

Oscillations of methane combustion over alumina-supported palladium catalysts under oxygen-deficient conditions

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Abstract

The oxidation of methane over Pd/Al₂O₃ catalysts in flow systems has been investigated at temperatures in the range 250–600°C and with O₂/CH₄ ratios between 0.5 and 10.0. Oscillatory behaviour in the evolution of heat of reaction was observed for mixtures close to the stoichiometric composition. The frequency of oscillation increased with rising temperature. The amplitude also depended on both temperature and feed gas composition, and was greatest under conditions such that the consumption of oxygen was almost complete. The oscillatory behaviour may be attributed to the periodic or aperiodic changes in a Pd–PdO_x active phase, modulated by the specific reaction environment at elevated temperature. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Although the oxidation of methane over supported noble metal catalysts has been reinvestigated recently [1–10], few of these studies [4,5,10] have involved the use of stoichiometric or methane-rich mixtures. Such studies are important because of possible changes in the kinetic behaviour of the catalyst with mixtures at the stoichiometric composition and because these mixtures are likely to be encountered in

the neutralisation of industrial and auto-exhaust gases. Although oscillatory behaviour has been observed during the oxidations of H₂, CO and other reducing gases over supported noble metal catalysts [11,12], an oscillatory reaction during methane oxidation over a Pd-film catalyst has been reported only recently [13]. Revelation of regimes of oscillatory behaviour in catalytic processes may lead to new insights into the reaction mechanisms and achieve a better understanding of the operation and improvement of the practical catalysts [14].

A small platinum coil encapsulated with supported noble metal catalyst, e.g., a ‘pellistor’ as used in flammable gas detection [15], is a suit-

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able tool to investigate catalytic oxidation kinetics and oscillatory behaviour [16]. The coil acts both as an internal heater and as a heat-sensing element, and has a highly sensitive and rapid response to small changes in the temperature of the catalyst. The detecting device consists of a matched pair of elements, the active bead carrying the catalyst and a compensating non-active bead. The size of the beads is so small (≤ 1 mm in diameter) that possible spatial variations caused by regions of different catalytic activity during the oscillation can be greatly reduced. Both of the elements are connected into a Wheatstone Bridge circuit in which the bridge supply maintains the detector at the required operating temperature. As a flammable gas is oxidised on the heated surface of the catalyst bead, the exothermic nature of the reaction produces a rise in its temperature, which is detected by an increase in electrical resistance of the Pt coil. The magnitude of the signal produced by the detecting system for a particular gas concentration will depend mainly on the rate of reaction and the accompanying enthalpy change [17].

Using this system, we have investigated possible non-steady-state phenomena during methane oxidation in close-to-stoichiometric mixtures over supported Pd/Al₂O₃. Since CO and H₂, whose oxidation over noble metal catalysts may give rise to oscillations, are produced from methane under oxygen-deficient conditions at elevated temperature, their possible influence on the oscillation of methane oxidation has also been investigated by the temperature-programmed reaction method using a fixed-bed reactor system.

2. Experimental

2.1. Materials

PdCl₂ (laboratory reagent grade) was obtained from BDH and γ -Al₂O₃ (BET surface area 170 m²/g, for catalyst support) was sup-

plied by Tianjin Chemicals. Coils (8 turns, ϕ 0.5 mm \times 1 mm) of Pt wire (0.037 mm diameter, Johnson Matthey, 99.97%), each welded to a transistor header, were kindly donated by City Technology. Catalysts of 15 mass% Pd on γ -Al₂O₃ were prepared as previously described [18]. Part of the resulting slurry of catalytic material was deposited onto the coils of Pt wire, forming 'elements' similar to pellistors, and the remainder was dried at 120°C for several hours, crushed and sieved (40–60 mesh) to form the catalyst bed. Both of the precursors were calcined in air (550°C, 5 h), then conditioned in a reducing mixture (12% CH₄ in air, 750°C, 0.5 h), and further stabilised in air (550°C, 5 h). The average Pd crystallite sizes from XRD measurement were ca. 73 nm. The Pd surface area and dispersion calculated from CO chemisorption measurement were respectively 58 m²/g and 11%. Inert beads were prepared from a slurry of α -Al₂O₃ in poly(dimethylsiloxane) and were shown to be inactive to methane oxidation.

