacks sensitivity and is inconvenient to set-up and calibrate. Alternatively mass spectrometry is used but these instruments are usually expensive and bulky.

Tunable infrared laser absorption spectroscopy provides a promising solution and quantum cascade lasers (QCL) have become the most widely used tunable infrared laser source in recent years. They have been used for the detection of a wide range of trace gases in various areas of scientific research such as atmospheric monitoring, industrial emissions, plasma diagnostics, vehicle exhaust monitoring, isotope ratio analysis and breath analysis [1-8]. This has been primarily due to their room temperature operation in a single device at

wavelengths suitable for the detection of fundamental vibrations of many trace gas species of interest. Additionally, they have high output power and improving spectral tunability.

One of the trace gases of interest for catalysis research is carbon dioxide (CO₂). For infrared absorption detection of carbon dioxide, the anti-symmetric vibrational band ν_3 centred around 2350 cm⁻¹ (4.25 μ m) is usually the most convenient to analyse. However, in this spectral region, it is difficult to manufacture quantum cascade lasers due to lattice matching requirements. Previously cryogenically cooled lead –salt diode lasers have been used to detect CO₂ in this vibrational band. Pulsed QCLs and cryogenically cooled continuous wave QCLs have been used in this region for CO₂ detection but now continuous wave distributed feedback quantum cascade lasers (cw DFB QCL) operating at or just below room temperature have recently become commercially available. External cavity quantum cascade lasers (ECQCL) [9,10] are also available in this region but for single species with resolved vibration-rotational spectral structure the narrower tuning range of the DFB lasers is sufficient. Cw DFB QCLs also have the advantage of intrinsic linewidths in the kHz range [11]. Previous work has described the CO₂ analyser for ¹³CO₂/¹²CO₂ isotope measurements [12].

This paper describes the first application of a QCL CO₂ analyser being used to study catalytic oxidation reaction kinetics as a proof of concept. The QCL CO₂ sensor was tested using CO oxidation over a low surface area Pt catalyst at atmospheric pressure as a probe reaction where the CO₂ concentration range was expected to be in the tens to hundreds of ppm. The CO₂ analyser and performance are described, followed by a description of the experimental set-up for a catalytic reactor. The measurement results are then described before the discussion and conclusion on the capabilities and potential of QCL analysers for studies of low surface area catalysts under high pressures.

2. Quantum cascade laser CO₂ analyser

Parts of the laser spectrometer have been previously described and further details relevant to the application are given here [13]. The P(46) vibration-rotational line of the ν_3 anti-symmetric vibrational stretch at 2306.926 cm^{-1} was used for all measurements. This had a linestrength at room temperature (298 K) of $S = 2.637 \times 10^{-19}\text{ cm molecule}^{-1}$ [14]. As can be seen from the simulated spectrum in *figure 1*, this is one of the weaker lines of the ν_3 band. The laser was originally designed for wider applications such as the simultaneous detection of $^{13}\text{CO}_2$ and $^{12}\text{CO}_2$. The quantum cascade laser (Hamamatsu) operated in continuous wave (cw) and in a single longitudinal laser mode due to its distributed feedback (DFB) structure. The spectral range from 2305 to 2313 cm^{-1} could be accessed by reducing the laser temperature from $25\text{ }^\circ\text{C}$ down to $5\text{ }^\circ\text{C}$. This was achieved by mounting the laser onto an air-cooled thermoelectric cooling element (TEC). The laser operating temperature was stabilised by a temperature controller. In order to minimise power consumption it was decided to operate around $25\text{ }^\circ\text{C}$ with the compromise of a weaker CO₂ absorption line. A current controller was used to drive the stabilised QCL current up to the manufacturer's recommended maximum of 1 A with a lasing threshold of 0.9 A. The divergent laser beam was collimated to around 3 mm diameter using an anti-reflection coated aspheric lens of focal length about 4 mm with an output power of the laser of around 2 – 3 mW. A wedged calcium fluoride beam splitter was used to divide the laser output so that a reference signal could be obtained before the beam passed through the gas cell. Both beams were focussed by off-axis parabolic (OAP) mirrors onto 1 mm^2 (HgCdZn)Te photodetectors. These were cooled by two-stage thermoelectric coolers and both detector outputs were fed to 1 MHz bandwidth preamplifiers. The laser signal on the detectors had to be attenuated by the use of insulating tape so that the power was reduced to below $10\text{ }\mu\text{W}$. The signals from the

detector/preamplifiers were fed to a 16-bit data acquisition card (DACQ) at a sampling rate of 200 kHz. A schematic of the QCL spectrometer is shown in *figure 2*.

