Further studies on oscillations over nickel wires during the partial oxidation of methane

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Oscillatory reactions over nickel wires during the partial oxidation of methane were investigated in a tubular continuous flow reactor made of quartz at atmospheric pressure. A modified thermocouple was designed to measure the temperature while the interposed nickel coil worked as a catalyst. Significant effects on the oscillations were observed by varying the system temperature and the feed gas composition, and by cutting off one of the reactant gases temporarily.

KEY WORDS: methane partial oxidation; oscillations; nickel wires.

1. Introduction

The partial oxidation of methane under catalytic conditions has received increasing attention recently, mainly because of its potential use as a commercial source of syngas [1–5], while the steam reforming of methane, which is the dominant industrial process currently in use, suffers from high energy requirements, a higher H_2/CO ratio than is required and poor selectivity for CO product [6,7]. The complexity of the reaction pathways involved in the catalytic partial oxidation of methane can result in oscillatory kinetics under certain circumstances. Such oscillations have been observed over palladium catalysts [8–11] and supported nickel catalysts [12–14]. There has also been a report [15] of oscillations occurring over an Nd_2O_3/MgO catalyst containing an exposed chromel–alumel thermocouple. However, the oscillatory mechanism is still not understood in detail, although it is generally accepted that the cyclic oxidation/reduction process is responsible for the oscillation [13,14].

Our previous study showed that chromel–alumel thermocouples, when no other catalyst was present, can act as effective catalysts for the methane/oxygen reaction oscillating at temperatures between 700 and 740 °C, where nickel was found to be the active ingredient [16]. In this paper we report further investigations into the oscillatory reaction kinetics over nickel wires during the partial oxidation of methane. A modified thermocouple was designed to measure the temperature while the interposed nickel coil worked as a catalyst. The oscillations were studied in detail over wide ranges of parameters in terms of reactant and product concentrations and reactor temperatures. By varying the reaction conditions, the regime of oscillatory behavior was revealed.

2. Experimental

The catalytic reaction was carried out under atmospheric pressure by flowing an argon/methane/oxygen mixture over a nickel wire coil, located centrally in a 10 mm i.d. quartz tubular reactor that was heated in a tubular furnace [16]. The effluent gas from the reactor outlet after reaction was analyzed with a 16-channel quadrupole mass spectrometer (QMS-200D, European Spectrometry Systems), which was connected to the atmospheric pressure part of the system via a set of differentially pumped needle valves. The mass spectrometric data, together with the thermocouple measurements, were logged by a real-time, computerized data acquisition system (Sensorlab V.5, Fisons Instruments, Vacuum Generators Quadrupoles). To prevent condensation of water vapor product, the needle valves and connecting tubulations were heated to about 200 °C. Mass flow controllers (ASM Model AFC-260) were used to control the flow rates of the feed gases in known proportions prior to reaction. The flow rates of the argon/methane/oxygen mixtures were in a range from $30:29:1$ to $30:22.5:7.5\,\mathrm{cm^3\,min^{-1}}$.

A modified thermocouple was designed and made in the laboratory for the experiment, based on the law of intermediate metals for thermocouples [17]; if one or both of the junctions of a thermocouple are opened, and one or more metals are interposed, the resultant electromotive force (e.m.f.) is not altered provided that

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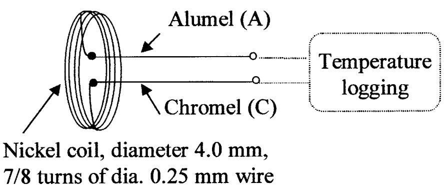

Figure 1. Modified thermocouple with a nickel coil catalyst.

all the new junctions are at the same temperature as the original junction between which they are positioned. This modified thermocouple, shown in figure 1, was used to measure the reaction temperature while the nickel coil worked as a catalyst. The reactor tube temperature without reaction inside was measured by means of stopping one of the reactant gases while keeping the power supplied to the furnace unchanged.

Methane (purity 99.0%) and oxygen (purity 99.6%) were purchased from Aldrich Chemicals. Argon (purity 99.9%) was supplied by BOC Gas. The nickel wire (diameter, 0.25 mm, 99.98% Ni) was purchased from Johnson Matthey. It was spot-welded with 0.5 mm diameter chromel and alumel wires separately. The compositions of the chromel and alumel wires, obtained from Goodfellow without further treatment before use, were 90% Ni/10% Cr and 95% Ni/5% (Al + Mn + Si), respectively.

3. Results

3.1. Oscillatory behavior over a nickel filament

Using the modified thermocouple with a nickel filament interposed (shown in figure 1), oscillations in reactant and product concentrations coupled with temperature oscillations were observed. With the feed gas controlled at an $Ar/CH_4/O_2$ flow ratio of $30:22.5:7.5\,cm^3\,min^{-1}$, the reaction producing CO_2 and H_2O was first observed when the temperature reached 800 °C. In general, after the oxidation reaction started, it was observed that an induction period of 2 min was required before oscillations commenced. This induction period was found to be dependent on the temperature and as the temperature was increased, the induction period decreased. Subsequently, stable and repeatable oscillations became established 5–10 min after the induction period was seen.

