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Comparison of conventional versus microwave heating of the platinum catalysed oxidation of carbon monoxide over EUROPT-1 in a novel infrared microreactor cell

Ian Silverwood[*], Gordon McDougall[**], Gavin Whittaker

School of Chemistry, University of Edinburgh, Joseph Black Building, West Mains Road, Edinburgh, Scotland, United Kingdom

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Abstract

The oxidation of carbon monoxide over a 6.3% Pt/SiO$_2$ catalyst (EUROPT-1) is studied under conventional and microwave heating and found to display similar activity. The capability of the cell to observe the adsorbed gases spectroscopically is also demonstrated.
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1. Introduction

The use of microwaves to heat chemical reactions began in the 1980s [1] and has attracted interest ever since. Today, laboratory-scale microwave ovens are increasingly common in the realm of liquid phase organic synthesis with considerable enhancements in rate [2] often arising from the utilisation of this method. This effect is generally agreed to result from the superheating of solvents which may occur in a microwave system [3] and a number of reviews on liquid-phase organic reactions have been presented [4,5].

Microwave ovens may also allow greater efficiency due to the fundamental differences in the mechanism of heating of materials under microwave irradiation from conventional heating [6]. It is possible to heat only the target rather than maintaining an oven or vessel at an elevated temperature and this has led to its use in the sintering of ceramics [7,8] as well as its more familiar use in food processing [9]. Heating solid phase and heterogeneous reactions with microwave radiation has also shown differences from conventional heating [10–12], although agreement on the source of these effects has not yet been reached.

The catalytic oxidation of carbon monoxide is of considerable importance in a number of fields. In addition to the elimination of CO emission in both vehicle exhausts and other combustion sources [13], interest exists in areas such as purification of gas streams [14] and regeneration of closed-cycle CO$_2$ lasers [15]. Conventional heating of the reaction is well understood [16], although reports of the application of microwave heating are limited to the work by Perry et al. [17–19]. Their research concerns carbon monoxide oxidation over γ-alumina supported Pt and Pd catalysts under conventional and microwave heating. In contrast to reports relating to other heterogeneous catalytic reactions [10,20], no rate enhancement was observed, and it was suggested that the difficulties of thermometry in microwave fields may result in inaccurate measurements of activity.

Use of a silica supported platinum catalyst for CO oxidation under microwave heating has not previously been reported and it is possible that the dielectric properties of the support may cause dissimilar results. This work was thus undertaken to investigate the effects of microwave irradiation upon such a catalytic system using EUROPT-1, a well characterised 6.3% Pt/SiO$_2$ catalyst [21].

2. Experimental

The microreactor cell used for the experiments has been described in detail previously [22] and consists of a parallel plate applicator which surrounds a ceramic sample holder. The sample

* Corresponding author (pre-publication). Tel.: +44 131 650 4733; fax: +44 131 650 6453.
** Corresponding author (post-publication). Tel.: +44 131 650 7284; fax: +44 131 650 6453.
E-mail addresses: Ian.Silverwood@gmail.com (I. Silverwood), G.McDougall@ed.ac.uk (G. McDougall).

holder has a gas tight seal to the applicator plates and connections for admission of the reactant gases outwith the microwave field. This allows the atmosphere surrounding the catalyst to be controlled and the cell operated as a flow reactor. Resistive cartridge heaters are held in the applicator plates to allow conventional heating.

Self-supporting catalyst wafers were formed by pressing circa 30 mg of the finely powdered EUROPT-1 catalyst under 10 tonnes in a 13 mm die for 10 s. A 1 mm diameter shielded thermocouple, passed through the ground applicator plate, was placed in contact with the sample.

Gas flow to the cell was controlled using four MKS mass flow controllers; carbon monoxide (99.5%) was supplied by Argo; He (99.996%), H_2 (99.99%) and compressed air were supplied by BOC. EUROPT-1 was provided by Johnson Matthey.

Mass spectrometry of the exhaust gases was conducted with a Macrovision Plus quadrapole analyser, with associated vacuum and sample admission systems, from Spectra. The gas inlet was via a fused silica capillary inserted into the cell's outlet gas connection so that the sampling point was within 5 cm of the catalyst sample. This arrangement should ensure that the effluent gases reach the sampling point in less than 0.5 s.