CH₄, O₂ and N₂ (99.99%, BOC) were used, through a vacuum system, to prepare gas mixtures with the desired O₂/CH₄ ratios which were stored in steel cylindrical vessels (35 dm³, maximum pressure 6 kg/cm²). The concentration of CH₄ in the prepared mixture was held constant at 2% with a balance of N₂ and the O₂/CH₄ ratios were in the range 0.5 to 10. Before being introduced into the reaction system, the mixtures were further purified by passage through 5 Å molecular sieve and activated carbon.

2.2. Apparatus and procedure

A conventional flow reaction system was used for the kinetic measurements with elements. A catalytic element and a non-catalytic compensating element were mounted in a diffusion head reactor [19] with the compensator upstream, so that reactive gas reached the sensing element by diffusion. The temperatures of the elements were controlled and monitored using a Wheatstone

bridge network with the beads connected in series. For a matched pair of beads whose resistance is R at temperature T , the reaction rate r is related to the observed signal V by

$$r = V\{(RdW/dT)/(EdR/dT) - E/R\}/2f\Delta H$$

where E = voltage drop across the two beads; f = fraction of heat ΔH absorbed by the bead and detected by the internal coil; dR/dT = temperature coefficient of resistance of the Pt coil and dW/dT = temperature coefficient of the power dissipated by the bead.

In each experiment, prior to introducing the reaction mixtures into the reactor system, the elements were held in flowing air at the required temperature until a stable baseline was achieved. A four-way valve located upstream in the reactor system was used to switch between air and the reaction mixture (100 cm³/min).

For the temperature-programmed oxidation reaction system, a U-type reactor (4 mm i.d. \times 350 mm) was mounted centrally in a vertical tube furnace with a programmable temperature controller. The temperature of the catalyst was monitored by a chromel–alumel thermocouple (ϕ 0.5 mm) located inside the reactor in the centre of the catalyst bed (100 mg, length ca. 7 mm). The concentrations of CH₄, CO₂ and CO in the feed and exhaust gases were analysed on-line using an FTIR spectrometer (ATI Mattson Research Series). Absorbances at 3016, 2355 and 2170 cm⁻¹ were used for analysis of CH₄, CO₂ and CO respectively. WinFIRST software was used for collection of data and calculating peak areas. Calibration plots were established from the analysis of standard gas mixtures (0.1% to 2.0% in air) prepared using Woesthoff gas mixing pumps (SA18/3 and SA27/3F). The conditioned catalyst sample was heated from room temperature in flowing air (100 cm³/min) to 220°C and sustained for 0.5 h, and then in reactive mixtures (100 cm³/min) with linearly ramped temperature (2.5 K/min) up to \geq 500°C.

3. Results

3.1. Oxidation activity of Pd/Al₂O₃ in O₂–CH₄–N₂ mixtures and observations of oscillatory behaviour

Measurements of the catalytic activity of Pd/Al₂O₃ catalysts for oxygen-rich and methane-rich mixtures, shown in Fig. 1 as the response of catalytic elements as a function of temperature, established that methane is oxidized over Pd/Al₂O₃ at temperatures \geq 250°C. With O₂/CH₄ ratios \geq 2.3, Fig. 1a, stable responses were obtained reaching a maximum ca. 450°C, above which rates of reaction became controlled by bulk gas diffusion with characteristically insensitive to the changes of catalyst temperature [19]. No oscillation during methane oxidation could be found with O₂/CH₄ ratios \geq 2.3 at temperatures in the range 250–600°C. With O₂/CH₄ ratios $<$ 2.1, however, the response or the activity fluctuated and oscillations were observed at temperatures above 350°C. In the strong oscillatory regime, Fig. 1b, the upper and lower bounds of response, respectively 46 mV and 16.5 mV at 400°C, bracketed the signal (38.9 mV at 400°C) produced from the oxidation of the same concentration of CH₄ in air, Fig. 1c. All the features of the waveforms were repeatable, so long as the reaction conditions were reproduced precisely.

When the reactant gas was introduced under conditions leading to oscillations there was an ‘induction period’ before oscillatory behaviour commenced, Fig. 2. This period was dependent on the temperature; for example, ca. 0.5 min at 500°C (Fig. 2a) and $>$ 1 min at 400°C (Fig. 2b) for an O₂/CH₄ ratio of 1.9. Subsequently, the stable and repeatable oscillation became established over a period of 5–30 min.

