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Oscillatory behaviour observed in the rate of oxidation of methane over metal catalysts

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Abstract

The oscillatory behaviour during the complete/partial oxidation of methane over a range of metal catalysts has been reviewed, including palladium, cobalt, nickel and nickel/chromium alloy. Emphasis has been placed on the understanding of the mechanism of the rate oscillations over catalyst surfaces.

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1. Introduction

The oxidation of methane over metal catalysts can result in almost complete oxidation to CO_2 and H_2O, as happens with palladium [1–12], or partial oxidation to CO and H_2, which occurs predominantly with nickel [13–17], cobalt [18] and some of the other noble metals [19–22]. The overall reactions can be represented as follows:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g),\quad \Delta H^\circ(1000\,K) = -801.2\,kJ\,mol^{-1} \tag{1}$$

$$CH_4(g) + \tfrac{1}{2}O_2(g) \rightarrow CO(g) + 2H_2(g),\quad \Delta H^\circ\ (1000\,K) = -23.0\,kJ\,mol^{-1}. \tag{2}$$

Although the partial oxidation reaction is only slightly exothermic, the position of equilibrium will favour the products because of the large increase in entropy involved.

Oscillations in the rate of these reactions have been observed for a variety of catalysts including supported palladium [23–27], palladium wire and foil [28], supported nickel [29–31], nickel wire and foil [32,33], nickel/chromium alloy [34–37] and cobalt wire and foil [18]. It is generally thought that these oscillations arise from repetitive cycles of oxidation and reduction of the metal surface, the detailed nature of each oscillation depending upon the relative activities of the oxidised and reduced surfaces. During methane oxidation the reaction over the metal or oxide surface is likely to involve some of the following elementary steps. An asterisk (*) has been used to represent adsorption at a co-ordinatively unsaturated metal atom or group of atoms.

(i) Dissociative adsorption of methane on the metal surface:

$$CH_4(g) \rightarrow CH_3{}^* + H^* \rightarrow CH_2{}^* + 2H^* \rightarrow CH^* + 3H^* \rightarrow C^* + 4H^* \tag{3}$$

or

$$CH_4(g) + O^* \rightarrow CH_3{}^* + OH^*, \text{etc.} \tag{4}$$

(ii) Dissociative adsorption of methane on the oxide surface:

$$CH_4(g) + 2O^* \rightarrow O^*{-}CH_3 + OH^*, \text{etc.} \tag{5}$$

Here, O^* has been used to signify an oxygen atom in the oxide lattice.

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(iii) Dissociative adsorption of oxygen:

$$O_2(g) + 2^* \rightarrow 2O^* \quad (6)$$

(iv) Surface reactions and desorption of products:

$$C^* + O^* \rightarrow CO^* \quad (7)$$

$$CO^* \rightarrow CO(g) \quad (8)$$

$$CO^* + O^* \rightarrow CO_2(g) \quad (9)$$

$$H^* + H^* \rightarrow H_2(g) \quad (10)$$

$$H^* + O^* \rightarrow OH^* \quad (11)$$

$$H^* + OH^* \rightarrow H_2O(g) \quad (12)$$

$$OH^* + OH^* \rightarrow H_2O(g) + O^* \quad (13)$$

The dissociative adsorption of methane on metal surfaces usually requires a significant activation energy [38–42] and it might be expected that methane would be able to compete with oxygen for vacant adsorption sites only when the gas phase methane/oxygen ratio was very high. However, the dissociative adsorption of methane at high temperatures may be facilitated by the presence of oxygen on the surface, as in reactions (4) and (5). The presence of oxygen adatoms on palladium is known to suppress the dissociative adsorption of methane [43,44], which would seem to rule out reaction (4), but this reaction could be important at higher temperatures where methane oxidation is occurring.

The aim of the present paper is to review studies on the oscillatory behaviour during the complete/partial oxidation of methane over metal catalysts. Oscillations in the rate of oxidation of methane over palladium, nickel and nickel/chromium alloy, and cobalt are examined. Emphasis has been placed on the understanding the mechanism of the rate oscillations over the metal surfaces.

2. Methane oxidation over palladium

2.1. Relative activities of oxidised and reduced surfaces

It is known that the oxidation of methane to CO_2 and H_2O occurs over both palladium oxide and the reduced metal surface but there is some disagreement in the literature about which form is more active. Hicks et al. [1,2] and Oh et al. [6,7] argue that the metal surface is the most active whereas Burch et al. [3–5], Farrauto et al. [8,9] and Primet et al. [10–12] consider the oxide surface to be more active than the metal.

The activation energies for reaction occurring on both the oxidised and reduced states of a palladium catalyst supported on α-alumina have been measured by Lyubovski and Pfefferle [45]. They obtained a value of 73.2 kJ mol^{-1} for the oxide in the temperature range 350–560 °C, and a much higher value of 157.3 kJ mol^{-1} for the reduced state in the temperature range 690–830 °C. At the higher temperatures, the metal-catalysed reaction was found to be faster than the oxide-catalysed reaction despite the much lower activation energy required for the latter process. This can be explained if the reaction over the oxide surface is confined to a few defect sites. On the basis of Lyubovski and Pfefferle's results, it would seem that the oxide surface is the better catalyst at low temperatures, where the activation energy is the controlling factor, but the metal surface is superior at higher temperatures, where the pre-exponential term in the rate equation becomes important.

2.2. Reaction occurring over the oxide under steady-state conditions

Studies conducted by Fujimoto et al. [46] have shown that methane oxidation rates on palladium oxide obey the following rate law at temperatures below 330 °C:

$$\text{rate} = k[CH_4]^{1.0}[O_2]^{0.0}[H_2O]^{-1.0}$$

where k is the rate constant for the reaction. The first order dependence on the methane concentration indicates that the dissociative adsorption of methane is the rate-determining step. By contrast, the reaction is zero order in the oxygen concentration, showing that the surface concentration of oxygen remains large and constant during the oxidation reaction. The presence of water vapour appears to inhibit the reaction showing that reactions (12) and (13), which involve hydroxyl groups, may be reversible. Fujimoto et al. concluded that the kinetics of methane oxidation at relatively low temperatures involved the activation of methane on site pairs consisting of oxygen adatoms and oxygen vacancies on the surface of PdO_x. This could explain the small pre-exponential factor for the oxide-catalysed reaction, as discussed earlier.

Isotopic scrambling, using ^{18}O labelled PdO/ZrO_2 catalysts, has been used by two groups of workers [47,48]. When CH_4 and $^{16}O_2$ were pulsed over the catalyst, ^{18}O was the main oxygen isotope appearing in the CO_2 and H_2O product molecules during the initial stages of the reaction. The following mechanism was proposed:

$$CH_4 + Pd + Pd^{18}O \rightarrow Pd{-}CH_3 + Pd^{18}OH, \text{etc.} \quad (14)$$

This overall reaction can be represented as:

$$CH_4 + Pd + 4Pd^{18}O \rightarrow 5Pd + C^{18}O_2 + 2H_2{}^{18}O \quad (15)$$

Thus, starting with one methane molecule and one Pd metal atom on the oxide surface, the overall effect is to produce another four metal atoms. In this way, methane may be able to reduce the oxide to the metal under oxygen-deficient conditions.

