

Oscillatory behavior during the partial oxidation of methane over nickel foils

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Received 11 April 2002; accepted 18 June 2002

The study of the partial oxidation of methane over nickel foils has been carried out over a wide range of reactor temperatures (748–930 °C) and feed-gas compositions (Ar/CH₄/O₂), ranging from 30:29:1 to 30:12:18 cm³ min⁻¹ at atmospheric pressure. The product formation shows pronounced oscillations. A modified thermocouple was designed to measure the temperature while the interposed nickel foil worked as a catalyst. The oscillations have been attributed to the cyclic reduction and oxidation of the nickel surface in the specific reaction environment at elevated temperatures.

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

1. Introduction

The partial oxidation of methane to produce carbon monoxide and hydrogen has increasingly received attention in recent years [1–6], mainly because of its potential use as a commercial source of syngas (CO + H₂). The dominant industrial process currently in use is the steam reforming of methane, which has disadvantages because of its high energy requirements, a higher H₂/CO ratio than is required and poor selectivity for CO [7,8].

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 [9–12] and supported nickel catalysts [3,13,14]. There has also been a report [15] of oscillations occurring over an Nd₂O₃/MgO catalyst containing an exposed chromel-alumel thermocouple.

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, and nickel was identified as the active catalyst [16]. In this paper we report on the further investigation into the oscillatory reaction kinetics over nickel foils during the reaction of oxidation of methane. The oscillations were studied in detail, and wide ranges of the feed-gas composition as well as the reactor temperature were investigated. By varying the reaction conditions, the regime of oscillatory behavior has been revealed. The

data thus obtained could lead to new insights into the reaction mechanisms of such complicated processes.

2. Experimental

The catalytic reaction was carried out under atmospheric pressure by flowing an argon/methane/oxygen mixture over a piece of nickel foil. The foil was located centrally in a 10 mm i.d. quartz tubular reactor, parallel to the tube axis. The reactor was heated in a tubular furnace and oscillations were generally observed at temperatures between 748 and 930 °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 (Sensorlab V.5, Fisons Instruments, Vacuum Generators Quadrupoles). To prevent condensation of water vapor produced during the reaction, the needle valves and connecting tubulations were heated to about 200 °C. Mass flow controllers (ASM model AFC-260) were used to control the feed-gas flow rates in known proportions prior to reaction. The feed gases used were mixtures of argon/methane/oxygen in flow-rate ratios ranging from 30:29:1 cm³ min⁻¹ to 30:12:18 cm³ min⁻¹, whereas the total flow rate was kept at a constant of 60 cm³ min⁻¹ throughout the experiment.

A modified thermocouple was designed for the experiment, based on the law of intermediate metals [17], which states that if one or both of the junctions of

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a thermocouple are opened, and one or more metals are interposed, the resultant electromotive force (e.m.f.) is not altered provided that all the new junctions are at the same temperature as the original junction between which they are positioned. This modified thermocouple could be used to measure the reaction temperature while the nickel foil acted as a catalyst. The temperature of the reactor tube without reaction occurring inside was measured by means of stopping one of the reactant gases, while keeping the power supplied to the furnace unchanged.

The modified thermocouple was made by spot-welding a piece of rectangular nickel foil (5 mm long \times 4 mm wide, thickness 0.05 mm, 99.98% Ni, obtained from Goodfellow) with 0.5 mm diameter chromel and alumel wires separately. The two welded spots were located near the longer edge of the rectangular foil and 3 mm apart. The thermocouple was then connected to the temperature display and logging system. The compositions of the chromel and alumel wires, also from Goodfellow, were 90% Ni/10% Cr and 95% Ni/5% (Al + Mn + Si) respectively. Methane (purity 99.0%) and oxygen (purity 99.6%) were purchased from Aldrich Chemicals. Argon (purity 99.9%) was supplied by BOC Gas.

3. Results and discussion

3.1. Initiation of oscillatory behavior over nickel foils

Figure 1 shows the start of oscillations over a piece of rectangular nickel foil where the feed-gas ratio was kept at $\text{Ar}:\text{CH}_4:\text{O}_2 = 30:25:5 \text{ cm}^3 \text{ min}^{-1}$. When the temperature was raised to 720 °C, methane conversion increased significantly as well as the product yield. The first oscillation appeared as a spike when the temperature reached 748 °C. After 2.5 min the second spike came while the temperature approached a constant value. Further spikes appeared with similar forms but they came at irregular intervals. After about 25 min the oscillations became regular.

