

Rate oscillations during partial oxidation of methane over chromel–alumel thermocouples

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A chromel–alumel thermocouple has been found to catalyse the methane/oxygen reaction, the main products being CO, H₂ with some CO₂ and H₂O. Regular oscillations in both reactants, products and temperature have been observed at temperatures around 700 °C. Similar behaviour has been obtained using nickel wires.

KEY WORDS: methane partial oxidation; oscillation; chromel–alumel thermocouple

1. Introduction

The partial oxidation of methane to produce CO and H₂ has received much attention in recent years [1–21], mainly because of its potential use as a commercial source of syn-gas. The dominant industrial process currently in use is the steam reforming of methane, which suffers from high energy requirements, a higher H₂/CO ratio than is required and poor selectivity for CO [22,23].

The complexity of the reaction pathways involved in the partial oxidation of methane can result in oscillatory kinetics under certain circumstances. Such oscillations have been observed over palladium catalysts [24–27], and supported nickel catalysts [11,28,29]. There has also been a recent report [30] of oscillations occurring over an Nd₂O₃/MgO catalyst containing an exposed chromel–alumel thermocouple.

In this paper we report the observation of oscillatory reaction kinetics when a methane/oxygen mixture was passed over a chromel–alumel thermocouple. Contrary to the results of Tyulenin et al. [30], the thermocouple was active when no other catalyst was present. The oscillations were observed in the reactant and product concentrations as well as in the temperature, and are thought to be caused by the cyclic oxidation and reduction of nickel. Similar results have also been obtained with a nickel wire. These results have important implications for catalytic studies that use a chromel–alumel thermocouple for temperature measurement.

2. Experimental

The catalytic reaction was carried out under atmospheric pressure by flowing an argon/methane/oxygen mixture over

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a thermocouple, or nickel wire, mounted centrally along a 10 mm i.d. quartz tube. The reactor was heated by a tubular furnace and oscillations were generally observed at temperatures between 650 and 730 °C. The gas composition after reaction was determined with a 16-channel quadrupole mass spectrometer (QMS-200D, European Spectrometry Systems), which was connected to the high pressure part of the system by a set of differentially pumped needle valves. The mass spectrometry data, together with the thermocouple readings, were recorded by a real-time, computerized data acquisition system. To prevent condensation of water vapour the needle valves and connecting tubulations were heated to about 200 °C. Mass flow controllers (ASM model AFC-260) were used to mix the feed gases in known proportions prior to reaction. The gas flows used were 30, 29.5 and 0.5 ml min^{−1} for Ar, CH₄ and O₂, respectively.

The thermocouple was made by spot-welding together 0.5 mm diameter chromel and alumel wires, obtained from Goodfellow. The compositions of the chromel and alumel wires were 90% Ni: 10% Cr and 95% Ni: 5% (Al + Mn + Si), respectively. Nickel wire (diameter, 0.25 mm) was purchased from Johnson Matthey. In some experiments the thermocouple was exposed to the reactants and in others it was sheathed by a quartz capillary tube with a chromel–alumel or nickel coil wrapped round it, as shown in figure 1.

3. Results

3.1. Observation of the oscillatory phenomena

Oscillations in the rate of reaction of methane with oxygen were first observed over a chromel–alumel thermocouple which was inserted into an empty quartz reactor. As the temperature was slowly increased from room temperature to 1000 °C there was a high rate of reaction, producing mainly CO and H₂, but no oscillations were observed until the furnace was switched off. Oscillations then appeared in both

products and reactants as the temperature dropped from 800 to 700 °C. These are illustrated in figure 2, where it can be seen that peaks in the CO and H₂ signals correspond to minima in the CH₄ and O₂ signals. This demonstrates that an oscillatory reaction is occurring, involving the partial oxidation of methane to CO and H₂. Oscillations were also observed in the temperature recorded by the thermocouple.