2.3. Oscillations occurring during methane oxidation

König et al. [23,24] were the first to observe oscillations in methane oxidation over palladium. They used ellipso-

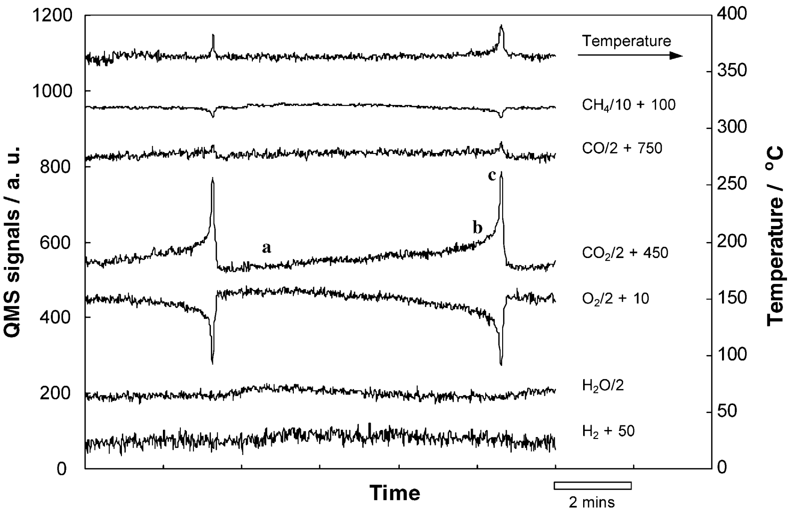

Fig. 1. Oscillations of methane oxidation over palladium foil in the temperature range of 345–390 °C; methane/oxygen ratio = 5:1.

metry to follow the growth of a PdO layer on the surface of a thick palladium film during methane oxidation at 500 °C. Oscillations were observed only when the methane/oxygen ratio of the gas mixture was greater than 2, and the temperature was greater than 470 °C. There was an induction period before the oscillations were observed during which a porous oxide layer formed on the surface. The surface was observed to oscillate between a highly active oxide state and a less active metal-rich state. The period of the cycles seemed to get slightly shorter as the reaction progressed and eventually the surface became so rough that it was impossible to obtain reliable ellipsometric data.

Periodic phase changes associated with the oscillatory reaction kinetics have also been observed using thermogravimetric analysis and XRD techniques [27]. From a study of methane oxidation over supported Pd and Pt catalysts, Deng and Nevell [25,26] have concluded that oscillations occur only under oxygen-deficient conditions, which cause the surface to undergo cycles of oxidation and reduction. When oxygen is in excess, the catalytic surface is predominantly oxidised and stable.

Zhang et al. [28] have used a quadrupole mass spectrometer (QMS) to analyse the products of methane oxidation occurring over palladium wires and foils. Typical oscillatory behaviour reported for reaction in the temperature range 345–390 °C is shown in Fig. 1. It should be noted that the QMS signals for the different gases have been vertically offset by the factors shown to the right of each plot to avoid overlapping. It can be seen that the catalyst has relatively low activity for most of the time with periodic bursts of high activity. The temperature (top line in figure) is seen to rise and fall with the activity of the catalyst, as would be expected for a highly exothermic reaction.

The main features of the oscillation observed in the CO_2 signal are marked in Fig. 1 by the letters (a–c), and these can be explained in the following way.

(i) At point (a), the catalyst is thought to consist mainly of palladium metal covered in a layer of adsorbed oxygen. The rate of methane oxidation is at a minimum, showing that the metal is a poorer catalyst than the oxide.

(ii) Between points (a and b), the surface slowly becomes oxidised to the non-stoichiometric oxide PdO_x, and the rate of methane oxidation rises.

(iii) The isotopic scrambling experiments discussed in Section 2.2 show that the methane oxidation reaction abstracts oxygen from the newly formed oxide lattice. Thus, as the rate of methane oxidation increases and the oxygen pressure falls, there must come a point where the rate of removal of oxygen atoms from the oxide lattice exceeds the rate of their replacement through dissociative adsorption of oxygen. This is thought to occur around point (b), and produces an increase in the number of oxygen vacancies in the oxide lattice. According to Fujimoto et al. [46], these are the best sites for dissociative adsorption of methane to occur (see Fig. 2). Thus, the rate of methane oxidation will increase still further, as observed between points (b and c). This results in the rapid reduction of the oxide to the metal. This process is exacerbated by the rise in temperature accompanying the methane oxidation reaction, which accelerates the reaction even further.

(iv) At point (c), the reduction of the oxide is thought to be almost complete and the carbon dioxide signal falls rapidly to a value commensurate with the activity of a palladium metal surface. At the same time, the oxygen

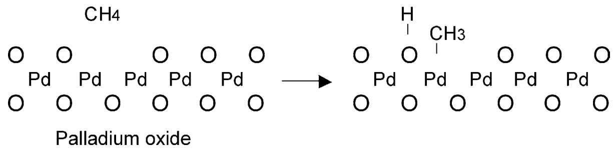

Fig. 2. Diagram of preferential site for dissociative adsorption of CH_4 on oxide surface.

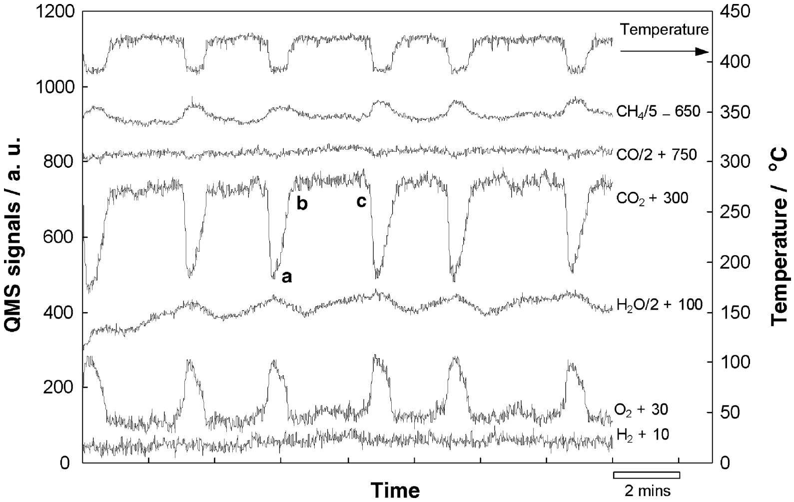

Fig. 3. Oscillations of methane oxidation over palladium wire in the temperature range of 389–425 °C; methane/oxygen ratio = 14:1.

signal rises and the process of re-oxidation begins once more.