The intrinsic linewidth of the laser has been estimated to be less than 36 kHz at a laser power of around 25 mW [11]. This was determined from the minimum of the two-sample variance of the laser frequency difference between two adjacent measurement points on the side of an absorption lineshape. Additional noise contributions to the linewidth are made by the laser current controller.

The gas sampling cell was constructed out of aluminium and had an absorption pathlength of 54.2 cm and an internal diameter of 2.2 cm giving an overall cell volume of around 206 cm³. Wedged CaF₂ optical windows were mounted at both ends of the cell to minimise étalon effects. A mass flow controller provided a 10 sccm gas flow into the cell and a pressure controller connected to a diaphragm vacuum pump controlled the gas pressure in the cell. The gas temperature was monitored on the surface of the cell outlet and the readings fed to the data acquisition card. A particulate filter was also installed into the inlet gas line to remove any particles arising from the catalytic reactor.

In order to remove laser intensity variations and the effects of absorption by atmospheric carbon dioxide, the ratio of the two detector signals was taken. The optical pathlength of the main beam outside the gas sampling cell was set within a few mm to be the same as the pathlength of the reference beam in order to cancel absorption due to atmospheric carbon dioxide. Also the light intensities at each detector were adjusted to be approximately equal.

A LabView program was written to control the laser operation by means of a voltage waveform of 200 points in a 1 ms time interval. The voltage was ramped to provide a current ramp through the laser giving a spectral sweep of around 0.14 cm⁻¹ for a 10 mA current ramp. The first 10 points of the each scan were always set below laser threshold in order to provide

a reference point for detector offsets and drifts. Scans were averaged and displayed within LabView. The reference signal was normalised to the main signal at points 49 – 51 and then a ratio of the two signals was taken to provide the transmission spectrum. Wavelength calibration was achieved by inserting a germanium étalon into the reference beam in order to convert from a points scale to a wavenumber scale. The transmission spectrum was fitted to a Lorentzian lineshape together with a second-order polynomial function for the background light intensity. The mole fraction (or volume mixing ratio) x in ppm of CO₂ was determined from the absorption peak area A (cm⁻¹), the pathlength L (cm), the linestrength at temperature T (K) and the gas pressure p (torr):

$$x_{CO_2} \text{ (ppm)} = \frac{kT}{p} \times \frac{A}{S(T)L} \times \frac{760 \times 10^{12}}{101325} \quad (1)$$

The final term converts from pressure units of Torr to Pa. k is Boltzmann's constant. An example of an absorption line with a Lorentzian lineshape fit is given in *figure 3* showing 12.75 ppm of CO₂ in He. The spectrum is for the average of 100 scans over a period of 0.1 s at a gas cell pressure of 100 Torr and a gas flow rate of 10 sccm. The absorption residual standard deviation was 3.3×10^{-4} . The limiting noise was due to optical fringes produced by the windows of the gas cell. Derived gas mole fractions were saved every 0.437 seconds (averaging time of 0.1 s plus 0.337 s line fitting). For a CO₂ mole fraction of 12.75 ppm in helium the measurement precision was estimated to be around 40 ppb derived from the square root of the two-sample variance.

3. Experimental Catalyst Measurement

The QCL CO₂ analyser was tested using CO oxidation over a low surface area Pt catalyst supported on yttria-stabilised-zirconia (YSZ) at atmospheric pressures as a probe reaction. The catalytic reactor was fabricated from a closed-at-one-end quartz tube and the supported

Pt catalyst was placed at the bottom of the reactor. The reactor volume was approximately 40 cm³. The outlet flow of the reactor was split, with approximately 70 ml (STP) min⁻¹ fed to the QCL CO₂ analyser; the remaining outlet flow was vented. The total flow rate could vary depending on the experimental conditions. The gas lines used were 1/8" PFA tubing. Swagelok fittings were used throughout the testing rig and the catalytic reactor. A schematic of the testing rig is shown in *figure 4*.