Depending on the reaction conditions, two types of oscillations were revealed, viz. periodic oscillation (Fig. 3a, e, f and g) and aperiodic oscillation (Fig. 3b, c and d) with different waveforms, amplitudes and frequencies. The re-

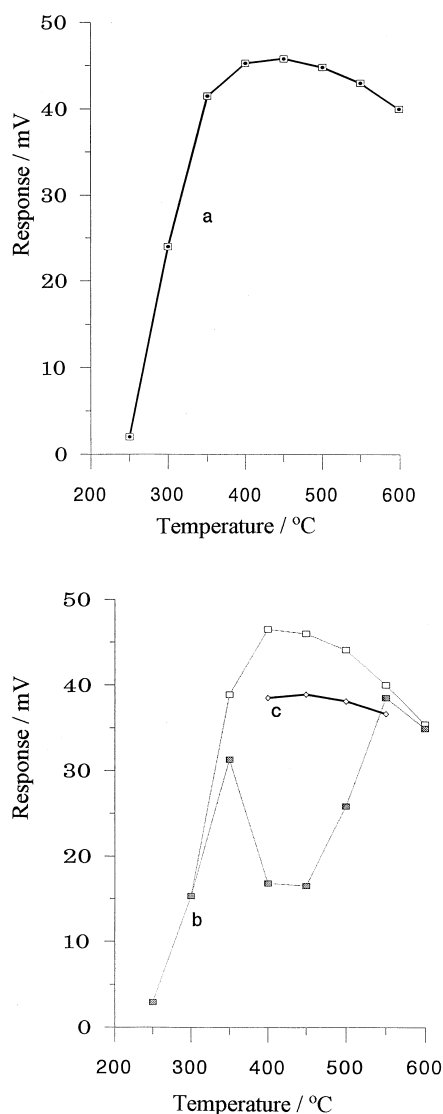


Fig. 1. Activities of Pd/Al₂O₃ for methane oxidation as a function of temperature. (a) 2% CH₄ in air; (b) O₂/CH₄ = 1.7; (c) 1.85% CH₄ in air. The double dotted lines show the upper and lower bounds of responses during oscillation.

sponses shown in Fig. 3a and b were typical waveforms for low O₂/CH₄ ratios respectively at lower and higher temperature while those in Fig. 3c and d were the corresponding waveforms for higher O₂/CH₄ ratios. The general trend of frequency of oscillation varied from ca 2/h (Fig. 3g) to more than 600/h (Fig. 3d). Various oscillatory waveforms were observed, such as relatively simple peaks (Fig. 3a), single

sharp peaks (Fig. 3e), double peaks (Fig. 3f) or even multiple peaks (Fig. 3g). There were two alternative basic features in the oscillation waveforms: either the direction of oscillations was 'downward', corresponding to relatively slow decrease followed by a very rapid restoration of the response, or the oscillations involved alternate enhancement and suppression. An unusual waveform was also found, Fig. 3g, showing two regular superimposed oscillations. In this case, regular high-frequency oscillation occurred for ca. 20 min, then ceased abruptly with a characteristically lower response which recovered slowly until triggering resumption of the high-frequency oscillation. This sequence was maintained for at least 6 h.

3.2. The effects of reaction conditions

The frequency, amplitude and waveforms of the oscillations were strongly dependent on O₂/CH₄ ratios, Fig. 4. As the ratio was reduced, there were general trends for the frequency to decrease and for the time spent at the upper level of response to increase. Irregular complex oscillations at higher ratios (up to 2.1)

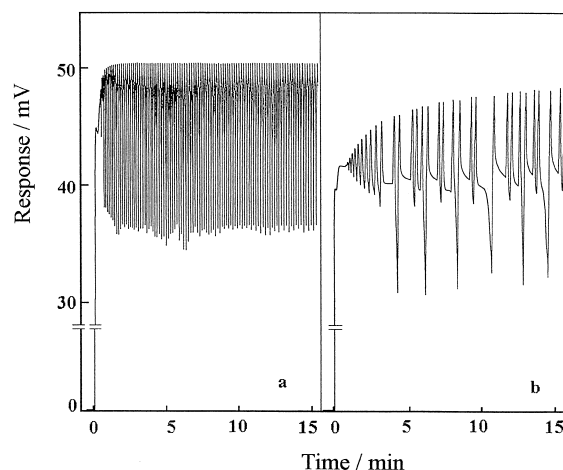


Fig. 2. Initial activities/response of Pd/Al₂O₃ and evolution of oscillation behaviour. (a) O₂/CH₄ = 1.9, at 500°C; (b) O₂/CH₄ = 1.9, at 400°C.