The oscillations just discussed were obtained with a methane/oxygen ratio of 5:1 and the oxygen partial pressure never approached zero. If there is a shortage of oxygen, a different type of oscillation is obtained, as shown in Fig. 3. Here, the methane/oxygen ratio was 14:1 and the oxygen signal was close to zero during periods of high catalytic activity. The temperature range (389–425 °C) was also slightly higher than in the previous experiment. Under these conditions, the catalyst appears to be in a high activity mode for most of the cycle with sudden drops in activity.

The main features of this type of oscillation are indicated by the letters (a–c) on the CO_2 signal in Fig. 3 and they can be explained by a modification of the scheme just given.

(i) Between points (a and b), the surface becomes oxidised and the rate of methane oxidation increases, as before.

(ii) At point (b), the oxygen signal has dropped to a value close to zero, showing that the reaction is using up all of the oxygen supply. The rate of methane oxidation then becomes constant between points (b and c). It might appear that a steady state has been established in which the rate of consumption of oxygen in the methane oxidation reaction is equal to the rate of supply of gas phase oxygen. However, there appears to be a small imbalance between these two rates that leads to a net removal of oxygen from the oxide. This is thought to produce a gradual reduction in the thickness of the oxide layer until the surface suddenly reverts to palladium metal at point (c). However, the sudden drop in activity could also be consistent with the model proposed in [28], in which the oxide exists as islands and methane oxidation occurs predominantly at the metal/oxide interface.

2.4. Variation of oscillation frequency with temperature

The frequencies of the oscillations observed by Zhang et al. [28] were found to increase markedly with the temperature of the catalyst, and this enabled activation energies to be calculated by plotting the logarithm of the mean cycle time against reciprocal temperature. The values measured for the first and second types of oscillation were 194 ± 6 and 68 ± 6 kJ mol^{-1}, respectively. The second value compares well with the activation energy of 73.2 kJ mol^{-1} calculated by Lyubovski and Pfefferle for reaction over palladium oxide [45], but the activation energy measured for the first type of oscillation is significantly higher than the value of 157.3 kJ mol^{-1} obtained by Lyubovski and Pfefferle for reaction over the reduced surface of their catalyst. Also, their measurements on the reduced surface were made at much higher temperatures than those used here, and it must be concluded that these particular activation energies relate to quite different processes.

It is evident that different processes are controlling the cycle time for the two types of oscillation. In the first type, the catalyst appears to be in the reduced state for most of the time and the rate of oxidation of palladium may therefore be the controlling factor. The opposite is true of the second type of oscillation, where the catalyst is in the oxidised state for most of the time and the rate of reduction of the oxide appears to be the controlling factor. It is not entirely clear why the activation energy for this latter process should be equal to the activation energy for methane oxidation over palladium oxide, although the two processes are necessarily linked. As we have already seen, the rate at which the oxide is reduced depends upon small differences between the rate of oxygen uptake and the rate of oxygen depletion resulting from oxidation of methane. It may be that the slow formation of small Pd nuclei is the limiting factor here.

3. Methane oxidation over nickel

3.1. Mechanism for production of CO and H_2

The reaction of methane and oxygen over nickel can result in either partial oxidation to carbon monoxide and hydrogen or full oxidation to carbon dioxide and water. Complete oxidation is expected to be the main reaction occurring over oxide surfaces whereas production of CO and H_2 is more likely to occur over the metal surface. It has been suggested [12,40] that the production of CO and H_2 is a secondary reaction resulting from the steam reforming of methane according to the equation:

$$CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g) \qquad (16)$$

However, this reaction must necessarily go through similar adsorption/desorption steps to those of the basic reactions (1) and (2) and it cannot therefore be regarded as requiring a separate reaction pathway. The primary reaction steps that produce CO and H_2 would still be reactions (7), (8) and (10).

Tulenin et al. [34,35] have studied methane oxidation over a mixed oxide catalyst (Nd_2O_3/MgO) in the presence of a Ni/Cr alloy wire. They found that CO and H_2 could be produced at much lower temperatures than was possible when only the Ni/Cr wire was present in the system. To explain this result, they proposed that methane activation was taking place over the oxide surface, probably by production of methyl radicals that then migrated to the nickel surface for further reaction. If this explanation is correct, it follows that the dissociative adsorption of methane must be the rate-determining process when the oxide catalyst is absent. Activation energies for adsorption of methane on nickel single crystal surfaces have been found to be 56 kJ mol^{-1} for Ni(1 1 1) and Ni(1 1 0), and 25 kJ mol^{-1} for Ni(1 0 0) [40–42] and these values are sufficiently large to make it possible that dissociative adsorption of methane is the rate-determining process.

3.2. Oscillations occurring during methane oxidation

Zhang et al. [32,33,37] and Tulenin et al. [36] have studied oscillations over nickel catalysts using quadrupole mass spectrometers to identify the various products formed. Fig. 4 shows the oscillations observed by Zhang et al. [32]

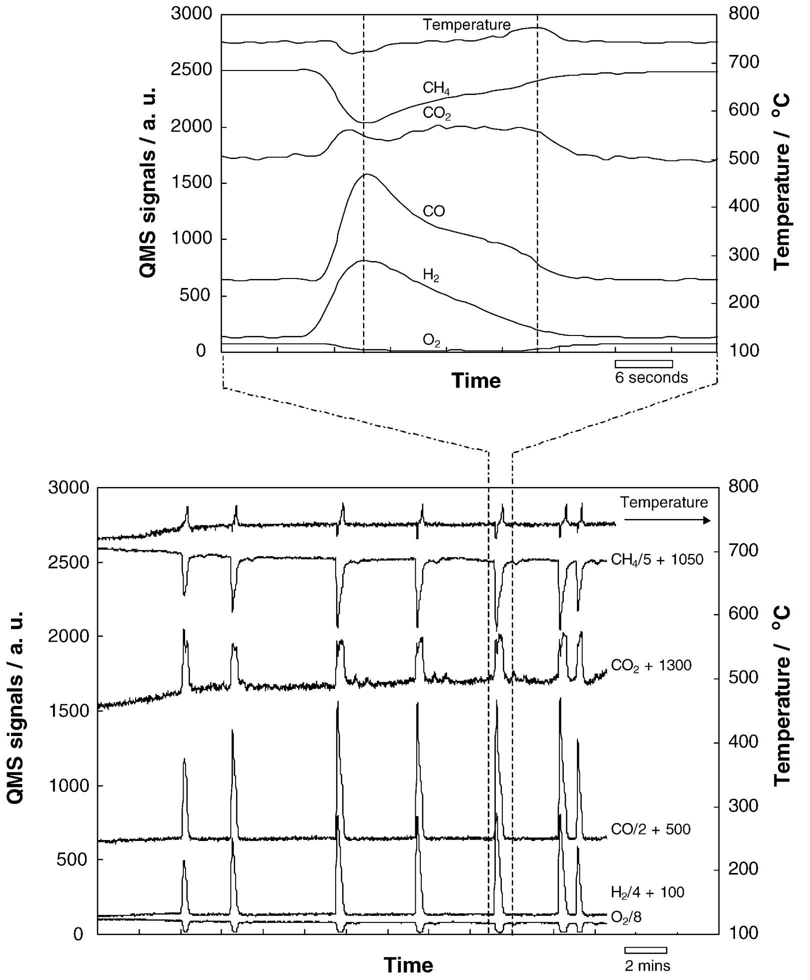

Fig. 4. Oscillations over nickel foil. Ar:CH_4:O_2 = 30:22.5:7.5 cm^3 min^{-1}; reactor temperature = 748 °C.