The catalyst was prepared by sputtering of a dense Pt film on a single crystal YSZ (111) support. The geometric projected surface area of the Pt film was approximately 37 mm². Atomic force microscopy (AFM) and scanning electron microscopy (SEM) analysis of a fresh Pt film showed very small surface roughness and no porosity. It is therefore expected that the actual Pt surface area is similar to the geometric projected surface. This was used for the calculation of the area specific reaction rates.

CO oxidation experiments were conducted at 340°C (temperature of the reactor) at a flow rate of 150 ml (STP) min⁻¹, this corresponds to a total molar flow rate of approximately 0.1 mmol s⁻¹. The reactants, provided by BOC were 5% CO/He and 20% O₂/He. Pure He (N5 grade) was also used as the balance gas in all reaction mixtures. The kinetics of CO oxidation were studied as a function of the oxygen and carbon monoxide mole fractions (x_{O_2} and x_{CO} respectively). These mole fractions were determined at the inlet of the reactor by gas chromatography (Varian CP3800). For the reaction kinetics with respect to oxygen, the CO mole fraction was kept constant at approximately 0.5 % (5 000 ppm) while the oxygen mole fraction varied between 0.3 - 6 % (3 000 – 60 000 ppm). For the reaction kinetics with respect to CO, the oxygen mole fraction was kept constant at approximately 0.7 % (7 000 ppm) and the CO mole fraction varied between 0.2 - 3 % (2 000 – 70 000 ppm). The area-specific reaction rates were calculated based on the outlet mole fraction of CO₂ (x_{CO_2-OUT}) measured by the QCL analyser and are given in mmol s⁻¹ m⁻². The reactor was operated under

differential conversion (below 1%, determined from the CO₂ outlet mole fraction) so that the inlet and outlet mole fractions of both CO and O₂ can be considered to be equal. The CO₂ mole fraction at the outlet stream varied between 30 – 900 ppm for the experiments presented here.

4. Results and discussion

Figure 5 shows the outlet mole fraction of CO₂, in ppm, (as obtained from the QCL CO₂ analyser) as a function of time under reactive conditions ($x_{\text{CO}} \approx 5\,000$ ppm and $x_{\text{O}_2} \approx 30\,000$ ppm) at 340 °C. As can be seen in this figure, oscillations of a frequency of approximately 0.02 Hz in the CO₂ mole fraction are observed. These oscillations are often encountered in CO oxidation and are due to the periodic formation and dissociation of Pt oxides [15]. Over time the oscillations stopped and the CO₂ mole fraction settled to a lower value (of approximately 450 ppm) for these conditions.

Figure 6 shows the steady state reaction kinetics for CO oxidation as a function of (a) the oxygen mole fraction and (b) the CO mole fraction. These measurements were taken after cessation of the oscillations. The reaction rates are given in $\text{mmol s}^{-1} \text{m}^{-2}$. As can be seen in *figure 6* the reaction follows first order kinetics in O₂ and negative order kinetics in CO for the entire range of oxygen and carbon monoxide mole fractions used in this work. This behaviour of CO oxidation is well documented and is indicative of competitive adsorption of CO and O₂ on the catalyst active sites. It has been found that in general for O₂ mole fractions between 0.5 - 5 % the reaction follows first order kinetics with respect to oxygen while it follows negative order kinetics with respect to CO for carbon monoxide mole fractions in the range of 1-5 % [16]. The results presented here are in reasonable agreement with these findings. Moreover, the reaction rates measured in this study (i.e. 0.1-3 $\text{mmol s}^{-1} \text{m}^{-2}$) are of the same order of magnitude as similar studies on a low surface area Pt catalyst performed

under UHV conditions (where the reactants were introduced in the UHV chamber with the appropriate high vacuum leak valves) [17].

The detection limit for CO₂ attained in these experiments was around 36 ppb obtained for 0.1 s averaging and for a CO₂ mole fraction of 2.5 ppm in helium. Improvements can be made by faster data processing which would allow more spectra to be averaged in the same time period. The measurement precision obtained in this work with the quantum cascade laser analyser is an improvement on that of 50 ppb in a 40 s integration obtained from a cryogenically cooled lead-salt diode laser spectrometer at 2291.6 cm⁻¹ with a 5 m absorption pathlength and balanced InSb liquid nitrogen cooled detectors [18]. It is also comparable with a precision of 50 – 100 ppb (in 1 s) obtained by similar system based upon a pulsed QCL at around 2310 cm⁻¹ and two 7 m multi-pass cells [3].