The microwave source used was an ASTeX AX-2100 microwave generator, a variable power 2.45 GHz source allowing remote control and generating up to 1 kW. The source was connected to a Thurlby Thandar TG215 function generator for power control and the power was varied sinusoidally between 0 and 200 W with 0.1 Hz frequency.

Catalyst wafers were pretreated by oxidation in 15 sccm air at circa 423 K for 1 h, followed by reduction under 15 sccm hydrogen at the same temperature. The samples were allowed to cool under hydrogen, then purged under 20 sccm He for 5 min before the reaction mixture of 5 sccm CO and 15 sccm air, corresponding to a 1:1.3 ratio of CO:O, was passed over the catalyst disc. The cell and catalyst were then raised to the desired temperature by conventional heating and the reaction system allowed to equilibrate.

Under conventional heating alone, IR data was averaged over a period of 30 s to give improved signal to noise. Where microwaves were applied in addition to conventional heating, data was collected with a time resolution of approximately 1 s. Recording was initiated and after a short period of circa 10–20 s at the set temperature, the oscillating microwave power was enabled for 120 s. The infrared spectrometer used for all data collection was a Bio-Rad FTS-6000 instrument fitted with a narrow band MCT detector.

3. Results

During an irradiation cycle, oscillations in the CO_2 production, sample temperature and spectral features caused by the modulation of the microwave power were clearly evident at almost all temperatures. The CO_2 pressure trace for such a period is reproduced in Fig. 1 along with the corresponding temperature recorded. The data corresponds to the introduction of microwave heating to the reacting system initially at 367 K. At this point, the CO conversion was approximately 0.7%.
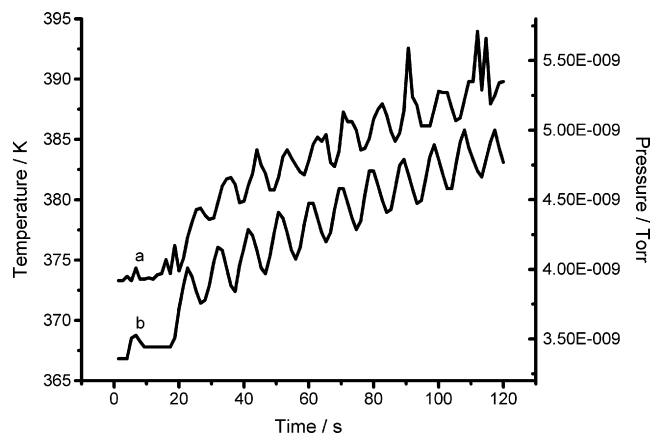

Fig. 1. CO_2 production (a) and recorded temperature (b) over EUROPT-1 under microwave heating as a function of time.

A significant jump was seen on enabling the microwave power, followed by smaller 0.1 Hz oscillations. This larger initial temperature step is believed to result from overshoot in the output from the microwave power supply when first switched on. The production of CO_2 increases with time as the microwave energy heats the sample, with oscillations clearly seen at 0.1 Hz, corresponding to the frequency at which the microwave energy is modulated. The CO_2 production appears to slightly lag behind the recorded temperature, possibly due to the self-sustaining nature of the reaction. Each microwave cycle raises the temperature by approximately 4.5 K and the CO_2 conversion by 0.05%. Over the 120 s irradiation the temperature rises in total by 18 K and the conversion by 0.2%.