when a mixture of argon, methane and oxygen (methane/oxygen ratio 3:1) was passed over a nickel foil at a temperature of 748 °C. Sudden bursts of activity can be seen in which the main products are CO, CO_2 and H_2. The water signal is not shown in this figure because its response tended to be sluggish due to adsorption on the walls of the system. The bursts came at irregular intervals at first, but after 25 min or so the oscillations became more regular. One burst of activity has been enlarged to show in detail the way in which the various signals vary with time. The CO and H_2 signals both show a fairly sharp peak followed by a pronounced shoulder, which may indicate that two different processes are occurring. The CO_2 signal responds in a different way from the CO and H_2 signals in that it peaks slightly before the CO and H_2 signals do and there is an ill-defined secondary peak that does not occur with the other two gases. The existence of a two-stage process is supported by the variation in temperature, which shows a pronounced dip corresponding to the CO and H_2 peaks, followed by a rise above the base temperature at the point where the CO_2 signal is still high but the CO and H_2 signals are almost back to their baselines.

The initial drop in temperature seems to indicate that the overall reaction occurring at this stage in the cycle is endothermic. One possible endothermic reaction is the steam reforming of methane reaction (16), but this reaction requires steam, which must come from the highly exothermic reaction (1). The net result would be to generate heat, not to absorb it. Another endothermic reaction that produces CO and H_2 is the reduction of nickel oxide according to the equation:

$$NiO(s) + CH_4(g) \rightarrow Ni(s) + CO(g) + 2H_2(g) \qquad (17)$$

The heat of formation of NiO at 298 K is -239.7 kJ mol^{-1} and the reduction of this oxide would be more than sufficient to make the overall process endothermic.

A similar type of oscillation has been observed by Tulenin et al. [36] using a Ni/Cr alloy wire as catalyst. However, there are significant differences between the two studies. In particular Tulenin et al. did not observe a dip in temperature corresponding to the CO and H_2 peaks. By calibrating the mass spectrometer signals for reactants and products Tulenin et al. were able to calculate the amount of oxygen deposited on the catalyst at any given time during the reaction. Their results, shown diagrammatically in Fig. 5, indicate that the oxygen stored on their catalyst was at a minimum when the CO and H_2 signals were at their maximum values and that fairly rapid oxidation of the catalyst occurred as the CO and H_2 signals decayed back to their baselines. During the period of low activity, there was a gradual decrease in the oxygen stored on the catalyst, showing that the oxide layer was being reduced. This latter process may be similar to that discussed for palladium in Section 2.3, where it was attributed to an imbalance between the rates of oxygen removal through methane oxidation and the rate of re-oxidation.

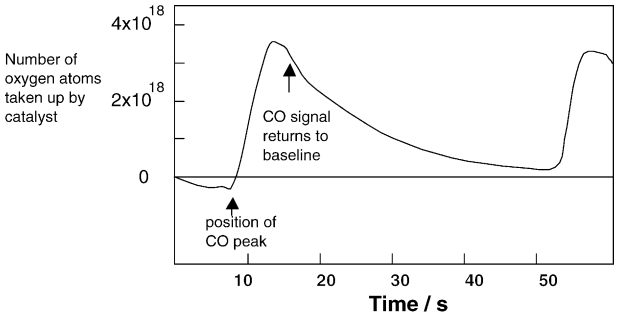

Fig. 5. Oxygenstored in Ni–Cr alloy catalyst as a function of time (CH_4:O_2:Ar = 75:20:5; flow rate = 40 cm^3 min^{-1}; furnace temperature = 750 °C) [36].

There appears to be a conflict between the two studies about the stage during the cycle at which reduction of the oxide occurs. The results of Tulenin et al. indicate that reduction occurs gradually during the period of low activity whereas Zhang et al. have provided evidence that reduction occurs at the start of a burst of high activity. In the work of Zhang et al. it is important to note that nearly all of the oxygen supply was used up by the reaction, even during periods of low activity when CO_2 and H_2O were the main products produced. Therefore, very little oxygen remained in reserve to feed the oscillations and the oxygen signal actually went to zero during bursts of high activity, indicating that the gas supply was unable to provide all of the oxygen that was needed. By contrast, the oxygen signal in the experiments of Tulenin et al. always remained high.

It is also possible that the (1 0 0), (1 1 0) and (1 1 1) crystal faces of nickel behave differently during methane oxidation. Only certain parts of the surface seem to undergo cycles of oxidation and reduction. For example, in the work of Zhang et al. the CO_2 signal always has a large, constant component that must come from parts of the surface where there are no cyclic changes in the oxide layer.

Further evidence that reduction of the oxide may be occurring during CO and H_2 evolution comes from experiments in which the methane supply has been temporarily stopped for a few minutes. Data obtained when a nickel wire was used as the catalyst are shown in Fig. 6 [33]. It can be seen that there was an almost instantaneous evolution of CO and H_2 after the methane supply was restored, which resulted in peaks that were much larger than those normally obtained when the methane supply had not been interrupted. This was accompanied by a fall in the temperature showing that the overall process was endothermic. Although there was a large initial drop in the oxygen signal, most of this drop could be attributed to the resumption of a constant rate of CO_2 and H_2O production, and only a small component was associated with the CO oscillations. It is significant that this oscillating component was the same size as that observed in later, normal oscillations.