Figure 2 shows four complete oscillation cycles in superimposed form, clearly showing the shape of the reactants, products and temperature peaks. The reactants, methane and oxygen, were observed to be in-phase with each other. The products, CO_2, CO and H_2, were also in-phase with one another, whilst being out-of-phase with the reactants. The minimum temperatures were seen always to coincide with the highest concentrations of the reactants and the lowest yields of the products. The period of oscillations for all product and reactant concentrations and for temperature was the same at about 31 s.

3.2. Effect of temperature on oscillations

Keeping the input flow rates of reactants at a constant ratio of $Ar/CH_4/O_2 = 30:22.5:7.5\,cm^3\,min^{-1}$, the temperature of the system was raised step by step and then decreased in steps to investigate the effects of temperature on the oscillations. Changes in the waveforms, frequencies and amplitudes of the oscillations in the reactants, products and temperature, and also in the product distribution, were observed when the temperature was altered. The results are depicted in figure 3.

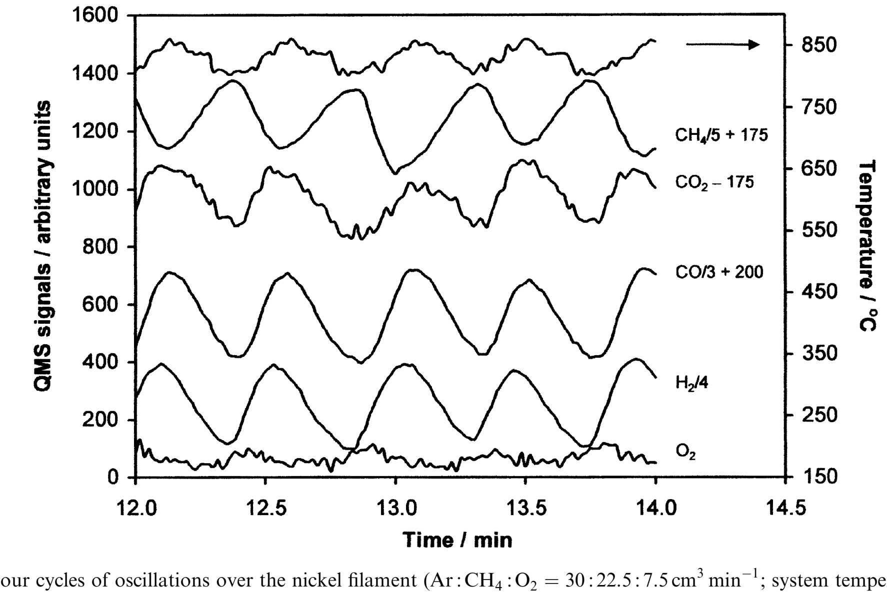

Figure 2. Four cycles of oscillations over the nickel filament ($Ar:CH_4:O_2 = 30:22.5:7.5\,cm^3\,min^{-1}$; system temperature 800 °C).

As the temperature was increased, in general, the frequency of temperature oscillations tended to increase