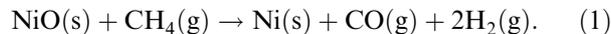
It was also observed that all the fresh catalysts needed an “induction period” of a few minutes. As long as the catalyst was “initialized” the oscillatory behavior could be observed immediately in the following runs after the temperature reached a certain level. This indicated that some initial reactions occurred on the metal surface which were essential in establishing the oscillations. The possible reactions could include the formation of NiO and dissociatively adsorption of methane on Ni to give carbon and hydrogen adatoms [16].

It can be seen, from a typical oscillation cycle as shown in detail in figure 1, that the CO and H₂ spikes are composed of two parts, a sharp peak followed by a shoulder, while the CO₂ spike had a sharp peak and a flatter second peak. Coinciding with the product signals, there was a big drop in the methane signal followed by a

slower increase. The temperature peaks were more complicated. There appeared to be a small rise from 751 °C up to 757 °C, followed by a quick fall to 722 °C. The temperature then climbed up to a maximum value of 797 °C before returning to the starting level of 751 °C, when it was ready for the next cycle.

The combustion of methane to produce carbon dioxide and water is a strong exothermic reaction ($\Delta H_{1000\text{K}}^0 = -801.2 \text{ kJ mol}^{-1}$) that could mainly contribute to the temperature rise. However, the low temperature level (722 °C), which was even lower than the reactor temperature (748 °C), clearly indicated that there must also be an endothermic reaction. The coincidence of the temperature drop with the production of CO and H₂ showed that the CO- and H₂-producing reactions are endothermic.

Endothermic reactions producing CO and H₂ in such an environment could include the CO₂ reforming of CH₄ and the steam reforming of CH₄. They, however, 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. An alternative endothermic reaction producing CO and H₂ involves at least some of the oxygen being provided by a surface oxide. The formation heat of NiO at 298 K is $-239.7 \text{ kJ mol}^{-1}$ and the participation of this oxide to produce CO and H₂ would be more than sufficient to make the overall process endothermic. The reaction could then be expressed as



It follows from this discussion that much of the oxygen required for reaction comes from reduction of nickel oxide, and the periodic oxidation/reduction of the nickel catalyst surface induces the oscillatory kinetics.

3.2. The effect of temperature on the oscillations

As the temperature increased, the waveforms, frequencies and amplitudes were all strongly affected, as shown in figure 2. The feed-gas composition was kept constant at a flow-rate ratio of $\text{Ar}:\text{CH}_4:\text{O}_2 = 30:25:5 \text{ cm}^3 \text{ min}^{-1}$ in these experiments.

It can be seen from figure 2 that the frequency of the oscillations tended to increase and the amplitudes to decrease as the temperature was raised. Thus, the period between spikes decreased from 40 s to 10 s and the amplitude was reduced 3–4 times as the reactor temperature was increased from 760 to 930 °C. With regard to product selectivity, the amount of CO₂ decreased while the amount of CO and H₂ increased as the temperature was raised. However, when the oscillations finally disappeared at a reaction temperature of 945 °C, corresponding to a reactor temperature of 930 °C, the CO₂ yield increased slightly while the CO and H₂ yields were lowered. This phenomenon provided