It is surprising that a nickel catalyst that has been exposed to oxygen for 8 min in the absence of methane can

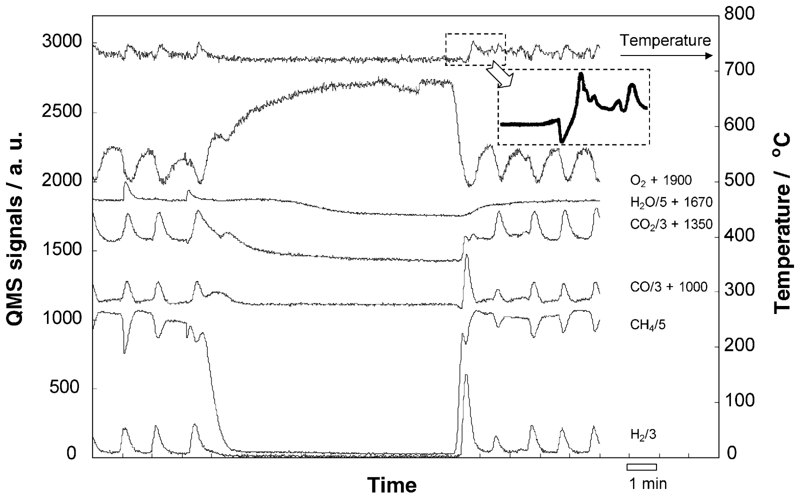

Fig. 6. Oscillatory behaviour over nickel wire before and after methane supply was temporarily switched off. Ar:CH_4:O_2 = 30:22.5:7.5 cm^3 min^{-1}; reactor temperature = 734 °C when reaction was terminated.

immediately start catalysing the production of CO and H_2 when the methane supply is restored. Such a surface would be expected to have a thick oxide layer and the nature of the sites where reaction can occur to give CO and H_2 is not entirely clear. The oxide is likely to form an epitaxial layer initially, in registry with the nickel surface, but strains will develop as it grows thicker and there must come a point where oxide crystallites with the normal bulk NiO structure will be formed. Metal sites suitable for production of CO and H_2 may be exposed during this process. As the reaction proceeds, these metal nuclei would be expected to grow until the whole of the oxide layer had been reduced to the metal.

3.3. The effect of oxygen concentration on the oscillations

Fig. 7 shows the changes that occur in the temperature, waveform, frequency and amplitude of oscillations taking place over nickel foil when the O_2/CH_4 ratio was increased from 0.03 to 1.5 at a constant reactor temperature and flow rate [32]. It can be seen that there is a sudden change in the mode of oscillation at an O_2/CH_4 ratio of approximately 0.5. Below this value, the frequency of the oscillations was high and roughly constant. There was also a significant drop in temperature that coincided with the CO, CO_2 and H_2 peaks, and this was followed by a rise in temperature. Both the temperature changes and the waveforms are similar to those shown in Fig. 4. At an O_2/CH_4 ratio ≥ 0.5, the oscillations change their character entirely: the frequency of the oscillations becomes much lower and the initial fall in temperature is no longer observed. The CO_2 peaks are also much stronger than they were at lower oxygen concentrations. It may be that this represents a changeover to the type of behaviour observed by Tulenin et al. [36], although the O_2/CH_4 ratio that they used was only 0.266.

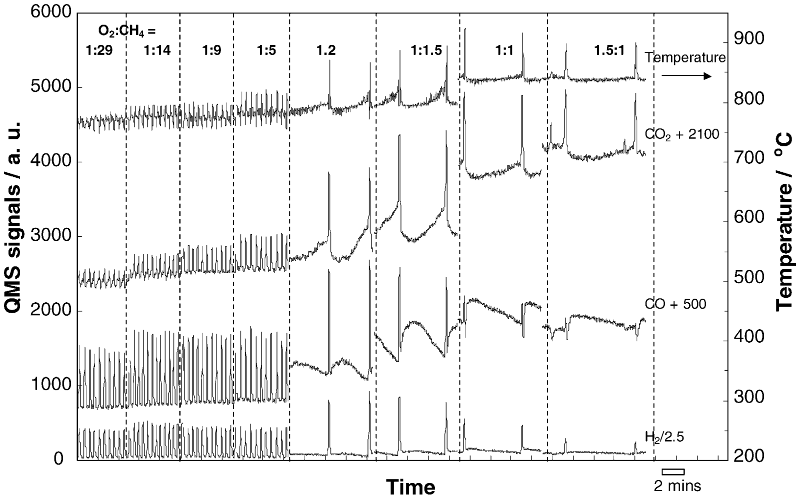

Fig. 7. Oscillations over nickel foil at different oxygen concentrations. Ar:CH_4:O_2 ranging from 30:29:1 to 30:12:18 cm^3 min^{-1}; reactor temperature = 785 °C.

4. Methane oxidation over cobalt

4.1. Oscillations occurring over cobalt foil during methane oxidation

Oscillations with cobalt foil have been observed by Zhang et al. [18] at temperatures in the range of 700–870 °C and for gas mixtures with methane/oxygen ratios ranging from 29:1 to 2:1. There was normally an induction period of about 1–2 min before oscillations commenced and another 5–10 min was required before the oscillations became stable and regular.

Some typical results obtained at the lower end of the temperature range with a methane/oxygen ratio of 5:1 are shown in Fig. 8. In many respects, the oscillations are similar to those shown in Fig. 4 for nickel but there are also some significant differences. For example, the CO and H_2 peaks appear to be made up of three components, whereas only two could be distinguished for nickel. The CO_2 signal also behaves quite differently, showing a sharp peak, corresponding to the first component, which is similar to the peak found with nickel, but then falling away steeply below the CO_2 baseline and only coming back up to the baseline after the burst of high activity was over.

The temperature dropped sharply as soon as the CO and H_2 signals began to rise, and three components could be distinguished, mirroring the structure found with the CO and H_2 signals. The drop in temperature indicated that all three components resulted from endothermic reactions, presumably the reduction of cobalt oxides to give CO and H_2. Whether or not these reactions were occurring on different crystal faces is not clear. The temperature finally rose to a peak at the point where the CO and H_2 signals had returned to their baselines, and this is probably an indication that re-oxidation of the catalyst was beginning to occur.

It should be noted that the strength of the H_2O signal followed changes in the CO and H_2 signals and not that of the CO_2 signal. This shows that some of the methane must be converted to CO and H_2O according to the equation:

$$CH_4(g) + \tfrac{3}{2}O_2(g) \rightarrow CO(g) + 2H_2O(g) \qquad (18)$$

This reaction is much more exothermic than the reaction producing CO and H_2 and makes it even more difficult to explain drops in temperature other than by reduction of the oxide.

As with the nickel experiments, most of the oxygen in the supply line was used up by a non-oscillating reaction producing CO_2 and H_2O and there was insufficient oxygen left to account for the rises in the CO and H_2O signals. For example, in Fig. 8, the oxygen signal dropped by approximately 100 units during a period of high activity whereas the CO and H_2O signals increased by approximately 1100 and 240 units, respectively. Thus, the rate of uptake of oxygen from the gas supply remained almost constant while the production of oxygen-containing products varied greatly. This shows that oxygen must be alternately stored and released from the catalyst surface. Reduction of the oxide seems to occur during bursts of high activity and re-oxidation then occurs during periods of low activity.