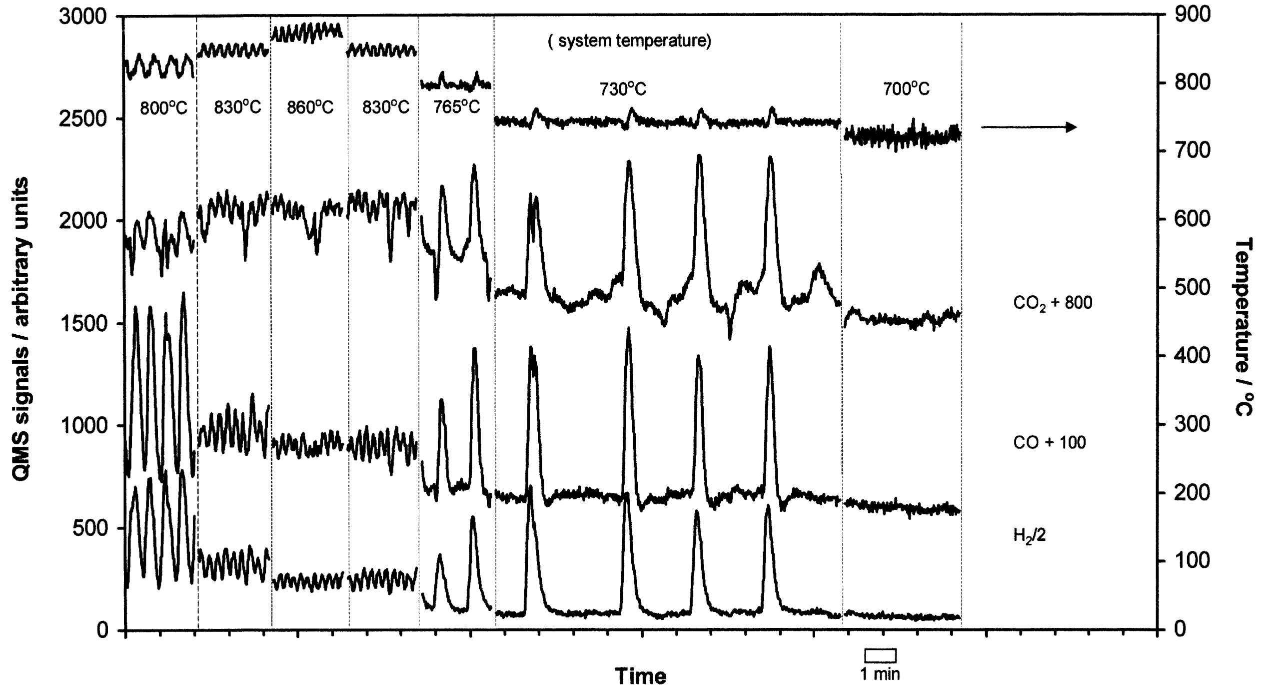

Figure 3. Oscillations over a nickel filament at different temperatures ($Ar:CH_4:O_2 = 30:22.5:7.5\,cm^3\,min^{-1}$; system temperature ranging from 700 to 860 °C).

whilst the amplitude of the oscillations tended to decrease. It was also observed that both CO_2 and CO levels were increased when the temperature was raised. This could be explained by the increase in reaction rates with increasing temperature. However, the CO reaction was more favored than the CO_2 reaction at higher temperatures, which could result in the higher CO/CO_2 ratio observed at the higher temperature.

A hysteresis phenomenon was also observed when the temperature was increased and then decreased. As the temperature was increased the oscillations started only above 800 °C, but small oscillations could still be observed even when the temperature was reduced to 690 °C. This result indicated that changes were occurring on the catalyst surface. Salomonsson *et al.* [18] also observed hysteresis in catalyst activity when the temperature was cycled up and down during oxidation over PdO_x. The hysteresis was connected with oxygen content and it was attributed to changes in properties of the O_2–Pd–PdO_x system.

3.3. *Effect of oxygen concentrations on oscillations*

Figure 4 shows the effect of varying oxygen concentrations on the waveforms, frequencies and amplitudes of oscillations, and the product distribution. It can be seen that, in general, the frequencies of oscillations tended to decrease whereas the amplitudes of the oscillations tended to increase when the oxygen concentration in the feed gas was increased. For example, when the O_2/CH_4 ratio was increased from 1:29 to 1:3, the period of the oscillations changed from 80 to 96 s and the CO_2 peaks became about three times larger whereas the amplitudes of the CO and H_2 peaks remained almost constant.

The changes in product selectivities were probably due to a change from oxygen-deficient to oxygen-rich conditions on the catalyst surface. This strong effect of feed ratios (O_2/CH_4) on the product selectivity was also observed by Trimm and Lam [19] and Mouaddib *et al.* [20] in the reaction of the oxidation of CH_4 to CO_2.

It was notable that the waveforms changed with the O_2/CH_4 ratio. This was especially marked for the temperature profile, as shown in figure 5. As can be seen, when the O_2/CH_4 ratio was kept at the lower value (1:29), significant decreases in temperature were observed just as the product peaks of CO_2, CO and H_2 appeared. Between peaks there was a general rise in CO_2 concentration and a gradual fall in CO concentration while the temperature increased slightly. In contrast, when the O_2/CH_4 ratio was higher (*e.g.*, 1:3), temperature rises were observed which corresponded with the product peaks. It was observed that this change in the temperature profile responded to the change in the product selectivity. With increasing O_2/CH_4 ratio, the ratio of CO_2 to CO increased. Since CO_2 was produced from a highly exothermic reaction while CO was formed in a slightly exothermic reaction or an endothermic reaction, the change in the proportion of each reaction changed the overall reaction heat and, in turn, the temperature profile. Thus, a higher CO_2/CO ratio in the peaks resulted in a temperature rise whereas