The reaction was then carried out under identical conditions to those just described except that the thermocouple was sheathed by a small quartz tube to prevent it from being exposed to the reactant gases. Under these conditions no oscillations were observed, proving that the chromel–alumel thermocouple material was responsible for catalyzing the reaction in the previous experiments.

3.2. Oscillations over bare thermocouples

In a further set of experiments a bare chromel–alumel thermocouple was inserted into the empty quartz reactor and the reactor temperature was kept at 700 °C. Figure 3 shows

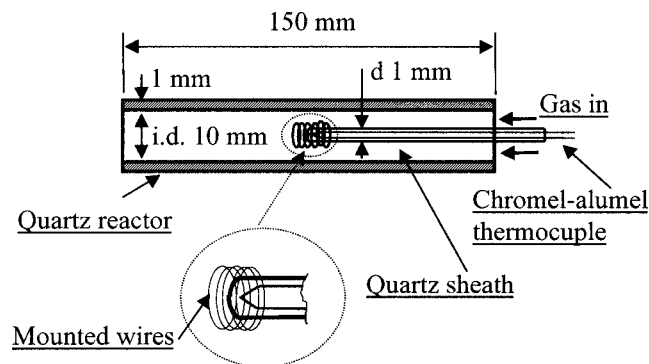


Figure 1. Chromel–alumel coils or a nickel coil mounted on the tip of the thermocouple sheath.

the oscillations in reactant and product signals obtained by monitoring the quadrupole signal for selected ions as a function of time. The temperature oscillations are also shown at the top of the diagram.

The oscillations started a few minutes after the temperature first reached 700 °C. As before, it was found that the products (in this case H₂, CO and CO₂) were in phase with one another while the reactants (CH₄ and O₂) were out of phase, having minima that coincided with product maxima. The period of the oscillations for both product and reactant signals was about 1.5 min. The profile of the CO₂ peak was different from the others, consisting of a single sharp spike, whereas the CO and H₂ peaks appeared to have two components, a sharp spike followed by a shoulder.

The temperature oscillated at the same frequency but showed a complex structure. At the start of a pulse there was a very rapid rise and fall in temperature which was over in about 1 s and was too fast to be recorded digitally because the scan time between recordings was of the order of 1 s. However, this temperature peak can be clearly seen on the analogue recorder trace shown in figure 4. After a rapid rise and fall, the temperature climbed up to a maximum value of 707 °C before declining to the level at which the oscillations started. The temperature was 700 °C when the oscillations started and it was found to return to the same level when the reaction was stopped.

3.3. Oscillations over chromel and alumel wires

There was always the possibility that the temperature oscillations that had been measured were affected by chemical reaction occurring at the thermocouple junction. To eliminate such an effect, the thermocouple was sheathed in a quartz capillary tube with one end closed, and a pair of chromel–alumel wires (each 10 cm long and 0.5 mm in di-