A rough estimate of the percentage of the surface that undergoes reduction to metallic cobalt can be obtained by assuming that the drop in the CO_2 signal, occurring just after the CO and H_2 signals have reached their peaks, is proportion to the amount of oxide that has been reduced. This is based on the observation that most of the CO_2 appeared to be generated over the oxide surface. The minimum value reached by the CO_2 signal was about 69% of its value prior to the burst of high activity, which indicates that approximately one third of the surface underwent reduction. Re-oxidation seems to begin soon after the CO and H_2 signals have peaked because there is a gradual increase in the CO_2 signal from this point onwards.

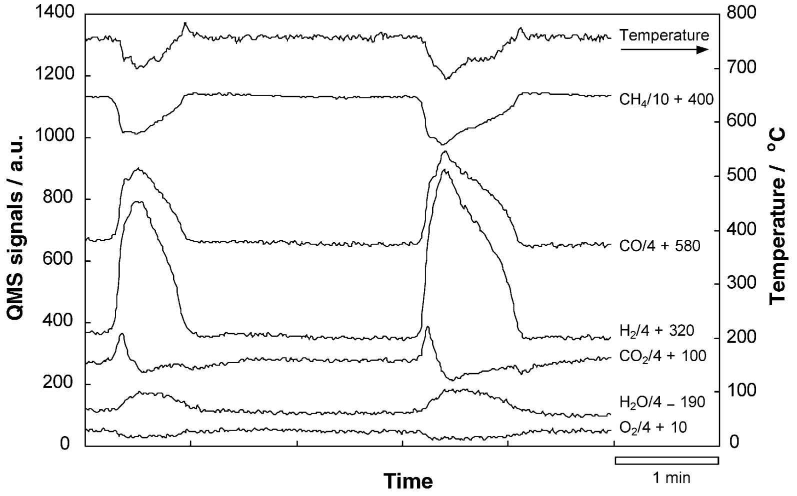

Fig. 8. Oscillations of methane oxidation over cobalt foil in the temperature range of 700–784 °C; CH_4:O_2:Ar = 30:25:5 cm^3 min^{-1}.

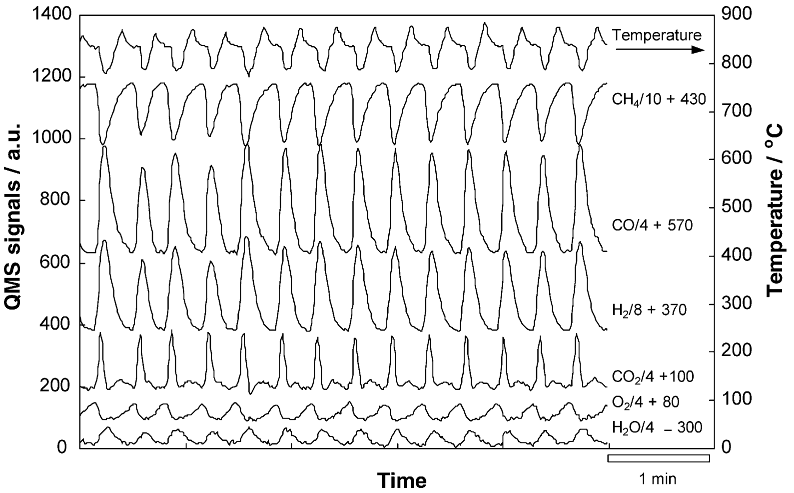

Fig. 9. Oscillations of methane oxidation over cobalt foil in the temperature range of 785–869 °C; CH_4:O_2:Ar = 30:25:5 $cm^3 min^{-1}$.

Fig. 9 shows the effects of increasing the reactor temperature by 85 °C or so. It can be seen that the frequency of the oscillations has increased enormously and the long periods of constant, low activity have almost disappeared. The periods of high activity have also been shortened from 60 to 15 s. Thus, both processes have been accelerated, but at different rates. This can be explained if the activation energy for the low activity reaction (assumed to be oxidation of cobalt metal) is greater than that for the high activity reaction (assumed to be reduction of the oxide by methane).

The temperature profile shown in Fig. 9 has a much more pronounced peak than the one shown in Fig. 8, and this peak occurs slightly earlier in the cycle, before the CO and H_2 signals have returned to their baselines. Although it coincides with a subsidiary peak in the CO_2 signal, this peak is too small to account for the whole of the rise in temperature, the main part of which must be attributed to re-oxidation of the surface.

4.2. Effects of interrupting the oxygen supply

Zhang et al. [18] found that there was a final burst of high activity when the oxygen supply was turned off, after which all oscillations ceased. When the oxygen supply was restored after a period of a few minutes the results shown in Fig. 10 were obtained. It is convenient to divide these results into the four stages outlined below.

Stage 1. There was an initial surge in the oxygen signal as the supply valve was opened and this coincided with a large CO_2 peak, a smaller CO peak, and a large rise in temperature. Significantly, the changes in the H_2 and H_2O signals were quite small, showing that the CO_2 and CO peaks arose mainly from oxidation of carbon already deposited on the surface and not from methane oxidation. Most of the sharp dip in the methane signal can be attributed to the temporary

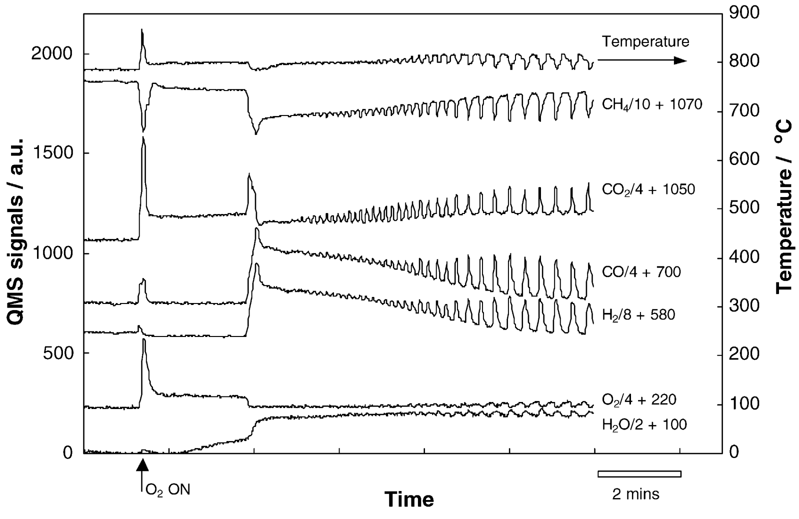

Fig. 10. Effects of turning oxygen supply off and on. Ar:CH_4:O_2 = 30:25:5 $cm^3 min^{-1}$; temperature ranging from 785 to 869 °C.