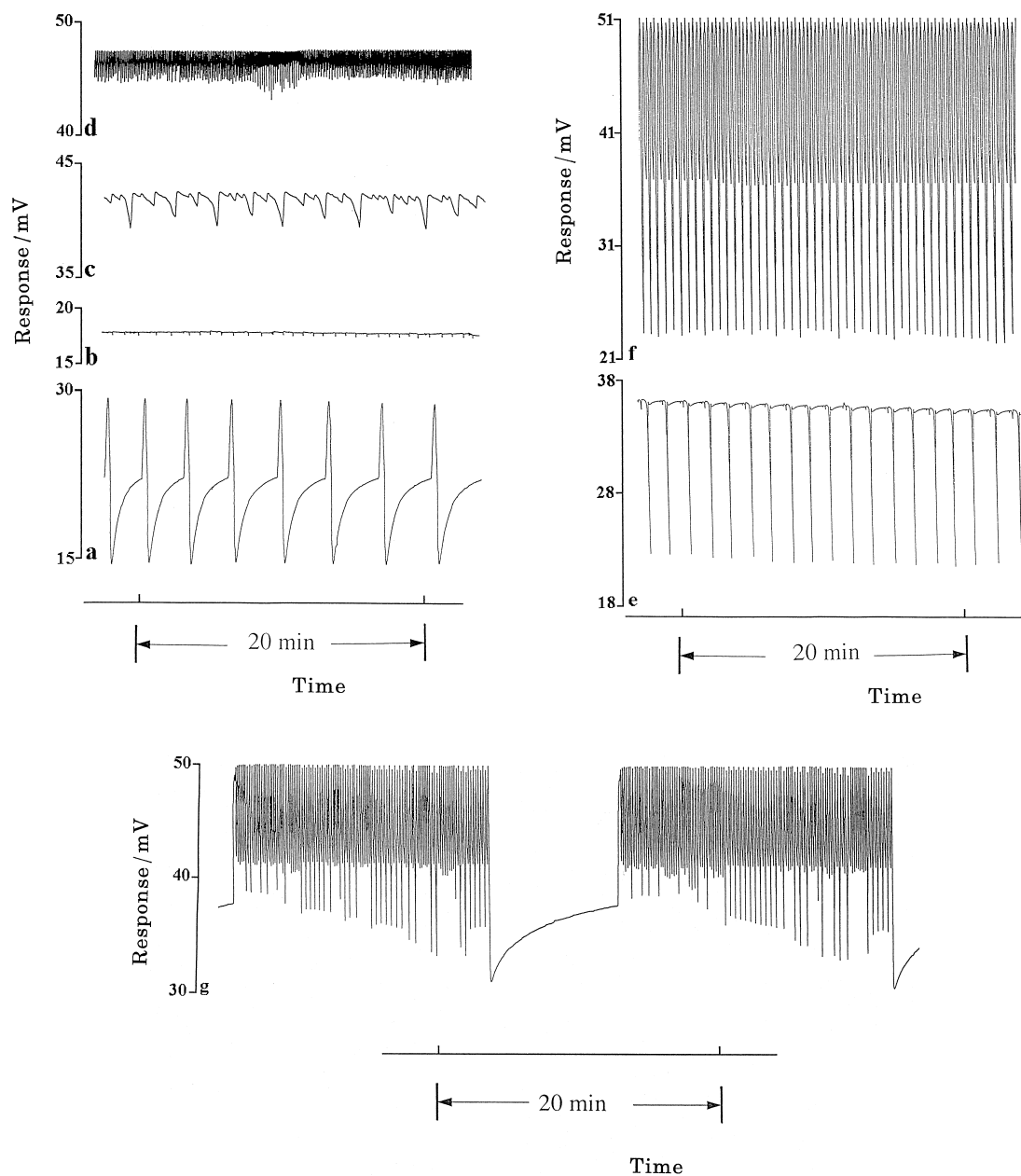


Fig. 3. Various forms of oscillation in the oxidation of CH_4 over $\text{Pd}/\text{Al}_2\text{O}_3$. Reaction conditions: (a) $\text{O}_2/\text{CH}_4 = 1.0$, 350°C ; (b) $\text{O}_2/\text{CH}_4 = 1.0$, 550°C ; (c) $\text{O}_2/\text{CH}_4 = 2.0$, 350°C ; (d) $\text{O}_2/\text{CH}_4 = 2.1$, 450°C ; (e) $\text{O}_2/\text{CH}_4 = 1.4$, 450°C ; (f) $\text{O}_2/\text{CH}_4 = 1.9$, 450°C ; (g) $\text{O}_2/\text{CH}_4 = 2.0$, 450°C .

were modified to simple regular peaks at ratios of ca. 1.0. The amplitude of oscillation passed through a maximum, with strong oscillations occurring for ratios in the range 1.0 to 1.9, Fig. 5. When the ratio was further decreased to 0.5,

oscillation behaviour ceased and the activity/response became unstable, particularly at temperatures between 400°C and 500°C , i.e., the response initially increased up to certain value, and then declined slowly. After individual ex-