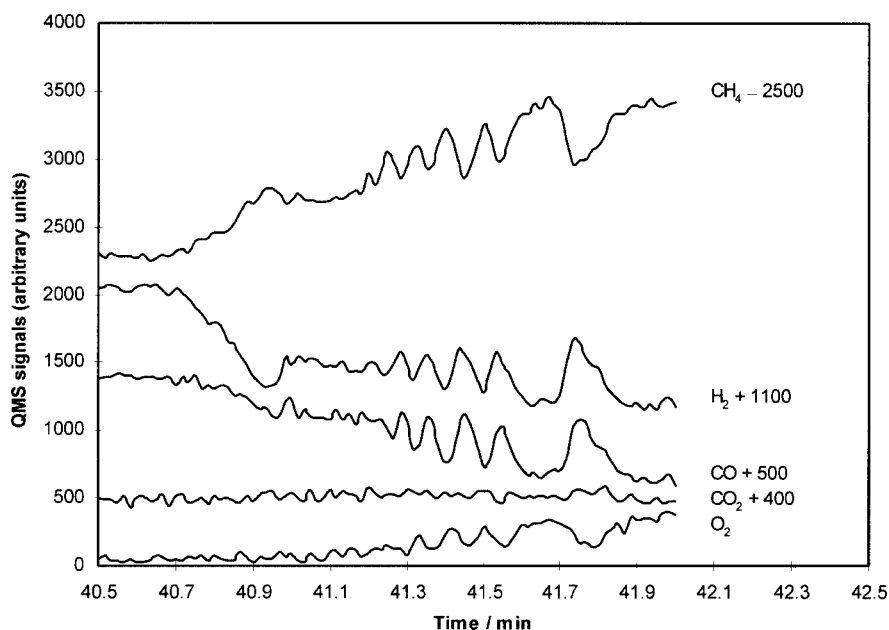


Figure 2. Oscillations observed with an Ar/CH₄/O₂ (30 : 29.5 : 0.5 ml min⁻¹) mixture as the temperature falls.

ameter) were coiled around the tip of the sheath to act as the catalyst, as shown in figure 1. Oscillations in reactants, products and temperature were observed, and are illustrated in figure 5.

It is noteworthy that the shoulders on the CO and H₂ peaks are more pronounced than they were when using the bare thermocouple, while the CO₂ peaks remain sharp. The period of the oscillations was about 1.8 min, which was sig-

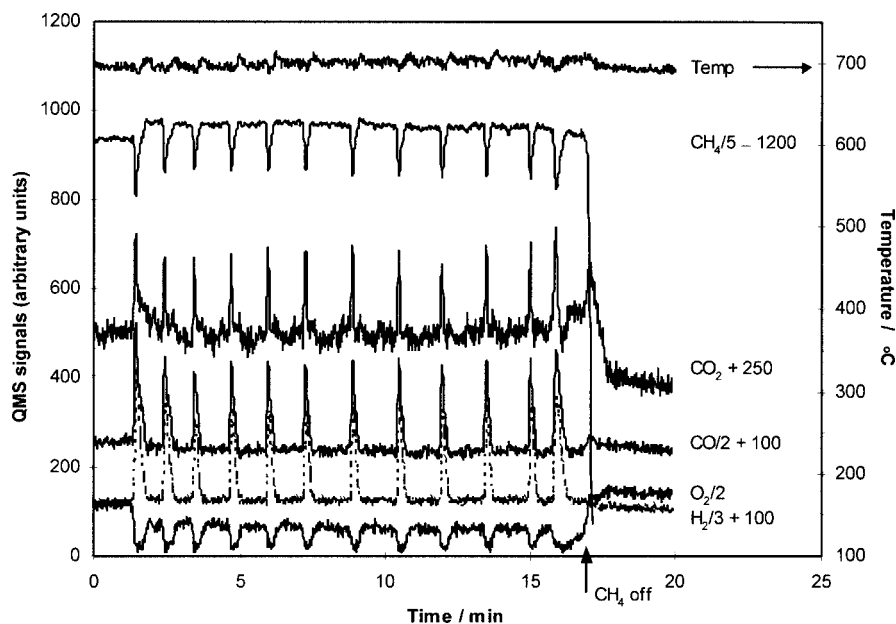


Figure 3. Oscillations observed over a bare chromel–alumel thermocouple. (Ar : CH₄ : O₂ = 20 : 29.5 : 0.5 ml min⁻¹, system temperature 700 °C.)

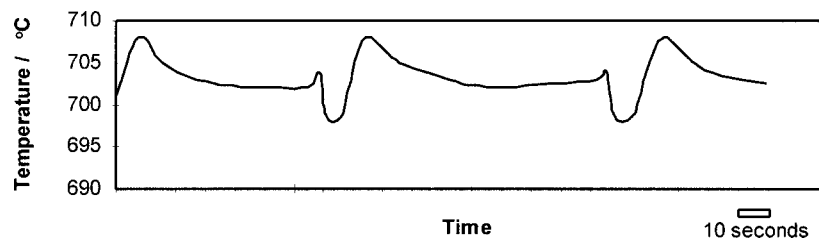


Figure 4. Two cycles of the temperature oscillation occurring over the bare chromel–alumel thermocouple.