Further improvements to the analyser can be made such as reducing the cell volume from around 200 cm³ down to less than 10 cm³. When this is combined with reduced sample pressures the sample volume can be reduced to below 1 cm³. The sensitivity can be increased by using longer optical absorption pathlengths. Cavity-ringdown or cavity-enhanced absorption spectroscopy are also possibilities to increase the absorption pathlength and thus the sensitivity. There have been several examples recently of these techniques being applied in the mid-IR range with cw QCLs [19]. Alternatively a multi-pass astigmatic Herriott cell has been used to obtain pathlengths of 75 m or more for CO₂ detection [20] but at the expense of larger cell volumes. Moving to a stronger vibration-rotation line of CO₂ such as the R(16) at 2361.466 cm⁻¹ ($S = 3.524 \times 10^{-18}$ cm molecule⁻¹) [14] would give over a ten times improvement in sensitivity.

The analyser is also capable of measuring ¹³CO₂/¹²CO₂ ratios [12] and will enable more detailed mechanistic studies of the catalyst activity to be studied. More interesting

isotopic studies for work using membrane catalytic systems would be to measure the oxygen isotopes e.g. $C^{17}O^{16}O$.

5. Conclusions

A trace gas analyser for carbon dioxide detection based on continuous wave quantum cascade lasers has been developed and tested on a catalytic oxidation reaction system. The results presented here show that the QCL CO_2 analyser is a very powerful tool for measuring the low reaction rates associated with low surface area model catalysts under real operating conditions (i.e. atmospheric pressures). Indeed the analyser can clearly follow the oscillations in the rate of CO_2 production due to the formation and dissociation of Pt-oxides. Even though the CO_2 concentrations studied here are in the ppm range the high sensitivity will enable the analyser to be used for the study of micro- and nano-patterned catalyst materials where much smaller catalyst areas and flows could be used requiring lower sample volumes and improved sensitivity. Improvements in the analyser will be based around reducing the cell volume for the study of smaller sample sizes and using cavity ring-down or cavity-enhanced absorption spectroscopy.

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Figures

Figure 1. Simulated $^{12}\text{C}^{16}\text{O}_2$ spectra for 1 ppb CO_2 mole fraction in air at a pressure of 760 Torr and 296 K with an optical cell path length of 1 m. The measurements in this work were made on the P(46) line where the laser temperatures are close to laboratory ambient.

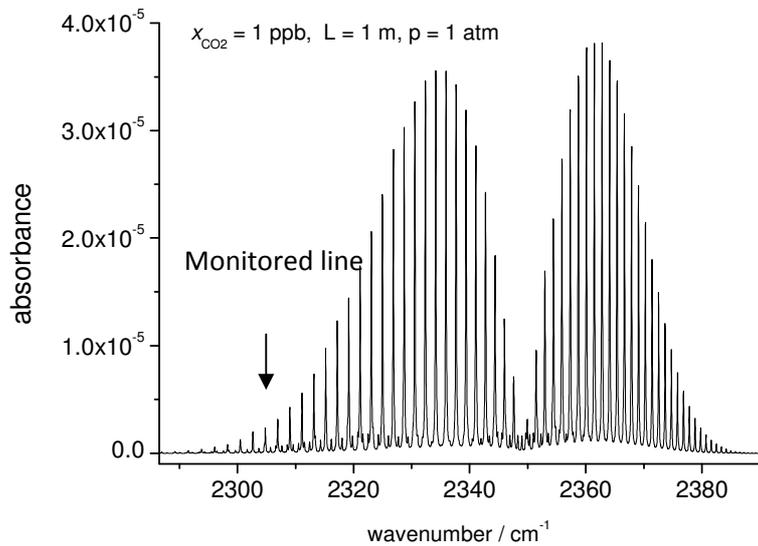
Figure 2. Schematic of the quantum cascade laser CO_2 analyser.

