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Non-steady activity during methane combustion over Pd/Al_2O_3 and the influences of Pt and CeO_2 additives

Youquan Deng, Thomas G. Nevell*

Centre for Chemistry, School of Pharmacy and Biomedical Sciences, University of Portsmouth,
St. Michael's Building, White Swan Road, Portsmouth PO1 2DT, UK

Abstract

Methane combustion over Pd/Al_2O_3 catalysts with and without added Pt and CeO_2 in both oxygen-rich and methane-rich mixtures at temperatures in the range 250–520°C has been investigated using a temperature-programmed reaction procedure with on-line gas analysis (FTIR). During the temperature loop under oxygen-rich conditions, there was an appreciable hysteresis in the activity of unmodified Pd/Al_2O_3, which was greatly enhanced over $Pd–Pt/Al_2O_3$. Over both catalysts the hysteresis was reversed under slightly methane-rich atmospheres, and as temperature was reduced, a sudden collapse or fluctuations in activity were shown respectively over $Pd–Pt/Al_2O_3$ and Pd/Al_2O_3. Such non-steady behaviour was almost eliminated over $Pd/Al_2O_3–CeO_2$. Under a very narrow range of conditions and over a Pd/Al_2O_3 packed bed, oscillation of methane combustion was observed. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Methane oxidation; Pd; Pt; CeO_2; Oscillations

1. Introduction

The non-steady behaviour [1,2] in activities of supported noble-metal catalysts used in methane oxidation has received little attention, even though the oxidation/combustion of methane over the supported and unsupported palladium catalysts has been the subject of considerable number of recent publications [3–12]. Some interesting phenomena have been reported, including structure sensitivity [3], hysteresis in the activity of Pd/Al_2O_3 attributed to the different temperatures required for the decomposition of PdO and reoxidation of Pd [4,5], strong influence of oxygen-to-methane ratio on activity and selectivities [6], and an increase in activity when PdO, supported on low surface area α-Al_2O_3, is reduced to Pd [13]. Recently, oscillations of methane oxidation under oxygen-deficient conditions were also revealed [8,14,15].

In this work, unusual phenomena associated with the temporal variations in activity during methane combustion over Pd/Al_2O_3 catalysts with and without modification by Pt or CeO_2 have been observed using a method of temperature-programmed methane oxidation (including temperature increasing and decreasing).

2. Experimental

Catalytically active precursors were deposited onto γ-alumina (BET surface area 170 $m^2\,g^{-1}$, Tianjin Chemicals) from aqueous solutions of ammonium tetrachloropalladate, ammonium tetrachloroplatinate

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*Corresponding author. Tel.: +44-1705-842119; fax: +44-1705-843565.

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and cerium(III) chloride (Johnson Matthey), giving catalysts Pd/Al_2O_3: palladium 15 mass%, area by CO adsorption 51 $m^2 g^{-1}$; $Pd–Pt/Al_2O_3$: palladium 7.5 mass%, platinum 7.5 mass%; $Pd/Al_2O_3–CeO_2$: palladium 15 mass%, CeO_2 15 mass%. The resultant catalyst precursors were dried (120°C, 2 h), crushed, sieved, and calcined in air (550°C, 5 h). This was followed by conditioning (CH_4 10% in air ca. 750°C, 0.5 h) and stabilising (air, 550°C, 5 h).

Gases used were methane (99.99%), nitrogen and oxygen (both 99.997%). The concentration of methane in reaction mixtures was held constant at 2.0% and the ratio of oxygen to methane was varied as required with a balance of nitrogen.

Bulk phases in the catalysts were determined by XRD measurement (Philips PW1710 BASED diffractometer with software PC-APD for data collection and calculation of average crystallite size).

A conventional flow reaction system operating at atmospheric pressure was used for the methane oxidation experiments. A U-type reactor (4 mm ID and 350 mm long) was mounted centrally in a vertical tube furnace heated by a programmable temperature controller. The temperature of 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, 40–60 mesh, 4 mm diameter×7 mm length). The CH_4, CO_2 and CO concentrations in the feed and exhaust gases were analysed on-line using an FTIR Spectrometer (ATI Mattson Research Series with WinFIRST software).