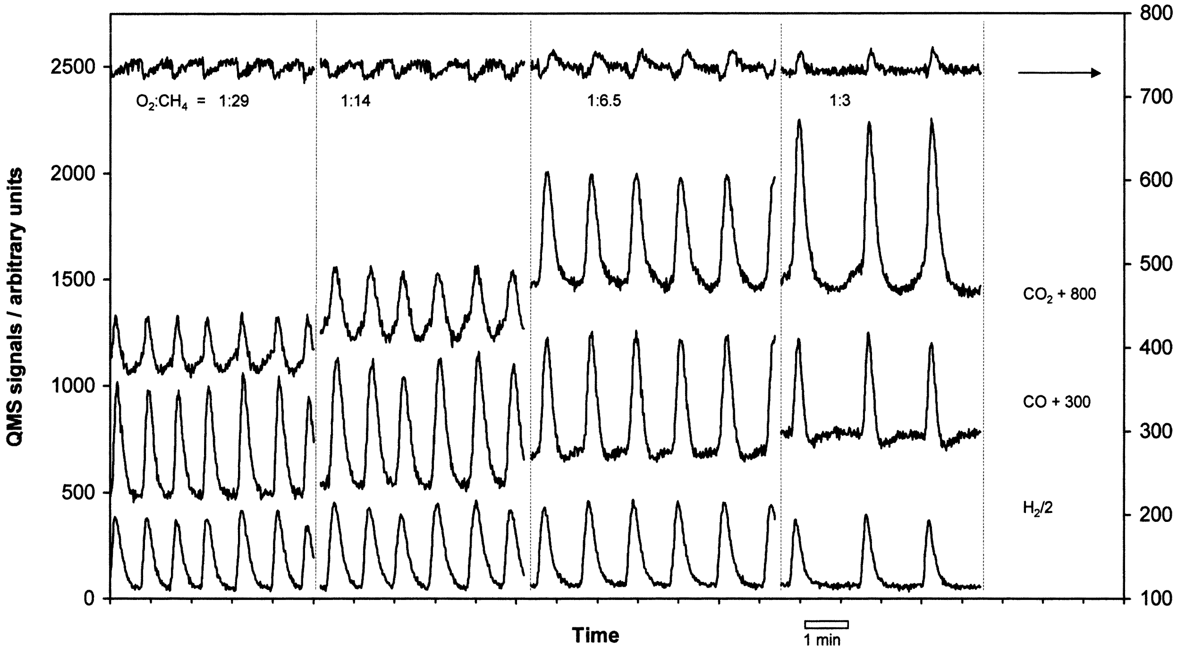

Figure 4. Oscillations over a nickel filament at different oxygen concentrations (system temperature 730 °C; Ar : CH_4 : O_2 ranging from 30 : 29 : 1 to 30 : 22.5 : 7.5 $cm^3\,min^{-1}$).

a higher CO/CO_2 ratio showed a temperature drop. This gave an indication of the difference in thermal dynamics between the reactions producing CO and CO_2.

3.4. *Effects of cutting off methane or oxygen gas supply temporarily*

In the following set of experiments, the supply of one of the reactant gases (methane or oxygen) was cut off temporarily for a few minutes while the other kept flowing and the system temperature remained unchanged. This operation led to the exposure of the catalyst in environments under extreme conditions, either oxygen-rich or methane-rich, in the gas phase at the elevated temperature level, and the possible reactions occurring on the catalyst surface. When the cut-off gas was restored, the changes on the surface could be revealed by the change in both gas-phase compositions and

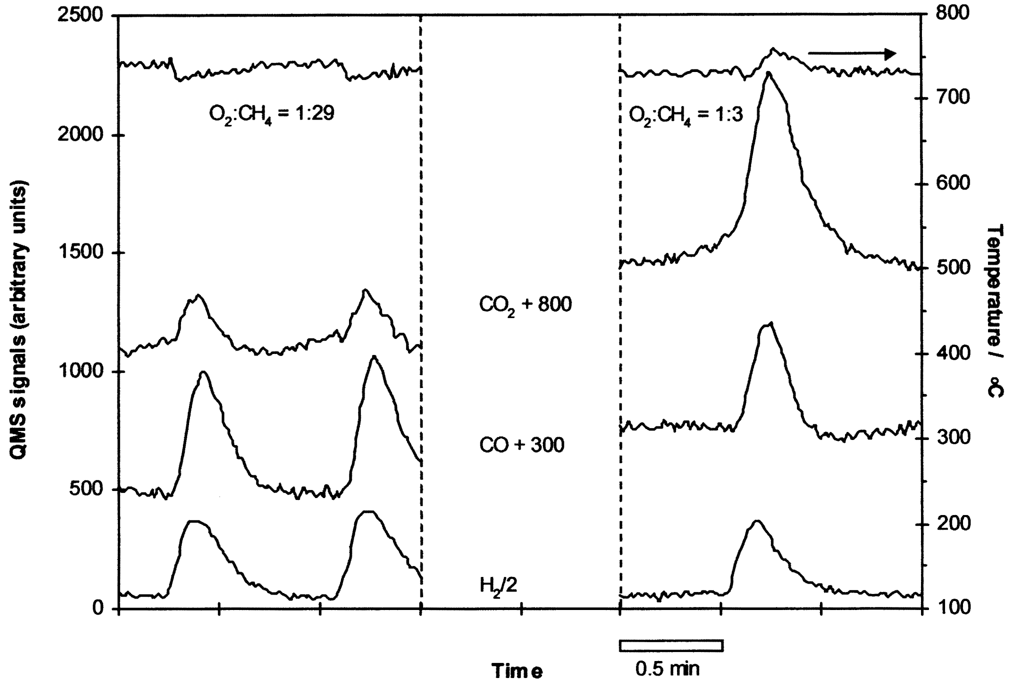

Figure 5. Changes in waveforms corresponding to the changes in the O_2 : CH_4 ratio (system temperature = 730 °C).