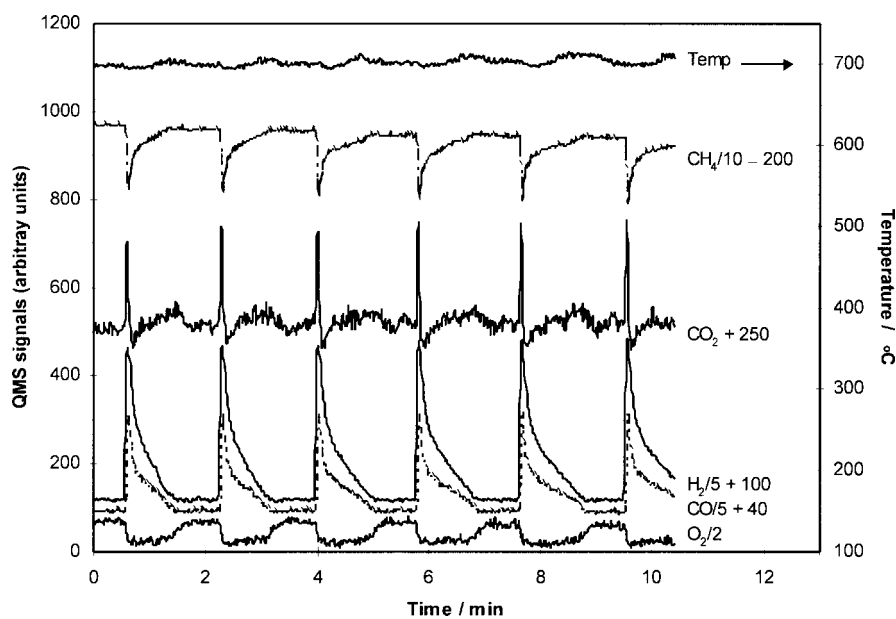


Figure 5. Oscillations observed over chromel and alumel wires. (Wires, 10 cm long each in 0.5 mm diameter; Ar : CH₄ : O₂ = 30 : 29.5 : 0.5 ml min⁻¹, system temperatures 702 °C.)