The production of CO_2 over the catalyst between 300 and 440 K is presented in Fig. 2. This shows the variation in the partial pressure of mass 44 recorded under both heating regimes. The data obtained from the conventionally heated experiment is plotted as a dashed line, and shows the CO oxidation increasing with temperature. Hysteresis is seen on cooling due to the reaction exotherm sustaining the reaction. The microwave heated data is shown as a series of solid traces, with the CO_2 level as a function of temperature recorded from the
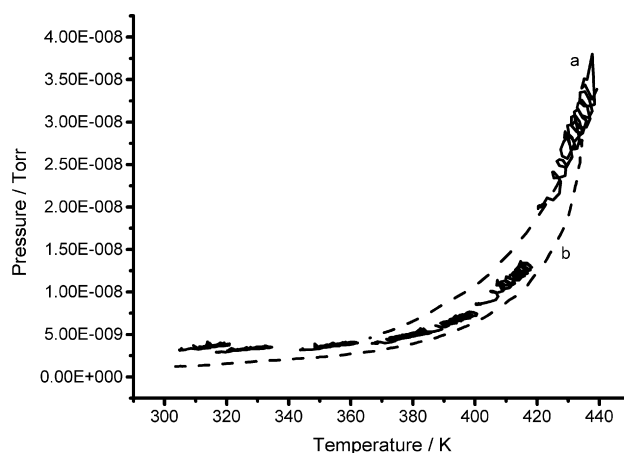

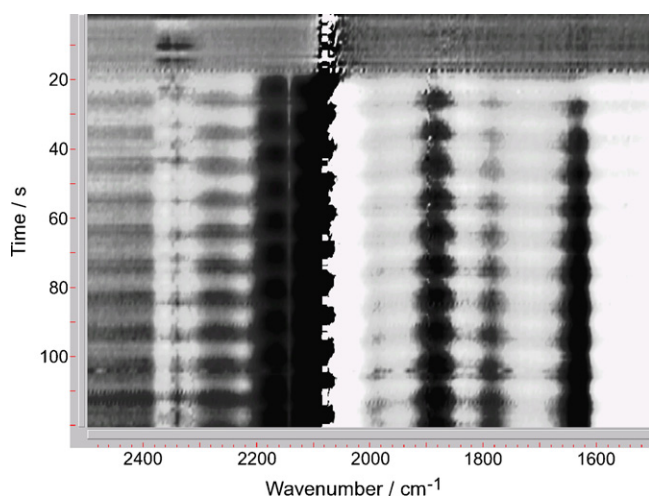Fig. 2. CO_2 production over EUROPT-1 under microwave (a, solid line) and conventional heating (b, dashed line).

Fig. 3. Time resolved IR spectra of CO oxidation of EUROPT-1 under microwave heating.
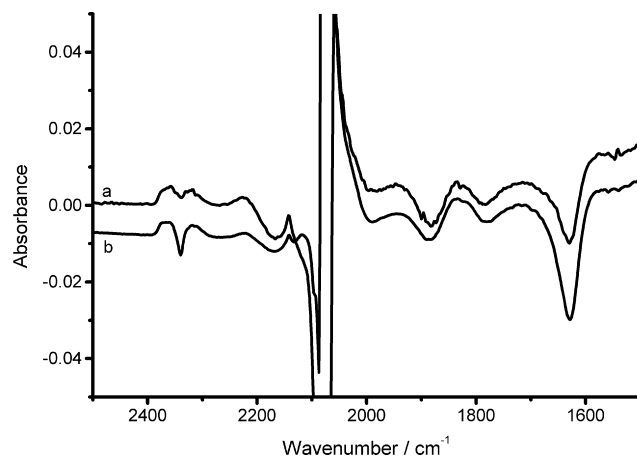

Fig. 4. IR spectrum for CO oxidation over EUROPT-1 after 90 s of microwave heating (a) and under conventional heating over a similar temperature range (b).

thermocouple in the cell during each 2 min irradiation cycle for a series of seven experiments over the temperature range studied.