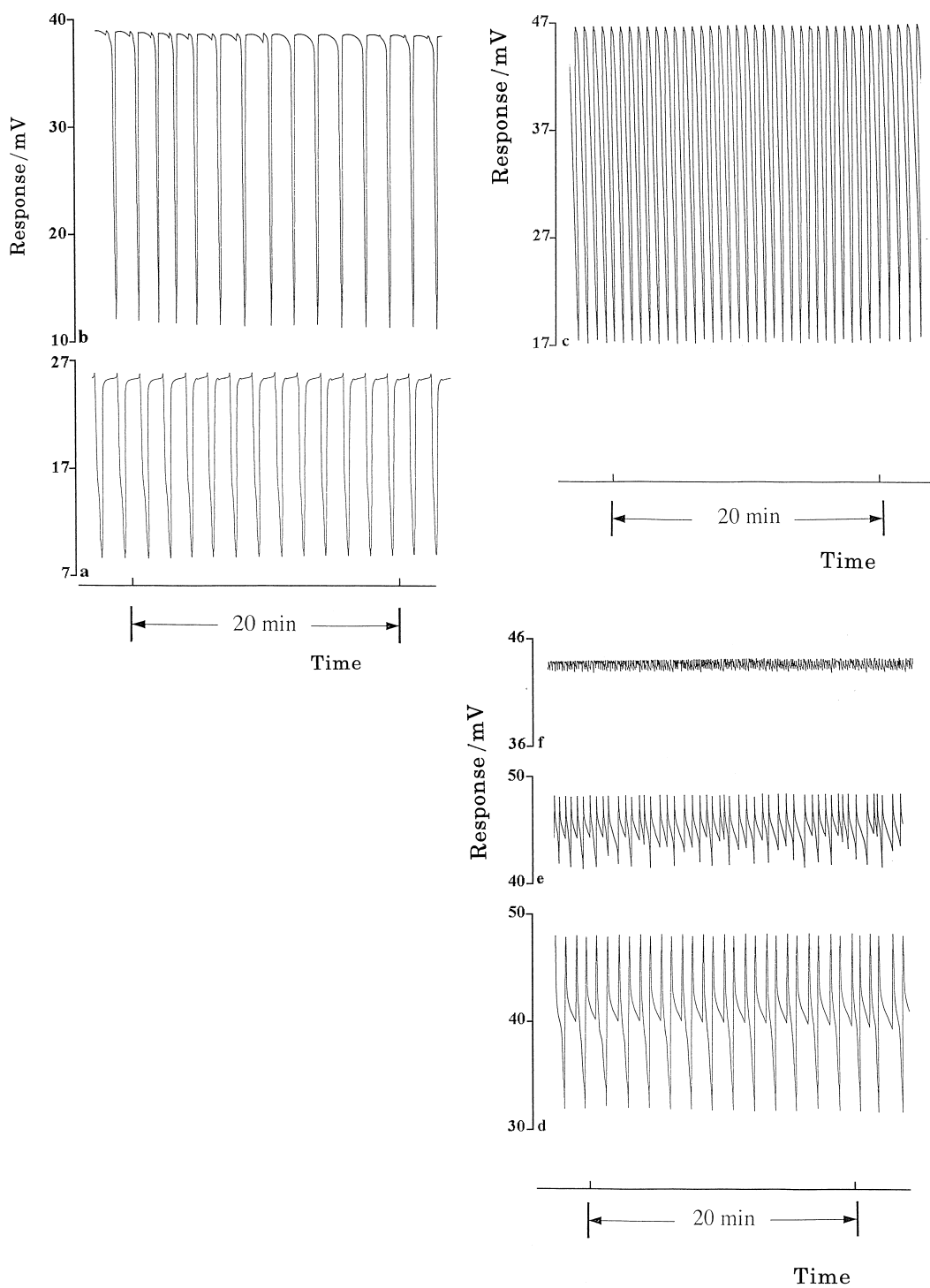


Fig. 4. Oscillation waveforms as a function of O_2/CH_4 ratios at $400^\circ C$. (a) $O_2/CH_4 = 1.0$; (b) $O_2/CH_4 = 1.4$; (c) $O_2/CH_4 = 1.7$; (d) $O_2/CH_4 = 1.9$; (e) $O_2/CH_4 = 2.0$; (f) $O_2/CH_4 = 2.1$.

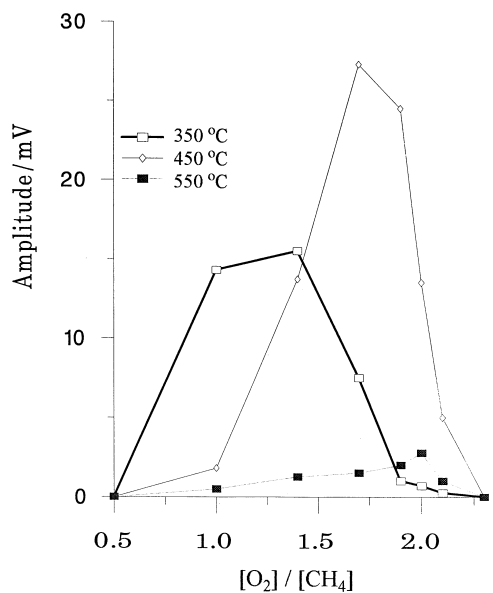


Fig. 5. Amplitude of the oscillation as a function of O_2/CH_4 ratio.

periments under these conditions, switching the gas flow back to air brought about a short-lived but substantial exothermic response, which was apparently caused by rapid catalytic combustion of deposited carbon species.

Oscillations were observed only at intermediate temperature, Figs. 1b and 6. Below 350°C methane oxidation proceeded slowly (low response), and without oscillation. Low-frequency oscillations were observed above 350°C with amplitude depending upon the O_2/CH_4 ratio. As the temperature was raised, the frequencies increased continuously for all the mixtures used. Quite regular waveforms with single peak were produced at the medium O_2/CH_4 ratios (1.4–1.7) and temperatures (350–550°C), for example, Figs. 3e, 4b and 4c. The amplitudes passed through maxima at temperatures which depended on the O_2/CH_4 ratios: ca. 400°C for $O_2/CH_4 = 1.0$ and ca 450°C for $O_2/CH_4 = 2.1$. The strongest oscillation was produced between 400°C and 450°C with $O_2/CH_4 = 1.7$, for which the amplitude was 64% of the maximum response. At higher temperatures, the amplitude decreased sharply and the waveforms became

irregular and complicated, dying away at ca. 600°C.

3.3. Methane oxidation in a fixed bed under an oxygen-deficient environment

Analyses of CH_4 , CO_2 and CO in products from oxygen-deficient mixtures passed through the fixed-bed reactor, Fig. 7 showed that, between 250 and 350°C, the conversion of CH_4 and the production of CO_2 were closely matched and increased with rising temperature. Reaction rates were similar for the two gas mixture compositions. Above a transition temperature, however, the conversion of CH_4 increased less rapidly and the corresponding increase in the production of CO_2 was even smaller. Such changes in reaction rate is, of course, not induced by the reaction temperature but by the gas phase composition. At slightly higher temperatures, detectable amounts of CO were formed. From a mass balance, almost all of the oxygen must have been consumed under these conditions. The temperatures for the transition