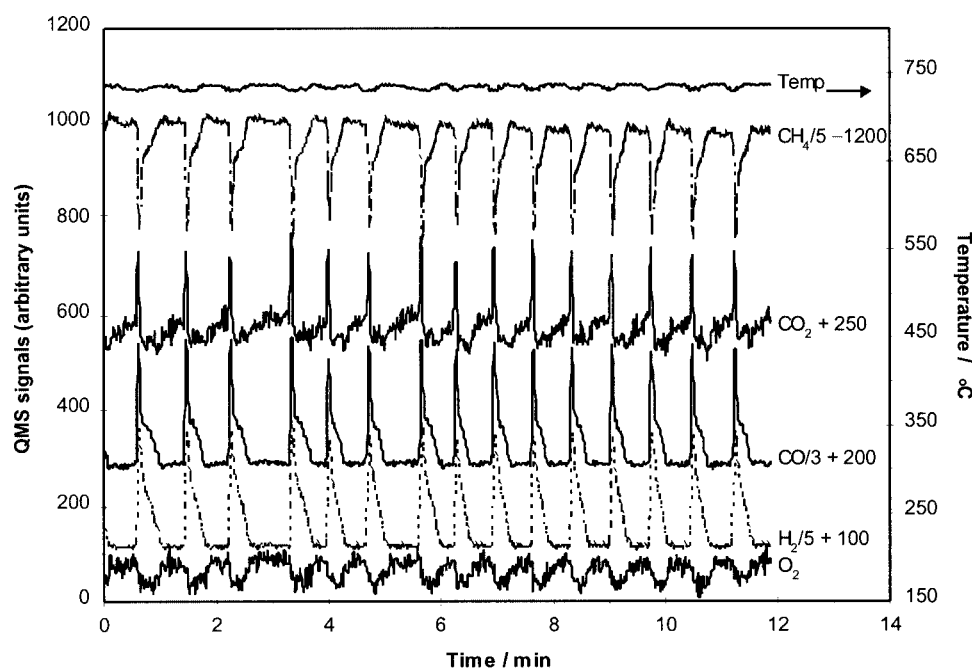


Figure 6. Oscillations observed over a nickel wire. (Ni wire, 20 cm long, 0.25 mm diameter; Ar : CH₄ : O₂ = 30 : 29.5 : 0.5 ml min⁻¹, system temperatures 730 °C.)

nificantly longer than that in the bare thermocouple run. The amplitude of the temperature oscillations was reduced from about 11 degrees to only 6–7 degrees and the peaks were much flatter, probably due to the heat capacity of the quartz sheath. The oscillations started at 710 °C. When one of the reactants was switched off to stop the reaction, the gas temperature returned to 702 °C.

3.4. Oscillations over nickel wires

When a length of nickel wire (20 cm long and 0.25 mm in diameter) was mounted on the tip of the quartz sheath in place of the chromel–alumel thermocouple wires, oscillations occurred under comparable conditions to those used in the runs already discussed. The results are shown in figure 6. The oscillations were observed between 734 and 740 °C and the oscillation period was 0.75 min. When the reaction was stopped the temperature fell to 730 °C.

4. Discussion

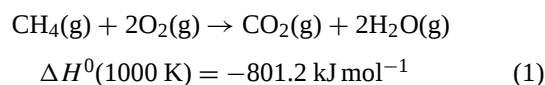
4.1. Comparison with previous work

Tyulenin et al. [30] have also observed oscillatory behaviour in the kinetics of methane oxidation over a chromel–alumel thermocouple but our results differ from their results in two important respects. First, Tyulenin et al. found the thermocouple to be active only in the presence of a Nd₂O₃/MgO mixed oxide catalyst. When this was absent the thermocouple showed zero activity. Secondly, the maximum production of CO and H₂ corresponded with a temperature rise in their experiments whereas it coincides with a temperature drop in our work. We can offer no explanation

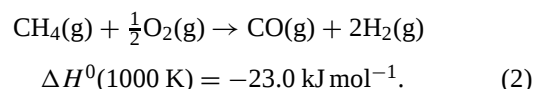
for these differences, but it should be noted that a drop in temperature, similar to that found in this work, has been observed by Hu and Ruckenstein [11] in oscillations observed during the partial oxidation of methane over a NiO/SiO₂ catalyst.

4.2. Exothermic and endothermic reactions

The main products formed during the gas pulses were CO₂, CO and H₂. Some H₂O was also formed but the response of the mass spectrometer to water vapour was rather sluggish and the data are not shown. The basic reactions that might produce these products are

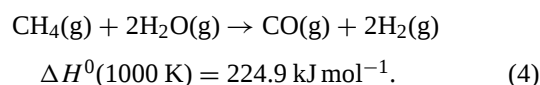
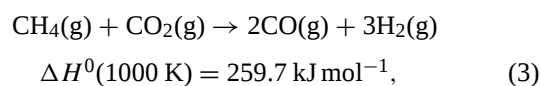


and



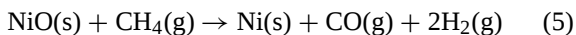
However, both of these reactions are exothermic and they cannot explain the drop in temperature that is observed during each pulse.

Alternative reactions producing CO and H₂ are the reforming reactions:



Although these are both endothermic, they cannot explain the temperature drop because they are secondary reactions which rely on the highly exothermic production of CO₂ and H₂O before they can occur.