Infrared spectra from the reacting system are a potentially more sensitive probe of the state of the catalyst under microwave heating than the conversion and temperature data. Fig. 3 shows the infrared spectra corresponding to the data presented in Fig. 1. The spectra are presented as a greyscale, time-resolved plot with higher absorbance values represented by the increasingly lighter shades. The background spectrum for the production of the absorbance spectra was recorded at the set temperature immediately prior to the acquisition of the data set and so the spectra are essentially featureless until the introduction of the microwave power at 20 s indicating the stability of the reaction system. The only significant feature evident during the initial 20 s is $\sim 2100\,cm^{-1}$. The overlapping absorbance of the gas phase and linearly adsorbed CO lead to near zero transmission at this point and so to intense miscancellation features at this wavelength in the ratioed data. A number of spectral features clearly develop with time under irradiation and oscillate in intensity in time with the applied microwave power and the changes in temperature and conversion noted in Fig. 1. These features are perhaps more evident in an individual absorbance spectrum extracted from the dataset and shown in Fig. 4a. This shows a spectrum collected after 90 s under microwave irradiation. The most intense feature in the region around $2079\,cm^{-1}$ is due to the linearly adsorbed CO and shows saturation. The gas phase CO_2 peaks are visible around $2340\,cm^{-1}$ and, in Fig. 3, increase in intensity with time due to the rising levels of CO oxidation as the temperature rises. A corresponding decrease in the gas phase CO can also be seen in the R-branch at $2167\,cm^{-1}$, although the large linear adsorbed CO peak obscures the P-branch. The adjacent positive feature at $2229\,cm^{-1}$ is caused by the heating of the gas phase resulting in an increased population of higher rotational states [22]. The features between 1950 and $1710\,cm^{-1}$ are due to changes in the bridged CO band [23], and a strong negative peak due to the desorption of water is seen at $1630\,cm^{-1}$.

4. Discussion

Even at low conversion, the CO_2 production is a sensitive measure of the effective catalyst temperature as the conversion increases significantly with rising temperature. In studies of microwave heating of heterogeneous systems, accurate and meaningful measurement of temperature is always an issue [17]. Here, the similarity of the gradient of each individual segment representing CO_2 production under microwave heating, shown in Fig. 2, to the corresponding section of the conventionally heated conversion curve suggest that the thermocouple accurately represents the effective temperature of the bulk catalyst. Furthermore, the increased CO_2 production in all the individual microwave experiments appears merely that to be expected from the equivalent temperature ramp from conventional heating. This suggests that for the EUROPT-1 catalyst, microwave heating is homogeneous or, if heterogeneous with the metal particle experiencing disproportionate heating compared with the support, then the rate of dissipation of heat to the support is sufficiently rapid that the bulk temperature measured is an accurate representation of the temperature of the active site for the catalytic reaction.

In the infrared spectra shown in Figs. 3 and 4, the behaviour of the adsorbed CO features will relate the temperature of the catalyst metal particles while the band from the desorption of water will be principally associated with the SiO_2 support making up the bulk of the catalyst. The extract at 90 s shown in Fig. 4a shows the consequence of the 15 K rise in temperature from the initial temperature of 367 K under microwave heating. Fig. 4b is the corresponding spectrum produced by the ratio of spectra recorded at 367 and 384 K under purely conventional heating. Like the effect of conventional and microwave heating on conversion shown in Fig. 2, there is again close correspondence between the changes apparent as a consequence of the microwave heating and those observed from the equivalent temperature rise produced by conventional heating. Only in the region around $2100\,cm^{-1}$ do the curves differ significantly and this may be attributed to the low photometric accuracy of the experiment at this point due to the near extinction of the linear CO feature.

These results appear to agree well with the earlier studies of CO oxidation over Pt/γ-alumina [17] where the rate of reaction was found to be comparable under both conventional and microwave heating and, in particular, that the metal crystallites were not significantly hotter than the support in a microwave heated reactor. Modelling of the maximum potential time dependant temperature difference that could be sustained between the support and the metal particles under reaction conditions similar to those employed here [18,24] also suggests that any temperature difference would be insignificant principally due to the rate of heat loss to the gas-phase. Nonetheless, instances of high differential metal/support temperatures and sufficient surface heating to cause irreversible modification of catalytic activity due to surface melting do appear well founded [25,26] and will be of interest to study by the methods employed here.

5. Conclusions

The rate of CO_2 production over the EUROPT-1 catalyst and the nature of the species absorbed on the catalyst surface in the temperature range 300–400 K appears unaffected by the method of heating used in as much as the increase in rate and change in surface composition noted when microwave heating is applied at a given temperature can be replicated by the equivalent temperature rise induced by conventional means. While reports of increased activity under microwave heating for other catalytic systems continue to require further explanation, there appears to be no enhancement for the CO oxidation reaction over platinum.

Acknowledgements

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