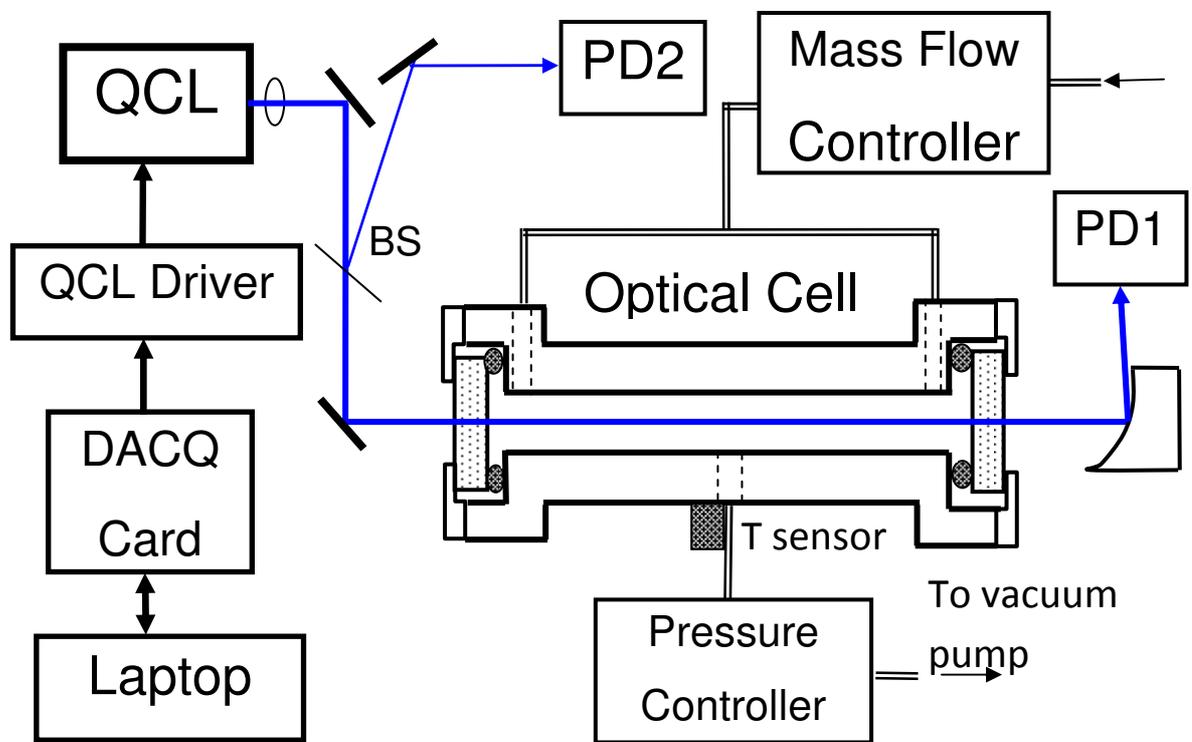
Figure 3. Fitted absorbance spectrum of CO_2 P(46) at 2306.926 cm^{-1} for a CO_2 mole fraction of 12.75 ppm in He and a cell pressure of 100 torr. A Lorentzian lineshape function was used for the fit and the fit residual is shown on the same scale. 100 averages in 0.1s were used.

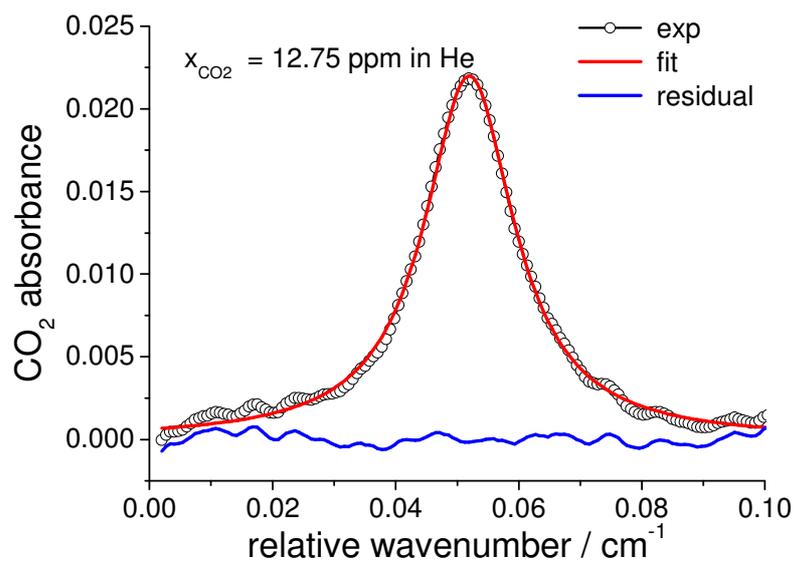
Figure 4. Schematic of the catalytic testing rig