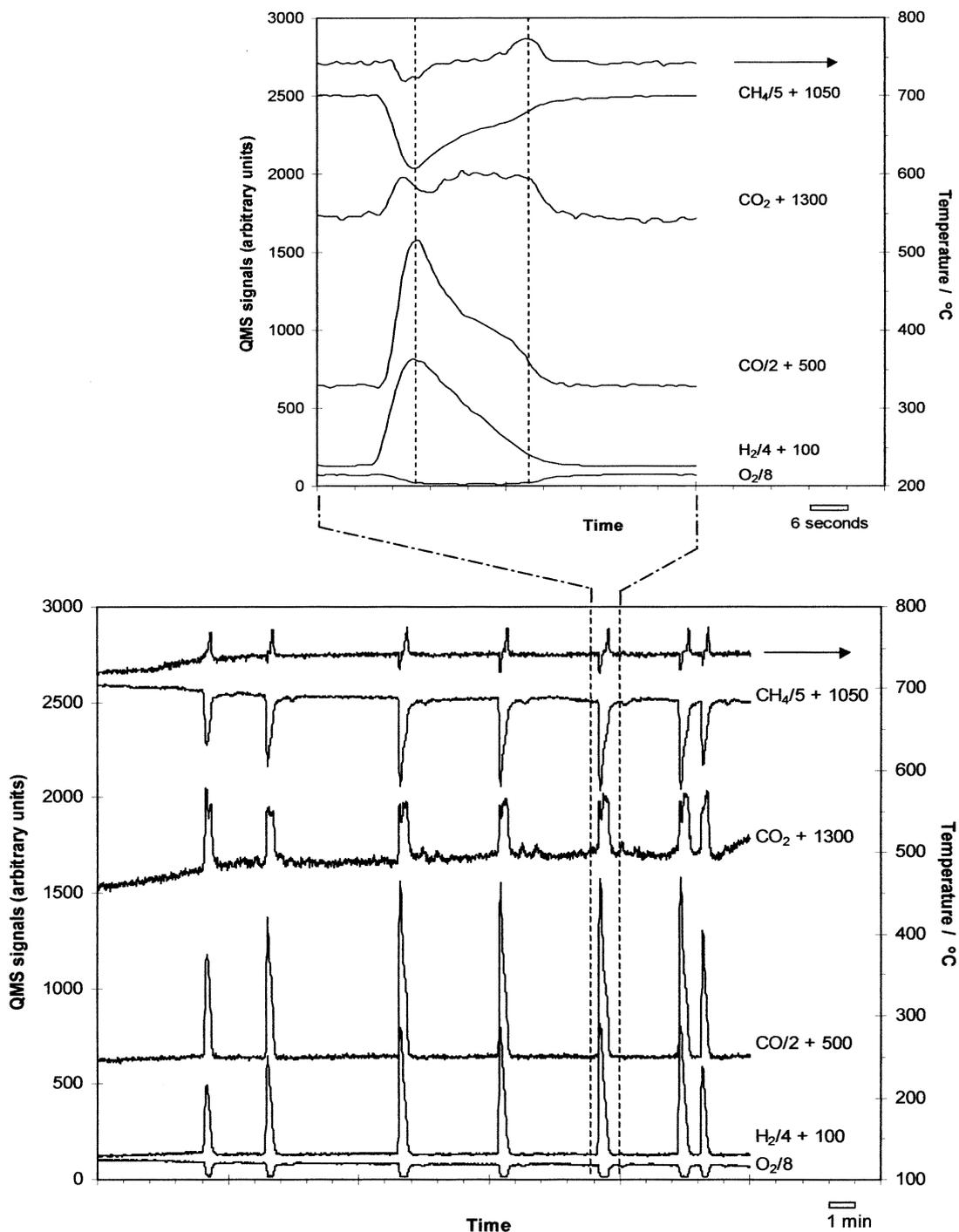


Figure 1. Oscillations over nickel foil (Ar:CH₄:O₂ = 30:22.5: 7.5 cm³ min⁻¹; reactor temperature = 748 °C).

further evidence of the phase changes occurring on the catalyst surface where one of the phases must be favorable to the production of CO and H₂.

Figure 3 shows the relation of the oscillation period (ω) to the system temperature (T). It is interesting to note that the points of $\ln(\omega)$ versus $1000\text{K}/T$ lie on a straight line, and the relation can be represented by the equation

$$f = \frac{1}{\omega} = A_0 e^{-(A/RT)} \quad (2)$$

where f is the oscillation frequency and ω the oscillation period in seconds.

By a comparison with the 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 $A_0 = 2.02 \times 10^6 \text{ s}^{-1}$ and $A = 165.1 \text{ kJ mol}^{-1}$.