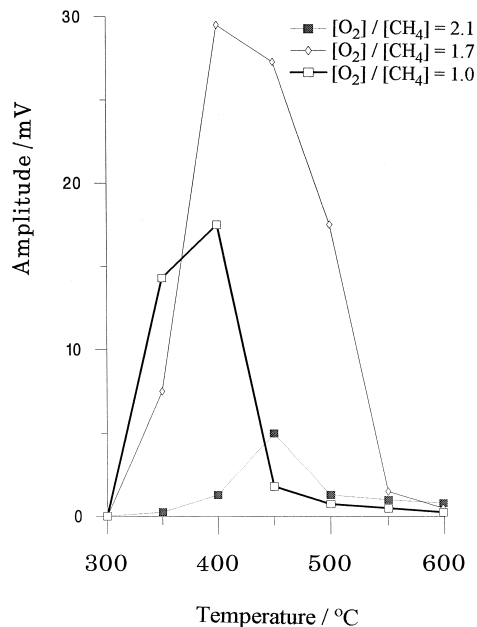


Fig. 6. Amplitude of the oscillation as a function of temperature.

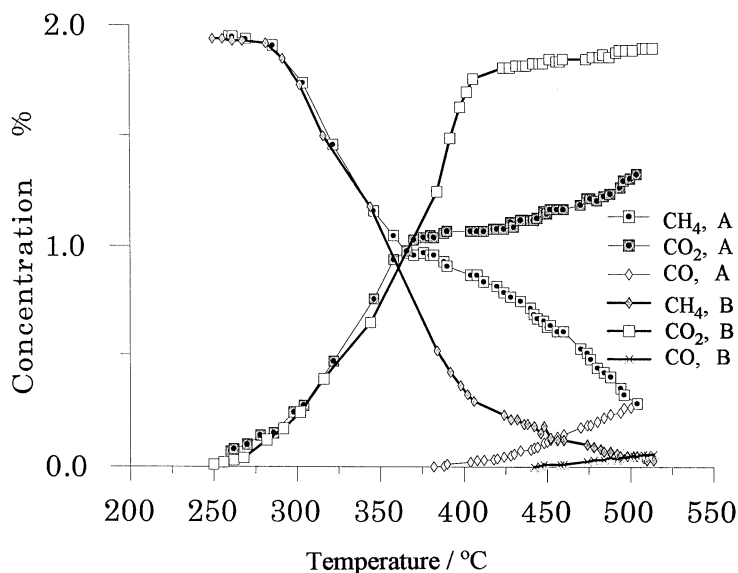


Fig. 7. Evolution of CH₄, CO₂ and CO as a function of temperature during the temperature-programmed CH₄ oxidation. (A) O₂/CH₄ = 1.0; (B) O₂/CH₄ = 1.7.

and for the formation of CO, and also the amounts of CO formed, were strongly dependent upon the O₂/CH₄ ratios. For example, these temperatures were respectively ca. 365°C and 385°C for O₂/CH₄ = 1.0, and ca. 405 and 445°C for O₂/CH₄ = 1.7. For the mixture O₂/CH₄ = 1.9, CO could be detected only above ca. 480°C. At the same temperature, much more CO was produced with lower O₂/CH₄ ratios. For example, at 500°C the CO concentration reached 0.3% with O₂/CH₄ = 1.0, which was four times higher than that with O₂/CH₄ = 1.7. In addition it can be seen that, above the minimum temperatures for CO formation, a slow but progressive increase in CO₂ and a corresponding decrease in CH₄ were observed even though the oxygen in the reactant mixture would have been completely consumed.

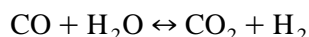
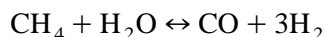
4. Discussion