In temperature-programmed experiments, each conditioned catalyst sample was initially heated from room temperature in flowing air (100 cm^3/min) to 200°C and sustained for 0.5 h. The reactant gas mixture (100 cm^3/min) was then introduced and the temperature increased linearly (2.5 K/min) up to ca. 520°C. Heating was then stopped and the reactor was allowed to cool naturally (ca. 10 K/min) with the flowing reactant gas mixture maintained, until methane oxidation ceased at 230–240°C.

3. Results

3.1. XRD characterisation

Compared with the ASTM values (d (Å)=2.246, 1.945, 1.376 for Pd, and d=2.265, 1.962, 1.387 Å for Pt), the three strongest lines of the XRD spectra of conditioned Pd/Al_2O_3 and $Pd/Al_2O_3–CeO_2$, Fig. 1(a) and (c), corresponded to metallic palladium (d (Å)= 2.246, 1.947 and 1.376 for Pd/Al_2O_3; d=2.245, 1.944 and 1.376 for $Pd/Al_2O_3–CeO_2$). Since the d values and relative peak intensities of Pd and Pt were so close, only overlapped but strong and slightly broadened peaks (d (Å)=2.249, 1.948 and 1.377) were obtained in $Pd–Pt/Al_2O_3$ (Fig. 1(b)). There were no detected phases of palladium or platinum oxides, indicating that such oxides were mainly or completely converted to Pd and Pt metals during conditioning with 10% methane in air. Some of the α-alumina phase (d (Å)=2.548, 2.084 and 1.603) was found in Pd/Al_2O_3 and $Pd–Pt/Al_2O_3$, and the peaks of α-alumina were slightly stronger in the former. In $Pd/Al_2O_3–CeO_2$, the α-alumina phase was not detected and only weak and broad peaks were observed for CeO_2 phase (d (Å)=3.118 and 1.629; d=1.91 was strongly overlapped with the Pd peak of d=1.944). In comparison with the Pd/Al_2O_3, the peaks of palladium metal in $Pd/Al_2O_3–CeO_2$ were considerably reduced. This may be attributed to the interactions between Pd and CeO_2, resulting in the increased dispersion of the metal. These results also confirmed that Pd (in particular) and Pt accelerated the transformation of γ-Al_2O_3 to γ-Al_2O_3 at elevated temperature [16]. It appears that CeO_2 may stabilise the structure of γ-Al_2O_3.

The calculated Pd crystallite sizes were 73 nm for Pd/Al_2O_3 and 30 nm for $Pd/Al_2O_3–CeO_2$, respectively. Due to overlapping of Pd and Pt peaks, it was very difficult to calculate individual crystallite sizes for these metals but, on the basis of the strong and sharp peaks of Pd and Pt, the metal crystallites in $Pd–Pt/Al_2O_3$ may be larger than those in $Pd/Al_2O_3–CeO_2$ but smaller than those in Pd/Al_2O_3.

3.2. The temperature-programmed methane oxidation over Pd/Al_2O_3, $Pd–Pt/Al_2O_3$ and $Pd/Al_2O_3–CeO_2$

For making comparisons, the temperature-programmed methane oxidation reaction with 2% methane in air, i.e. a strongly oxidising environment, was conducted. The catalytic activities were indicated by the evolution of CO_2 from the outlet of the reactor during the reaction, Fig. 2. As the temperature was increased, methane oxidation started at ca. 250°C for