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 [17–22], whereas methane has

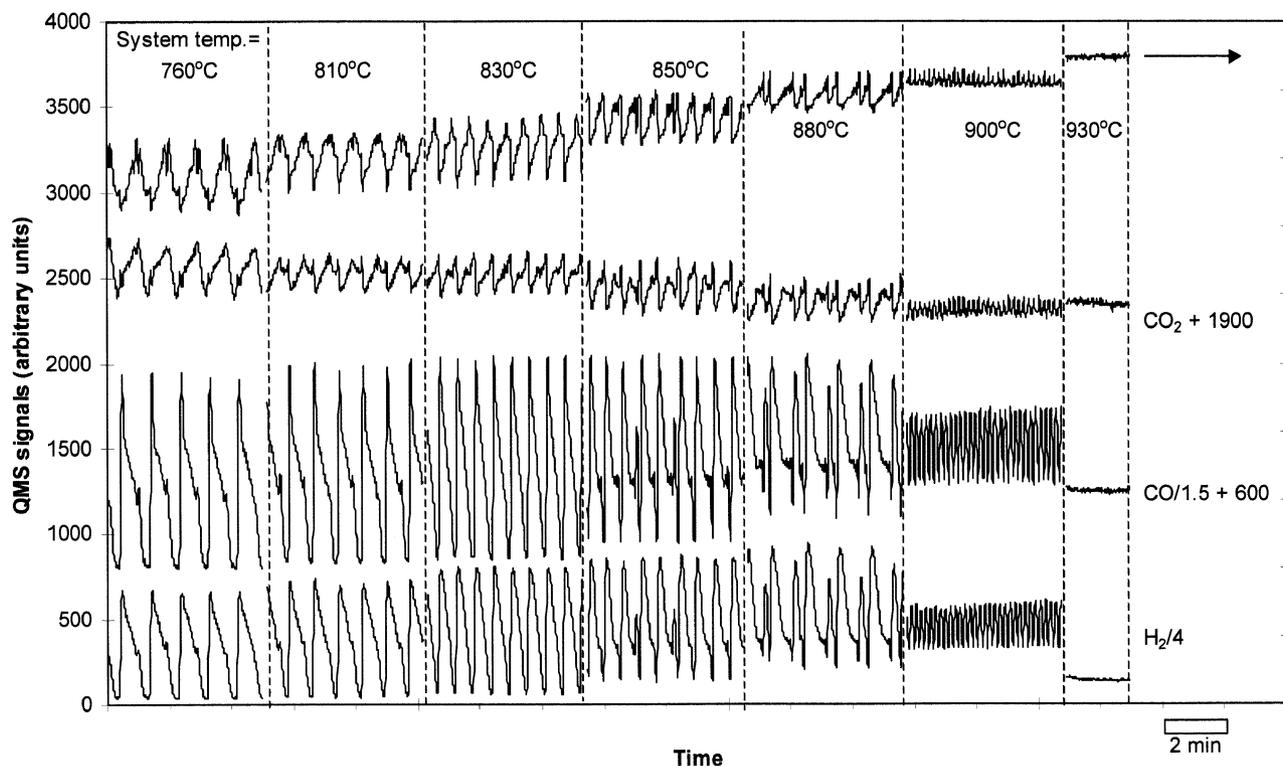


Figure 2. Oscillations over nickel foil at different temperatures (Ar:CH₄: O₂ = 30:25:5 cm³ min⁻¹; reactor temperature ranging from 760 to 930 °C).

an activation energy for adsorption of about 56 kJ mol⁻¹ on Ni(111) and Ni(110) and 25 kJ mol⁻¹ on Ni(100) [23–25]. Adsorption of methane on Ni(111) is believed to occur by a direct mechanism without passing through a precursor state [26]. In our reaction system the nickel surfaces are likely to include both (111) and (100) phases, and the possible carbon formation on metal surfaces in the presence of carbon-containing gases can change the

gas/metal interfaces. Thus, our calculated activation energy result (165.1 kJ mol⁻¹) is different from the data reported. Furthermore, the oscillation frequency f in equation (2) can only represent an apparent reaction rate where surely more than one reaction occurred in an oscillation cycle. That complexity makes it more difficult to compare the calculated activation energy with that obtained in either oxygen/nickel or methane/nickel