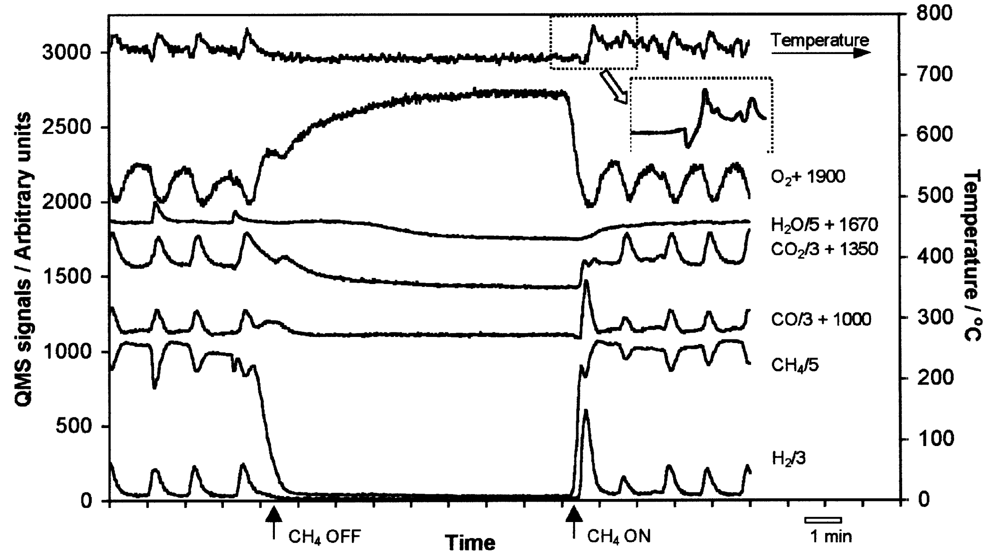

Figure 6. Oscillatory behavior over the nickel wire when the methane supply was switched off temporarily and on with gas mixture $Ar:CH_4:O_2 = 30:22.5:7.5$. The system temperature was 734 °C when the reaction was terminated.

temperatures, which could lead to new insights into the reaction mechanisms.

3.4.1. *Cutting methane supply off temporarily*

It was observed that, when the methane supply was cut off temporarily, the oscillation ceased. The oxygen signal gradually rose and there was a drop in the temperature of about 15 °C to a value found previously when no reaction occurred (see figure 6). When the methane supply was restored, there was an almost instantaneous evolution of CO and H_2, which gave very sharp peaks with a magnitude much greater than that obtained in the normal oscillations observed with a constant gas flux. The CO_2 and H_2O signals also rose to a high level but showed no significant peaks at this stage. This was accompanied by a fall in the temperature measured and in the methane signal when the reaction was occurring. The overall process must therefore be endothermic. This large jump in the CO signal was indicative that the oxygen was from the catalyst surface, because the drop in the oxygen signal at this stage was similar to the following oscillation cycles where the CO peaks were much lower. The oxygen from the surface was probably in the form of an oxide layer that was formed during the oxygen-rich period, but being reduced to the metal at this stage. In this case, the oxide layer must be fairly thick to be able to produce such a large quantity of CO and CO_2. It appeared that the overall process at this stage must be endothermic since a significant temperature drop was observed with the large peaks of CO and H_2 appearing (seen in the enlarged temperature profile in figure 6).

Following the first stage producing sharp peaks of CO and H_2, the system gradually settled down to exhibit regular oscillations which were similar to those before methane was switched off temporarily.

3.4.2. *Cutting oxygen supply off temporarily*

When the oxygen supply was cut off, there appeared a final oscillation with larger CO and H_2 peaks than usual and a smaller CO_2 peak. All oscillations ceased after this. The results seemed to indicate that the oxygen was competing with methane for adsorption sites and that excess oxygen could have an inhibitory effect on the partial oxidation of methane.

Figure 7 illustrates the results obtained when the oxygen supply was restored over a nickel filament with a 3:1 methane/oxygen gas mixture. An increase in oxygen signal accompanied by a decrease in methane signal was observed. These reactant changes were accompanied by the surge of a CO peak, intense CO_2 and H_2O increase, and a large rise in the reaction temperature. More significantly, hardly any change in H_2 signals was observed, showing that the oxidation of methane was not responsible for the CO and CO_2 increases. The process occurring was believed to be the oxidation of carbon, deposited on the catalyst surface during the period when only methane was present in the gas phase. The large drop in the methane signal can be explained in terms of the displacement of methane in the flow line by the sudden surge of oxygen and the large increase in products, and does not necessarily mean that methane is consumed during the reaction.

Following this process, there was a period of about 2 min when oxidation of the nickel surface appeared to be occurring. Evidence for this conclusion comes from the low oxygen signal detected, which should be higher if there was no reaction occurring. During this period, the CO_2 and H_2O signals were rising, and this could be an indication that full oxidation of methane to CO_2 and H_2O was beginning to occur over the oxide surface.