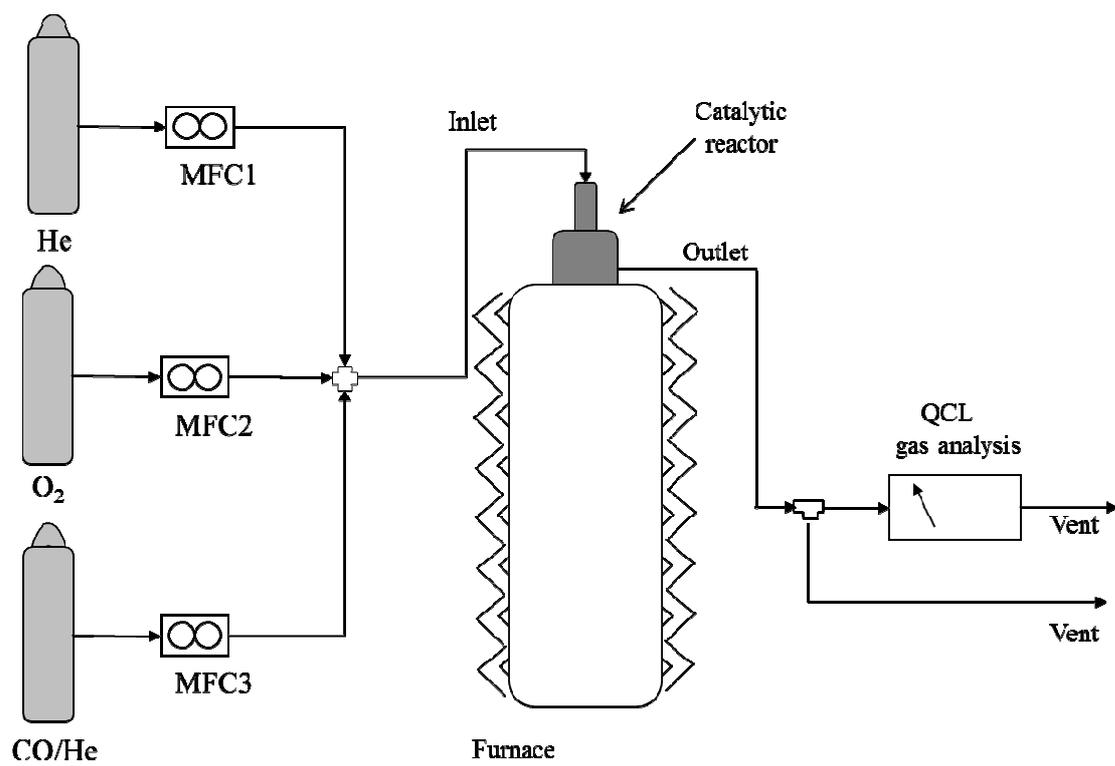
Figure 5. Mole fraction of CO₂ in the outlet stream as a function of time during CO oxidation of a Pt catalyst film at 340 °C using a flow rate of 150 ml (STP) min⁻¹. The reactant mole fractions were approximately 5 000 ppm and 30 000 ppm for CO and O₂ respectively.