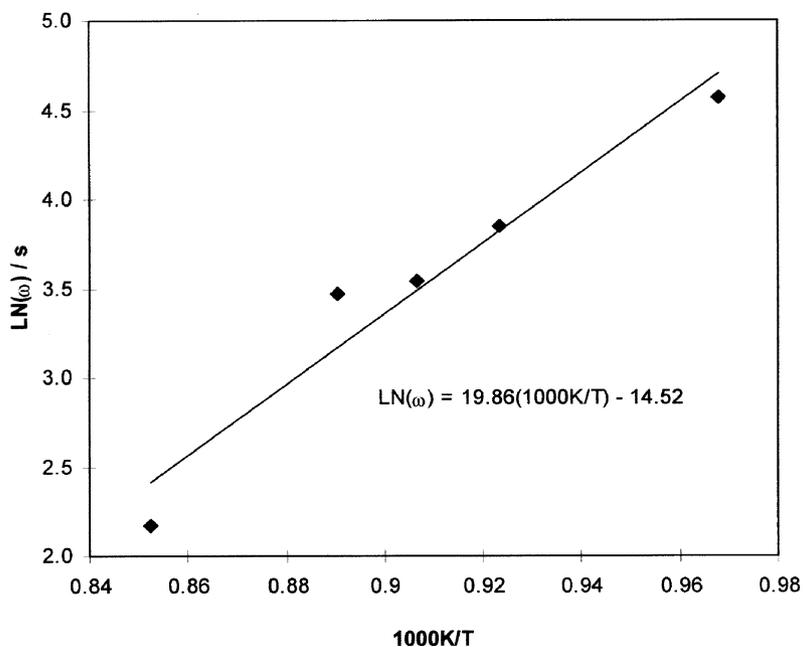


Figure 3. The relation of the oscillation period ω to the reactor temperature T for oscillations over nickel foils.

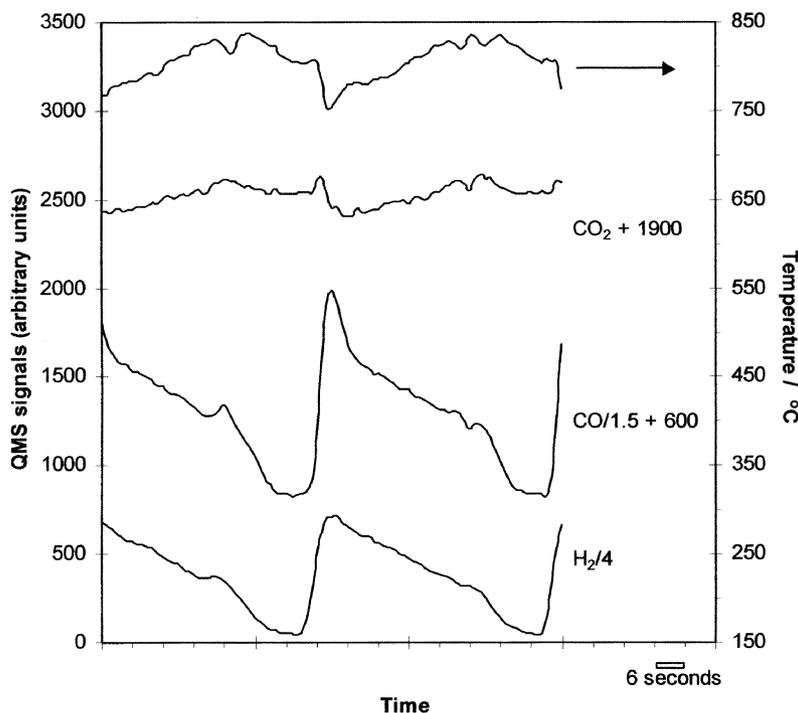


Figure 4. A cycle of oscillations over the nickel foil at 810 °C (Ar:CH₄: O₂ = 30:25:5 cm³ min⁻¹).

systems, while the mechanism of the oscillation is still not fully understood.

Figure 4 presents the details of a cycle, from which the changes in the waveforms can be seen clearly. It appears that the oscillatory behavior under this condition was more complex than that depicted in figure 1. During this cycle four stages can be distinguished in the CO and H₂ peaks: a sudden rise, then a drop followed by a more gradual drop, before a final rapid fall. The first rise and drop appeared to consist of a peak arising from one reaction and the more gradual drop was likely to be caused by a second reaction. The final rapid fall indicated a sudden stop to both reactions. The profile of the CO₂ concentration during the cycle was different, showing a sudden rise and fall, followed by a gradual increase and then a decrease in signal. The temperature profile was even more complex, showing a combination of reaction heats from all the reactions occurring. The temperature rise during reaction was mostly due to the highly exothermic reaction producing CO₂, and the temperature fall was due to the increase in the contribution from the reaction producing CO and H₂. It was observed that the lowest temperature reached (760 °C), corresponding to a sudden rise in CO and H₂, was much lower than the system temperature (810 °C). This big drop in temperature confirmed that the reaction corresponding to the high peaks of CO and H₂ was endothermic.