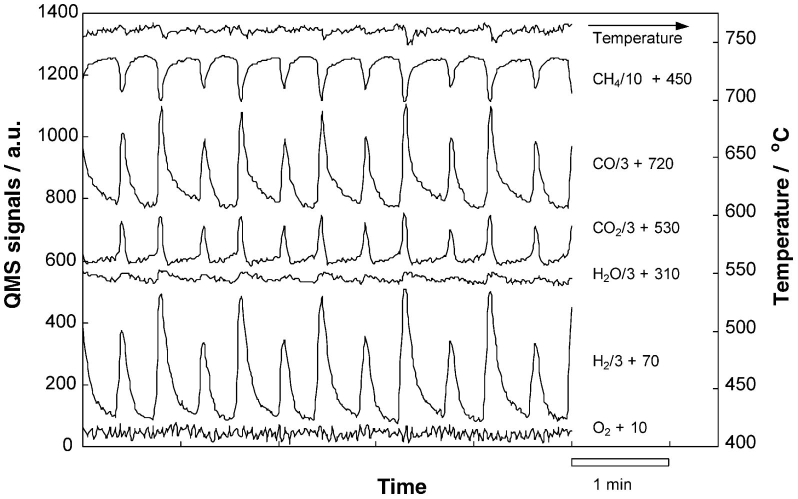

Fig. 11. Oscillations of methane oxidation over cobalt wire in the temperature range of 750–765 °C; Ar:CH_4:O_2 = 30:29:1 $cm^3\ min^{-1}$.

dilution of methane in the flow line, caused by the oxygen surge and the very large CO_2 peak.

Stage 2. The burst of high activity was followed by a period of lower activity, lasting slightly more than 2 min, during which there was a drop in the methane signal and the CO_2 signal remained at a constant value well above its baseline. There was also a steady rise in the H_2O signal. These results indicated that oxidation of methane to CO_2 and H_2O was taking place. However, calculations show that the fall in the oxygen signal was slightly greater than would have been expected if this was the only reaction occurring and it is possible that some oxidation of the surface was also taking place.

Stage 3. Stage 2 was followed by sharp rises in the CO, CO_2, H_2 and H_2O signals and a sharp fall in the CH_4 signal. The temperature also dropped by 37°C. The decrease in the oxygen signal was very small and was insufficient to account for the rise in the CO and CO_2 signals. On the basis of the discussion given in Section 4.1, the process occurring can be attributed to the reduction of cobalt oxide to the metal.

Stage 4. Up to this point, the behaviour of the system was similar to that observed in Fig. 8, apart from the initial oxidation of surface carbon. However, unlike the results shown in Fig. 8, the CO and H_2 peaks were followed by lengthy tails on which small, high frequency oscillations began to develop. All of the oxygen was consumed and a rough calculation[1] shows that approximately 50% of this oxygen was used up in producing CO_2 and H_2O, and about 40% went into CO production. This leaves a residual 10% that is available for re-oxidation of the surface, although this figure will be subject to very large error.

The long tails that follow the CO and H_2 peaks show that the re-oxidation process was much slower than it was in the experiment shown in Fig. 8. This could be the result of changes to the surface structure of the catalyst. After many oxidation/reduction cycles SEM photographs show that the surface of the catalyst can become quite rough and some consolidation due to crystal growth may have taken place during the period when the oxygen supply was turned off. Similar tails have often been observed near the start of experiments when the system has not had time to settle down into regular oscillations. This gives some support to the idea that the rate of re-oxidation may depend upon the roughness of the surface.

The high frequency oscillations appear to be the result of rapid oxidation/reduction cycles that were confined initially to small areas of the surface. The oscillations in the CO, CO_2 and H_2 signals slowly increased in strength until they were comparable in size to the large rises observed at the start of Stage 3, showing that the phenomenon had then spread to most of the area on which reduction had occurred initially. As mentioned in the previous paragraph, the redox process increases the roughness of the surface and this may help to explain the gradual rise in the proportion of the surface that takes part in the high frequency oscillations.

4.3. Bi-model oscillations

When very high methane/oxygen ratios were used there was a tendency for bi-modal oscillations to occur in which the CO_2, CO and H_2 signals showed alternate large and small peaks. This behaviour is shown in Fig. 11 for reaction occurring over a cobalt wire with a methane/oxygen ratio of 29:1. The simplest explanation for these results is that unsynchronised oscillations are occurring on two different parts of the surface. To agree with the observations the two oscillations would need to have exactly the same frequency.

It has also been observed in numerous experiments that the smaller peaks tend to come approximately, but not exactly, at the midpoint between two large peaks. For example, in

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[1] These calculations have been made using relative sensitivity factors (N_2 = 1.00) for O_2, H_2O, CO and CO_2 of 0.92, 1.17, 0.95 and 0.63 respectively.

Fig. 11, a small peak occurs 27 s after a large peak whereas the time interval between a small peak and a large peak is 24 s. In some other experiments, the time intervals were reversed, the time interval between a large and a small peak being slightly shorter than that between a small and a large peak. This shows that the relationship between the two oscillations is not entirely random. It may be that oscillations on neighbouring areas tend to synchronise and coalesce when the phase difference between them is small, and only oscillations where there is a large phase difference tend to survive as separate entities.

5. Summary and conclusions

Oscillations in the rate of oxidation of methane over metal catalysts occur when the surface of the catalyst undergoes cycles of oxidation and reduction. Only certain parts of the surface participate in the oxidation/reduction cycle, other parts apparently remaining permanently in the oxide state. For example, in experiments with a cobalt foil approximately one third of the surface was found to be responsible for all the oscillations.

Reactions over oxide surfaces produce mainly CO_2 and H_2O whereas reactions over metal surfaces can produce either CO_2 and H_2O (palladium) or predominantly CO and H_2 (nickel and cobalt). The switch from an oxide surface to a metal one often takes place quite suddenly and the events that trigger this process are not fully understood.

With palladium there appeared to be a gradual reduction in the thickness of the oxide layer until the underlying metal was suddenly exposed. This caused a sharp drop in the CO_2 and H_2O signals because the metal was a poorer catalyst than the oxide. Two modes of oscillation have been observed: (a) in the first mode, the catalyst was in a low activity state for most of the time with periodic bursts of high activity as the oxide layer slowly built up, whereas (b) in the second mode, the catalyst was in the oxide state for most of the time with sudden falls in activity when the oxide was suddenly reduced to the metal.

With nickel and cobalt the reduction of the oxide layer was accompanied by a sharp increase in the CO and H_2 signals. There was also a drop in temperature, showing that the reaction producing CO and H_2 was endothermic. The reduction process seemed to be triggered when the oxide layer reached a critical thickness. It has been proposed that this could be the point where the surface oxide layer re-crystallised to form crystallites of bulk oxide, thereby exposing some of the underlying metal atoms.

It was found that a nickel catalyst that had been exposed to oxygen for 8 min in the absence of methane could start producing CO and H_2 almost immediately when the oxygen supply was restored. This surprising result showed that a surface that had been exposed to pure oxygen still contained metal sites where dissociative adsorption of methane could occur, leading to reduction of the oxide.