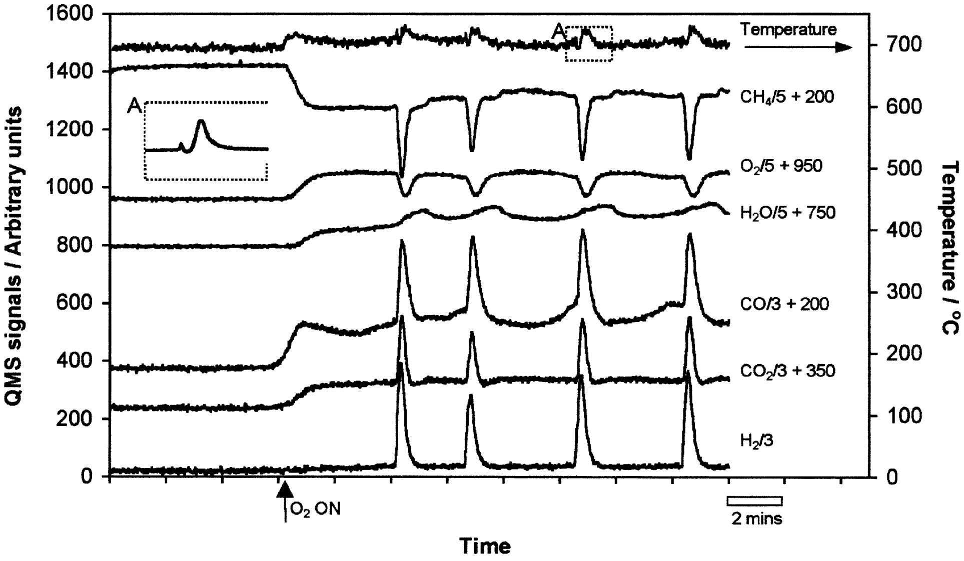

Figure 7. Oscillatory behavior over the nickel wire when the oxygen supply was switched off temporarily and on with gas mixture $Ar:CH_4:O_2 = 30:22.5:7.5$. The system temperature was 695 °C when the reaction was terminated.

After this stage, there was a gradual increase in only the CO signal and decrease in the O_2 signal, corresponding to a temperature drop of 8 °C, followed by a sudden evolution of CO, CO_2, H_2 and H_2O, which was accompanied by a 39 °C peak in temperature. On the basis of the previous discussion, this must be an indication that the oxidized surface had been reduced to the metal. It can also be deduced from the CO, CO_2 and temperature peaks that this reduction reaction occurred in two stages. It is not clear what process "triggered" the reduction; it could be that the oxide layer had reached a limiting thickness above which spontaneous recrystallization occurred, or that the reduction was initiated by the formation of metal nuclei above a certain critical size. A similar phenomenon was also observed with palladium catalyst where, after methane was introduced, an induction period was seen before any CO_2 and H_2O were formed. This has been attributed to the formation of metallic nuclei of palladium [21].

4. Discussion

4.1. Chemical reactions involved

In a previous paper [16] we presented the oscillatory behavior of methane partial oxidation over chromel–alumel thermocouples and nickel wires. The results led us to suggest that the oscillation arose because of chemical changes on the metallic surface and the temperature only followed the changes in the thermodynamic system.

Under the oscillation conditions investigated, the main products formed, when the peaks appeared, were CO_2, CO and H_2, and some H_2O was also formed. The basic reactions that might produce these products are as follows:

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$$

$$\Delta H^\circ\,(1000\,K) = -801.2\,kJ\,mol^{-1} \quad (1)$$

and

$$CH_4(g) + \tfrac{1}{2}O_2(g) \longrightarrow CO(g) + 2H_2(g)$$

$$\Delta H^\circ\,(1000\,K) = -23.0\,kJ\,mol^{-1}. \quad (2)$$

However, both of these reactions are exothermic and they cannot explain the drop in temperature that was observed in most of the cycles.

Alternative reactions producing CO and H_2 are the methane reforming reactions:

$$CH_4(g) + CO_2(g) \longrightarrow 2CO(g) + 3H_2(g)$$

$$\Delta H^\circ\,(1000\,K) = +259.7\,kJ\,mol^{-1} \quad (3)$$

$$CH_4(g) + 2H_2O(g) \longrightarrow CO(g) + 2H_2(g)$$

$$\Delta H^\circ\,(1000\,K) = +224.9\,kJ\,mol^{-1}. \quad (4)$$

Although these are both endothermic, they still cannot explain the temperature drop because they are secondary reactions that rely on the highly exothermic production of CO_2 and H_2O 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 $-239.7\,kJ\,mol^{-1}$ and the participation of this oxide in reaction (1) would be more than sufficient to make the overall process endothermic. The reaction would then become