3.3. The effect of oxygen concentration on the oscillations

By changing the feed-gas composition (O₂:CH₄ ratios) at a constant temperature of 785 °C where the total gas

flow rate was kept at a constant of 60 cm³ min⁻¹, the effect on the waveforms, frequencies and amplitudes could be observed. The results are shown in figure 5.

In general, two types of oscillations appeared with the increase in oxygen pressure in the feed gas. When the O₂:CH₄ ratio was kept at the lower value (<0.5), an increase in amplitudes of the oscillations was observed, but the frequency was reduced significantly with the increase in O₂:CH₄ ratios. In this lower O₂:CH₄ ratio range the waveforms were similar. When the O₂:CH₄ ratio was kept at a higher value (>0.5), the peak amplitude was decreased, whereas changes in frequencies were hardly observed with the increase in O₂:CH₄ ratios. In this higher O₂:CH₄ ratio range the waveforms were again similar but different from that in the lower oxygen pressure range. The trends of frequencies and amplitudes changing with the increase in O₂:CH₄ ratios are illustrated in figure 6.

The waveform changing with the O₂:CH₄ ratio was especially marked for the temperature profile. When the O₂:CH₄ ratio was kept at the lower value (<0.5) significant temperature drops were observed, just as the product peaks of CO₂, CO and H₂ appeared. Between peaks there was a general rise in CO₂ concentration and a gradual fall in CO concentration, while the temperature increased slightly. In contrast, when the O₂:CH₄ ratio was higher (>0.5) temperature rises were observed which corresponded with the product peaks. It was observed that this change in the temperature profile corresponded to the change in the product selectivity. With increasing O₂:CH₄ ratio, the ratio of CO₂ to CO increased. Since CO₂ was produced from a