The reverse experiment, closing off the oxygen supply for a few minutes, produced quite a different result with a cobalt foil. Oscillations did not start until 2 min after the oxygen supply was restored and when they did occur the CO and H_2 peaks had long tails, on to which high frequency oscillations were superimposed. Some annealing of the surface is thought to have occurred while the oxygen supply was closed and this has caused the rate of re-oxidation of the surface to become much slower; hence, the long tails on the CO and H_2 peaks. The high frequency oscillations seem to result from a redox process that occurred initially on only a small part of the surface and then gradually spread to other regions.

Bimodal oscillations in the CO, CO_2 and H_2 peaks were observed over a cobalt wire and these were ascribed to unsynchronised oscillations on two different parts of the surface.

References

[1] R.F. Hicks, M.L. Young, R.G. Lee, H. Qi, J. Catal. 122 (1990) 279.
[2] R.F. Hicks, H. Qi, M.L. Young, R.G. Lee, J. Catal. 122 (1990) 295.
[3] T.R. Baldwin, R. Burch, Appl. Catal. 66 (1990) 337.
[4] T.R. Baldwin, R. Burch, Appl. Catal. 66 (1990) 359.
[5] R. Burch, F.J. Urbano, Appl. Catal. A: Gen. 124 (1995) 121.
[6] S.H. Oh, P.J. Mitchell, R.M. Sievert, J. Catal. 132 (1991) 287.
[7] S.H. Oh, P.J. Mitchell, Appl. Catal. B: Environ. 5 (1994) 165.
[8] R.J. Farrauto, M.C. Hobson, T. Kennelly, E.M. Waterman, Appl. Catal. A: Gen. 81 (1992) 227.
[9] R.J. Farrauto, J.K. Lambert, M.C. Hobson, E.M. Waterman, Appl. Catal. B: Environ. 6 (1995) 263.
[10] P. Briot, M. Primet, Appl. Catal. 68 (1991) 301.
[11] E. Garbowski, C. Feumi-Jantou, N. Mouaddib, M. Primet, Appl. Catal. A: Gen. 109 (1994) 277.
[12] N. Mouaddib, C. Feumi-Jantou, E. Garbowski, M. Primet, Appl. Catal. A: Gen. 87 (1992) 129.
[13] R.J. Berger, G.B. Marin, Ind. Eng. Chem. Res. 38 (1999) 2582.
[14] E. Ruckenstein, Y.H. Hu, Appl. Catal. A: Gen. 183 (1999) 85.
[15] A. Slagtern, H.M. Swaan, U. Olsbye, I.M. Dahl, C. Mirodatos, Catal. Today 46 (1998) 107.
[16] V.R. Choudhary, A.M. Rajput, B. Prabhakar, A.S. Mamman, Fuel 77 (1998) 1803.
[17] F. van Looij, E.R. Stobbe, J.W. Geus, Catal. Lett. 50 (1998) 59.
[18] X.L. Zhang, C.S-M. Lee, D.M.P. Mingos, D.O. Hayward, Appl. Catal. A: Gen. 248 (2003) 129.
[19] P.D.F. Vernon, M.L.H. Green, A.K. Cheetham, A.T. Ashcroft, Catal. Lett. 6 (1990) 181.
[20] L.D. Schmidt, D.A. Hickman, J. Catal. 138 (1992) 267.
[21] D.A. Hickman, E.A. Haufear, L.D. Schmidt, Catal. Lett. 17 (1993) 223.
[22] P.M. Tornianan, X. Chu, L.D. Schmidt, J. Catal. 146 (1994) 1.
[23] D. König, W.H. Weber, B.D. Poindexter, J.R. Mcbride, G.W. Graham, K. Otto, Catal. Lett. 29 (1994) 329.
[24] G.W. Graham, D. König, B.D. Poindexter, J.T. Remillard, W.H. Weber, Top. Catal. 8 (1999) 35.
[25] Y.Q. Deng, T.G. Nevell, Faraday Discuss. 105 (1996) 33.
[26] Y.Q. Deng, T.G. Nevell, J. Mol. Catal. A 142 (1999) 51.
[27] U.S. Ozkan, M.W. Kumthekar, G. Karakas, J. Catal. 171 (1997) 67.
[28] X.L. Zhang, C.S.-M. Lee, D.M.P. Mingos, D.O. Hayward, Appl. Catal. A: Gen. 240 (2003) 183.
[29] Y.H. Hu, E. Ruckenstein, Ind. Eng. Chem. Res. 37 (1998) 2333.
[30] Y.H. Hu, E. Ruckenstein, Ind. Eng. Chem. Res. 38 (1999) 1742.

[31] J.G. Cohn, Ind. Eng. Chem. Res. 38 (1999) 1740.

[32] X.L. Zhang, D.O. Hayward, D.M.P. Mingos, Catal. Lett. 83 (2002) 149.

[33] X.L. Zhang, D.O. Hayward, D.M.P. Mingos, Catal. Lett. 86 (2003) 235.

[34] Yu.P. Tulenin, M.Yu. Sinev, V.V. Savkin, V.N. Korchak, Stud. Surf. Sci. Catal. 110 (1997) 757.

[35] Yu.P. Tulenin, M.Yu. Sinev, V.V. Savkin, V.N. Korchak, Y.B. Yan, Kinetika i Kataliz (Russ. Kinet. Katal.) 40 (1999) 405.

[36] Yu.P. Tulenin, M.Yu. Sinev, V.V. Savkin, V.N. Korchak, Catal. Today 91–92 (2004) 155.

[37] X.L. Zhang, D.M.P. Mingos, D.O. Hayward, Catal. Lett. 72 (2001) 147.

[38] A. Frennet, Catal. Rev. Sci. Eng. 10 (1974) 37.

[39] T. Engel, G. Ertl, Adv. Catal. 28 (1979) 1.

[40] T.P. Beebe, D.W. Goodman, B.D. Kay, J.T. Yates, J. Chem. Phys. 87 (1987) 2305.

[41] M.B. Lee, Q.Y. Yang, S.L. Tang, S.T. Ceyer, J. Chem. Phys. 85 (1986) 1693.

[42] I. Alstrup, I. Chorkendorff, S. Ullmann, Surf. Sci. 234 (1990) 79.

[43] F. Solymosi, A. Erdohelyi, J. Cserenyi, A. Felvegi, J. Catal. 147 (1994) 272.

[44] M. Valden, J. Pere, N. Xiang, M. Pessa, Chem. Phys. Lett. 257 (1996) 289.

[45] M. Lyubovski, L. Pfefferle, Catal. Today 47 (1999) 29.

[46] K.i. Fujimoto, F.H. Ribeiro, M. Avalos-Borja, E. Iglesia, J. Catal. 179 (1998) 431.

[47] C.A. Muller, M. Maciejewski, R.A. Koeppel, Catal. Today 47 (1999) 245.

[48] J. Au-Yeung, K. Chen, A.T. Bell, E. Iglesia, J. Catal. 188 (1999) 132.