$$NiO(s) + CH_4(g) \longrightarrow Ni(s) + CO(g) + 2H_2(g). \quad (5)$$

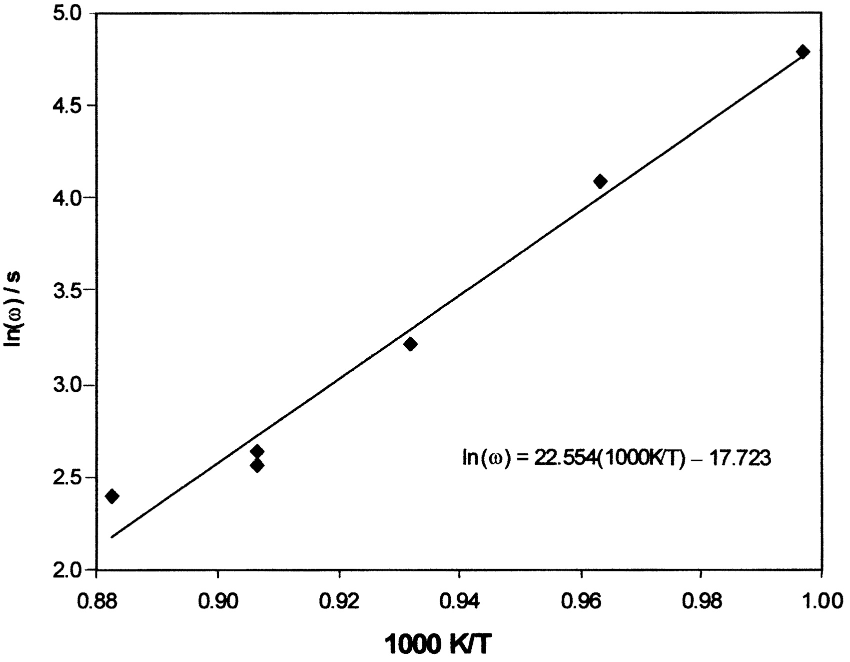

Figure 8. The relation of the oscillation period ω to the system temperature T for oscillations over the nickel filament.

Using a value of $-149.5\,\mathrm{kJ\,mol^{-1}}$ for the free energy of formation of nickel oxide at 1000 K, calculated from an equation given by Gurvich *et al.* [22], the free energy of reaction (5) is calculated to be $-70.2\,\mathrm{kJ\,mol^{-1}}$ at 1000 K, so that equilibrium will still favor the gaseous products.

It follows from this discussion that much of the oxygen required to form the CO and CO_2 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 O_2, CO and CO_2 signals at the start of each cycle, which shows that the drop in the O_2 signal accounts for less than one-third of the oxygen required to form the sharp CO and CO_2 peaks.

The drop in temperature indicated that there must be endothermic reactions occurring. The only reaction that meets this requirement is the reduction of nickel oxide by methane to produce CO and H_2. 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.

4.2. Activation energy

By varying the reaction temperature it was found that the frequencies and amplitudes of the oscillations in the reactants and products together with the product distribution were changed, seen in figure 3. It can be seen that the oscillation frequency increased when the system temperature was raised. This was indicative that the oscillation frequency could be a measure of the rate of the reaction which governed the overall oscillatory process. Figure 8 shows the relation of the oscillation period (ω) to the system temperature (T) according to the data shown in figure 3. It is interesting that the points of $\ln(\omega)$ *versus* $1000\,\mathrm{K}/T$ lie on a straight line, and the relation can be represented by the equations

$$\omega = \frac{1}{A_0}\,\mathrm{e}^{A/RT} \qquad (6)$$

and

$$f = A_0\,\mathrm{e}^{-A/RT} \qquad (7)$$

where f is the oscillation frequency, $f = 1/\omega$.

By comparison with the well-known Arrhenius equation, it can be seen that the oscillation frequency, f, represents the reaction rate during the oscillations, A_0 is the frequency factor and A the activation energy. For this oscillation system $A_0 = 4.98 \times 10^7\,\mathrm{s^{-1}}$ and $A = 187.5\,\mathrm{kJ\,mol^{-1}}$.

Studies on the reaction of nickel with oxygen have shown that the sticking coefficient of oxygen on Ni(100), Ni(111) and Ni(110) single crystal surfaces is close to unity at 300 K [23–28], whereas methane has an activation energy for adsorption of about $56\,\mathrm{kJ\,mol^{-1}}$ on Ni(111) and Ni(110) and $25\,\mathrm{kJ\,mol^{-1}}$ on Ni(100) [29–31]. Adsorption of methane on Ni(111) is believed to occur by a direct mechanism without passing through a precursor state [32]. Our surfaces are likely to include both (111) and (100) phases, and there may be some carbon covering the surface. Thus, our calculated activation energy result ($187.5\,\mathrm{kJ\,mol^{-1}}$) is different from the data reported.

4.3. The gas/solid interface

4.3.1. Estimation of reacting methane molecule number

The number of methane molecules reacting in a cycle can easily be estimated. If the volumetric flow rate of methane is $15\,\mathrm{cm}^3\,\mathrm{min}^{-1}$, for instance, the number of methane molecules flowing per minute is $15 \times 6.023 \times 10^{23}/22414 = 4 \times 10^{20}$. When the methane signal falls by an average of 4% for a period of 17 s, for instance, the number of methane molecules consumed during a pulse is approximately $4 \times 10^{20} \times 0.04 \times 17/60 = 4.5 \times 10^{18}$. This number of molecules is considerably greater than can be accommodated on the surface. The surface area of the wire cannot be more than a few cm^2 and a monolayer will contain approximately 10^{15} adatoms cm^{-2}. Thus the gas consumed is equivalent to more than 1000 monolayers. This also applies to the oxygen and shows that the oxygen must come from some form of oxide and not from an adsorbed layer.