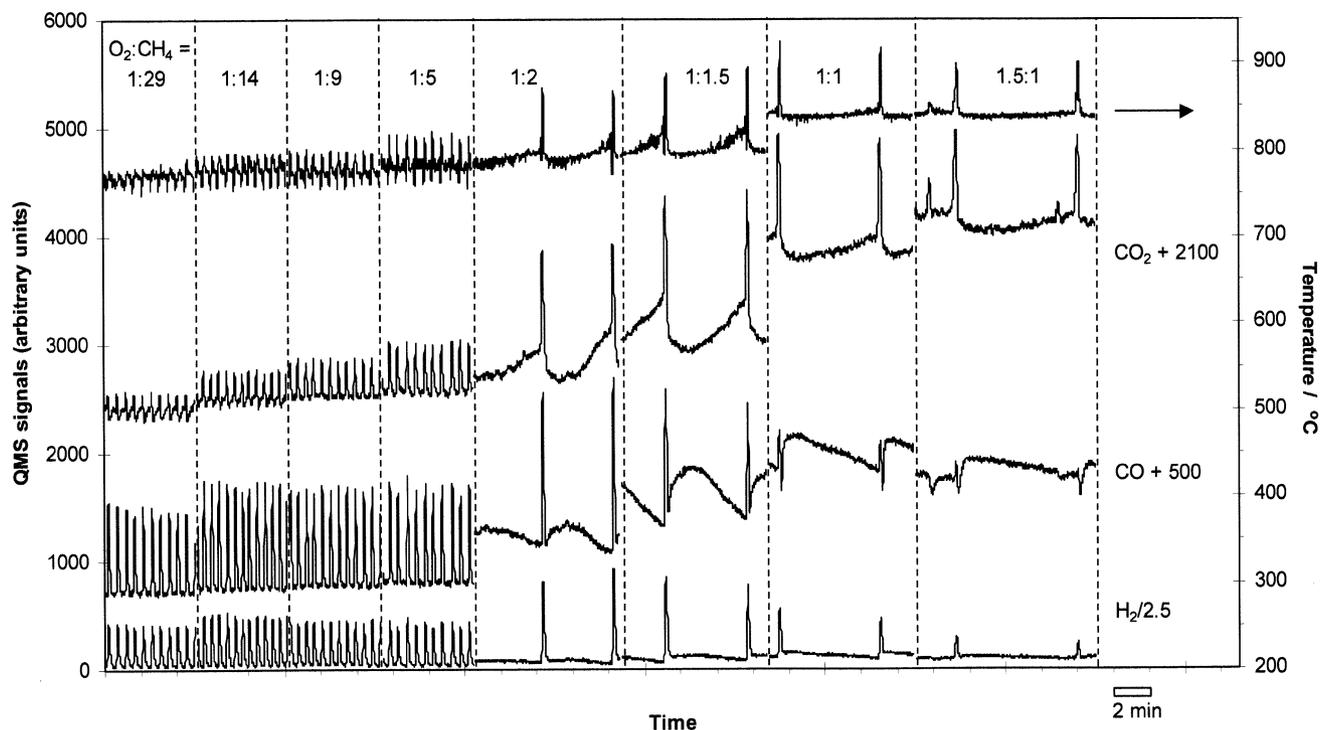


Figure 5. Oscillations over nickel foil at different oxygen concentrations (reactor temperature = 785 °C; Ar:CH₄:O₂ flow rates ranging from 30:29:1 to 30:12:18 cm³ min⁻¹).

highly exothermic reaction while CO was formed in endothermic reactions, the change in the proportion of each reaction changed the overall reaction heat and, in turn, the temperature profile. Thus, a higher ratio of CO₂/CO in the peaks resulted in a temperature rise while, by contrast, a higher ratio of CO/CO₂ showed a temperature drop. The changes in product selectivities may be attributed to catalyst phase changes with the oxygen pressure variation in the feed gas, as the nickel phase controlled the activity of the catalyst for a given reaction. This has been confirmed by the comparison

of the product selectivity over alumina-supported nickel catalysts at oxidized and reduced phases [27], although the reason why the significant change was observed here at the O₂:CH₄ ratio of about 0.5 is not clear.

4. Conclusions

Oscillations during the reaction of partial oxidation of methane have been investigated with a modified

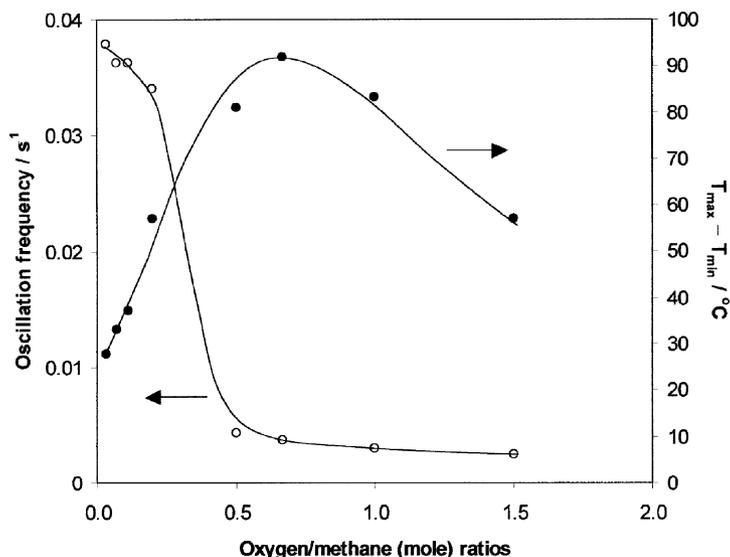


Figure 6. Variation of frequency and amplitude of the oscillations with feed-gas compositions over nickel foil (reactor temperature = 785 °C).

thermocouple designed to measure the temperature, while the interposed nickel foil worked as a catalyst. The oscillatory behavior has been observed for reactor temperatures in a range of 748 to 930 °C and feed-gas compositions with Ar/CH₄/O₂ gas ratios ranging from 30:29:1 to 30:12:18 cm³ min⁻¹. The oscillation frequency was increased but the amplitude was reduced with the rise in temperature. Changes in the feed-gas composition resulted in complex changes in frequencies, amplitudes and waveforms, as well as product selectivities. The oscillation is likely due to the cyclic reduction and oxidation of the nickel surface in the specific reaction environment at elevated temperatures.

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