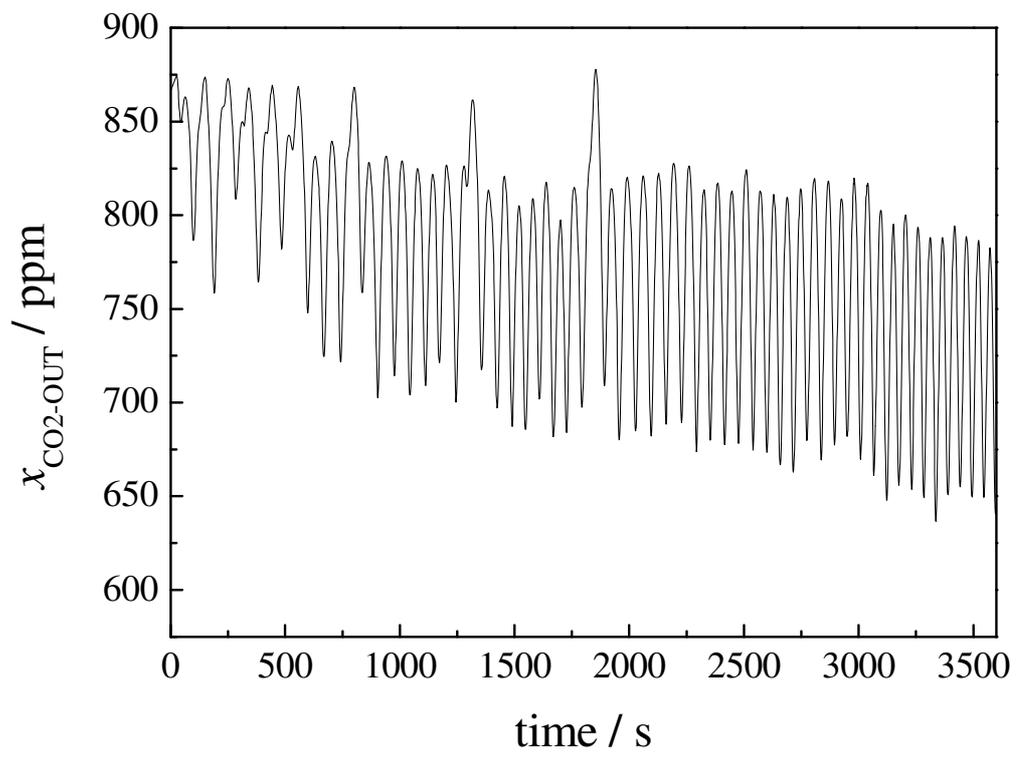
Figure 6. Reaction kinetics of CO oxidation on a Pt catalyst film at 340°C using a flow rate of 150 ml (STP) min⁻¹. a) Kinetics with respect to oxygen at a fixed $x_{O_2} = 5\,000$ ppm and b) kinetics with respect to carbon monoxide at a fixed $x_{CO} = 7\,000$ ppm.



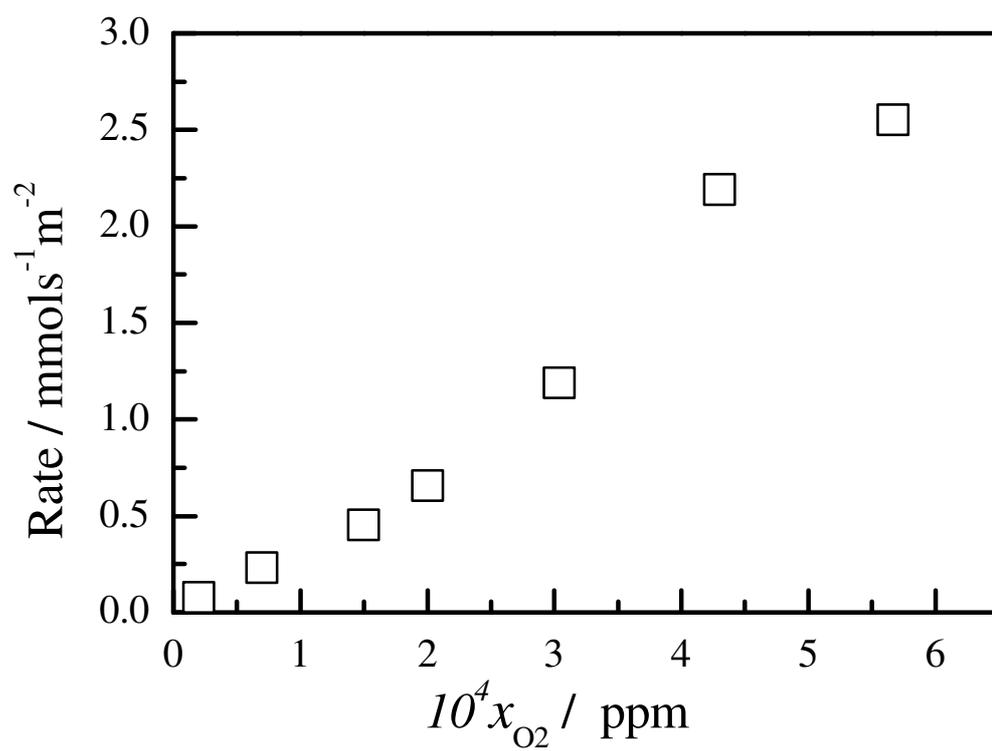








a)



b)