It is now accepted that oscillations in reactions over supported metal catalysts are caused by surface transformations occurring at the crystallite level [14], such as periodical oxidation

and reduction of the catalytic surface [20,21], or transitions between different surface phases [22,23], rather than from impurities in the feed gas. It is also established that the oxidised surface of metallic Pd is the most active form for methane oxidation [4,6,7,9]. Pd(II)O bulk oxide is somewhat active, while reduced metallic Pd is much less active. It has been observed that methane oxidation over Pt and Pd is a structure-sensitive reaction [1,2], and the suggested explanation was that this structure sensitivity was caused by the different reactivities of adsorbed oxygen. The three-phase system O₂(g)–Pd–PdO_x has been proposed to explain the hysteresis in the activity of Pd catalysts during methane oxidation [24]. These observations and proposals may also account for the most of the results in this work. In an oxidizing environment, e.g., O₂/CH₄ ratio ≥ 2.3, the catalytic surface is predominantly oxidized and the chemical state of the Pd active phase is relative stable, maintaining a relatively stable catalyst activity toward methane oxidation. Therefore, no oscillation could be observed. This also implies that the causes of oscillation during methane oxidation/combustion under

oxygen-deficient conditions was related to the transitions of Pd active phase. The possible occurrence of homogeneous oscillations in the absence of a catalyst can be ruled out, even though oxidation of methane is highly exothermic. However, with feed-gas compositions close to the stoichiometric value and at a sufficiently high temperature, the reactant gases may modulate the catalytic surface by influencing the PdO_x/Pd ratio in the active phase. Since, in each individual experiment, the catalyst was pretreated by air at the reaction temperature until a relatively stable state was achieved, the supported metal catalyst was in the predominantly oxidized state before it was exposed to the reaction mixture. The observed induction period before oscillations commenced, and the further time required for stable oscillations to be established, tend to support this explanation. The catalyst surface would have been modulated gradually from being oxidized into a state in which the phases of PdO and Pd coexisted, with corresponding fluctuations in activity.

During temperature-programmed oxidation, a slow but continuous increase in conversion of CH₄ to CO₂ and CO in the absence of oxygen may be attributed to the steam-reforming and water-gas shift reactions [5]:



The temperatures at which the oscillation of methane oxidation occurred are considerably below those at which CO was detected with CH₄-rich mixtures. Furthermore, oscillation was also observed with an O₂/CH₄ ratio of 2.1, from which CO was not produced at any temperature (250–600°C). Therefore CO and H₂, possibly derived from the partial oxidation of methane, are not related to the oscillation.

The oscillation of methane oxidation occurred only in a narrow window of reaction conditions, i.e., with temperature in the range 350–600°C and with the O₂/CH₄ ratios be-

tween 1.0 and 2.1. A summary of the dynamic behaviour of Pd/Al₂O₃ in the ‘temperature and O₂/CH₄ ratio’ phase plane is shown in Fig. 8. The increase in the frequency of the oscillation with rising temperature is due to the increase in the transformation rate of the chemical state of catalytic surface. The reason that amplitude goes through a maximum as the temperatures is raised may be related to the possible requirement that sufficiently rapid changes in the chemical state or structure of the catalyst surface can only take place at an elevated temperature. It may be significant that, at lower O₂/CH₄ ratios, the temperatures for maximum amplitude corresponded to those at which almost complete consumption of oxygen was achieved during methane oxidation.

In the oscillatory regime, the rate of conversion of methane during the upper bound of each oscillation was much higher than that for the same CH₄ concentration in excess air; this is partially consistent with the previous work on the oscillations of SO₂ and CO oxidations [25,26]. A full understanding of such a high activity state, even though it is unstable and short-lived, may lead to new insights into the improvement of industrial catalysts for total oxidation.

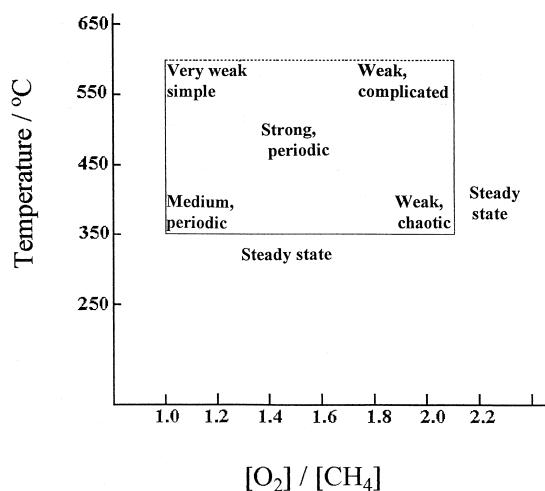


Fig. 8. Summary of the dynamic behaviour of Pd/Al₂O₃ in the temperature-O₂/CH₄ ratio phase plane.

Acknowledgements

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