To obtain an endothermic reaction it is necessary for at least some of the oxygen to be provided by a surface oxide. Bulk NiO has a heat of formation at 298 K of $-239.7 \text{ kJ mol}^{-1}$ and the participation of this oxide in reaction (2) would be more than sufficient to make the overall process endothermic. The reaction would then become



Using a value of $-149.5 \text{ kJ mol}^{-1}$ for the free energy of formation of nickel oxide at 1000 K, calculated from a formula given by Gurvich et al. [31], the free energy of reaction (5) is calculated to be $-70.2 \text{ kJ mol}^{-1}$ at 1000 K, so that equilibrium will still favour the gaseous products.

It follows from this discussion that much of the oxygen required to form the CO and CO₂ that appears in the peaks must come from reduction of nickel oxide. This is confirmed by a quantitative analysis of the rapid changes in the O₂, CO and CO₂ signals at the start of each pulse, which shows that the drop in the O₂ signal accounts for less than one third of the oxygen required to form the sharp CO and CO₂ peaks.

4.3. Analysis of the temperature profile

On this basis it is possible to give a reasonably detailed explanation of the three stages of reaction observed in the temperature profile shown in figure 4.

- (i) Each pulse starts with a rapid rise in temperature of about 1.5–2 °C, which coincides with very sharp CO, H₂ and CO₂ peaks. At this stage it is postulated that small crystallites of Ni begin to form as the NiO is reduced. Methane can dissociatively adsorb on these Ni sites to give carbon and hydrogen adatoms. The carbon adatoms then react with neighbouring oxide to produce a mixture of CO and CO₂. The hydrogen adatoms can either desorb as H₂ or react with oxide to form H₂O. The production of CO₂ and H₂O is highly exothermic and this is sufficient to cause a rise in temperature.
- (ii) The first stage is followed by a sharp drop in temperature of about 6 °C, which corresponds to shoulders on the CO and H₂ peaks. This is thought to occur because, as the size of the Ni islands increases, there is less oxide for the carbon atoms to react with and production of CO₂ ceases. The overall process is now represented by equation (5), which is endothermic, and the temperature begins to fall.
- (iii) Finally, there is a substantial rise in temperature of about 10 °C, which occurs just before the CO and H₂ signals return to their base lines. This must correspond to the slow re-oxidation of the nickel, although the reason why this occurs is not clear. The rate of production

of CO and H₂ over the reduced nickel surface slowly falls as the surface becomes re-oxidised and then the redox cycle starts all over again.

It should be noted that this model can work only if the oxide layer that begins to form on the reduced nickel surface is initially unreactive to carbon and hydrogen atoms, thus allowing the oxide layer to build up. At some critical stage this layer has to undergo a transformation which makes it much more reactive, thus initiating the reduction process. One possibility is that a strained epitaxial layer of nickel oxide is formed on the surface initially, which is relatively unreactive because there are no reduced nickel sites at which methane can adsorb. At some point during the build-up of such an epitaxial oxide layer a critical thickness would be reached at which the bond between the oxide and the metal surface would be broken and bulk nickel oxide would be formed. This process might well expose metal sites at which methane adsorption could take place.

5. Summary and conclusions

- (a) We have demonstrated that chromel and alumel wires can act as effective catalysts for the methane/oxygen reaction. The reaction is found to be oscillatory at temperatures between 700 and 740 °C, the main products being CO and H₂, although some CO₂ and H₂O is also produced. Thus, precautions should be taken when chromel–alumel thermocouples are used for temperature measurements, particularly when bare chromel–alumel thermocouples are inserted into catalyst beds in reaction systems where methane and oxygen are present.
- (b) Nickel was found to give similar results to those obtained with chromel and alumel wires and is thus likely to be the active ingredient.
- (c) The drop in temperature that occurs during a gas pulse is evidence that an endothermic reaction is occurring. The only reaction that meets this requirement is the reduction of nickel oxide by methane to produce CO and H₂. This process is followed by a rise in temperature, which is interpreted as the onset of re-oxidation of the metal, thus completing the redox cycle.

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