This also explains why the overall reaction process was endothermic, as observed by the temperature drop that accompanied the rise in the gas peak. Reaction (2) is slightly exothermic whereas reaction (5) is endothermic. This oxygen must be regular lattice oxygen because of the large number of molecules involved. Although the oxygen found at defect sites is more reactive and is known to be involved in the adsorption of water and methanol on oxide surfaces, there is insufficient of this type of oxygen to explain the results.

Since each pulse of product peaks used up oxygen accumulated on the surface, this oxygen must be replenished during the interval between pulses, which was when the build-up of the oxide layer must occur.

4.3.2. Estimation of contact of oxygen with nickel surface

An interesting feature of the results was the way in which the oscillations varied with the methane/oxygen ratio. As this ratio was decreased from 29:1 to 3:1, as seen in figure 4, the frequency of the oscillations decreased by a factor of two and the size of the CO_2 signal doubled. On the other hand, the size of the CO and H_2 signals remained approximately constant. This result clearly showed the effect of varying oxygen pressure in the gas phase.

It was also noteworthy that in many experiments virtually all of the oxygen was consumed during the rise of a $CO + H_2$ peak. For a purely surface reaction this implied that every oxygen molecule had collided and reacted at the surface. This hardly seems possible for a small length of nickel wire in a tube of 10 mm diameter. An estimation of the possibility has been made, as follows.

The total gas pressure is 1 atm. When the total flow rate is $60\,\mathrm{cm}^3\,\mathrm{min}^{-1}$ in a 1 cm i.d. tube, the gas linear flow rate is $1/(0.5)^2\pi = 1.27\,\mathrm{cm\,s}^{-1}$. Thus the contact time of the gas with the wire will be of the order of 1 s.

The mean free path, λ, of the oxygen molecules is given by the equation

$$\lambda = \frac{kT}{\sqrt{2}\sigma p} \tag{8}$$

where k is Boltzmann's constant, T the absolute temperature, p the gas pressure and σ the collision cross-sectional area. With a collision cross-section of $\sim 0.4\,\mathrm{nm}^{-2}$ and a temperature of 1000 K, $\lambda = 244\,\mathrm{nm}$, which is very small compared with the dimensions of the reactor tube.

The diffusion coefficient can be expressed as

$$D = \tfrac{1}{3}\lambda\bar{c} \tag{9}$$

where $\bar{c}$ is the mean velocity of the molecules and can be expressed as

$$\bar{c} = \sqrt{\frac{8kT}{\pi m}}. \tag{10}$$

Hence

$$D = \frac{1}{3}\lambda\sqrt{\frac{8kT}{\pi m}} \tag{11}$$

where m is the mass of one molecule. Under the same conditions for oxygen, $\bar{c} = 813.5\,\mathrm{m\,s}^{-1}$ and $D = 6.62 \times 10^{-5}\,\mathrm{m}^2\,\mathrm{s}^{-1}$.

The distance (d) moved by molecule in time t is given by

$$d = \sqrt{Dt}. \tag{12}$$

Hence in 1 s a molecule moves $\sqrt{6.62 \times 10^{-5}} = 8.13 \times 10^{-3}\,\mathrm{m} = 8.13\,\mathrm{mm}$.

For a 100 mm long nickel wire with a diameter of 0.25 mm, the effective reaction cross-sectional area would therefore be $0.025\pi \times 10 = 0.785\,\mathrm{cm}^2$. This is to be compared with the total cross-sectional area of the reactor tube, which is equal to $(0.5)^2\pi = 0.785\,\mathrm{cm}^2$. Hence all of the molecules should be able to collide with the nickel surface. These calculations show that it is possible for all of the oxygen to contact the surface under normal flow conditions.

5. Conclusions

Using a modified thermocouple with a nickel filament interposed, the oscillatory behavior was investigated for the partial oxidation of methane over a nickel catalyst. Regular oscillations in both reactants, products and temperature were observed at temperatures ranging from 700 to 860 °C and $Ar/CH_4/O_2$ gas ratios ranging from 30:29:1 to $30{:}22.5{:}7.5\,\mathrm{cm}^3\,\mathrm{min}^{-1}$. It was found that, when the reactor system temperature was increased, the frequency of oscillations tended to increase whereas the amplitude of the oscillations decreased. When the oxygen concentration in the feed gas was increased, the frequencies of oscillations tended to decrease whilst the amplitudes of the oscillations increased. The product distribution (CO_2/CO) was also significantly affected when the feed gas O_2/CH_4 ratio was varied. Temporarily cutting off either methane or oxygen supply revealed the changes occurring on the catalyst surface and the consequent effects on the oscillations. The oscillatory behavior was attributed to the cyclic oxidation and reduction processes occurring on the nickel metal surface, although it still remains unclear how the cycle was "triggered" to start again after the previous one was completed.

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