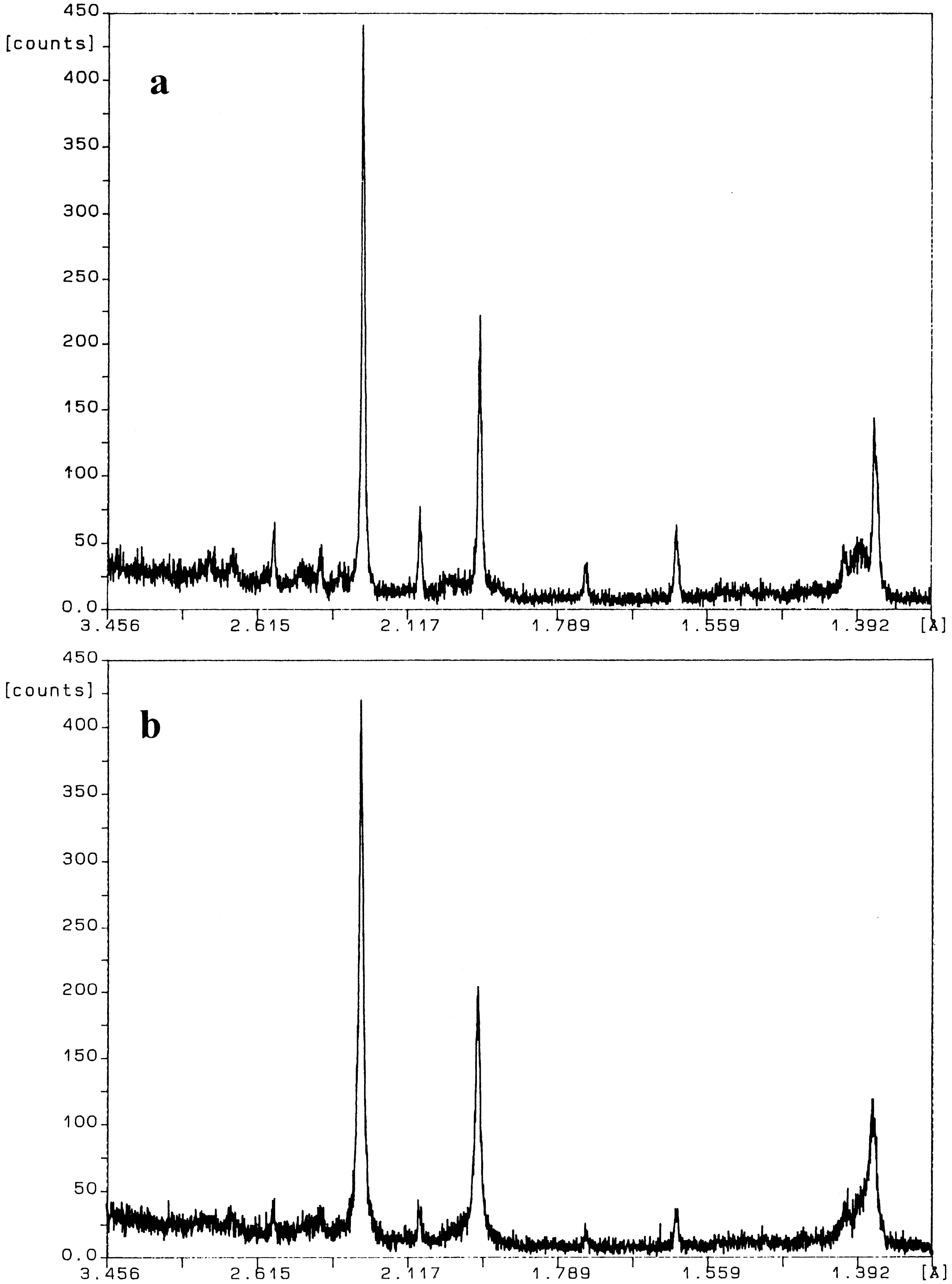

Fig. 1. XRD patterns of Pd/Al_2O_3, Pd–Pt/Al_2O_3 and Pd/Al_2O_3–CeO_2 conditioned in methane (10%)/air at 750°C: (a) Pd/Al_2O_3; (b) Pd–Pt/Al_2O_3; (c) Pd/Al_2O_3–CeO_2.

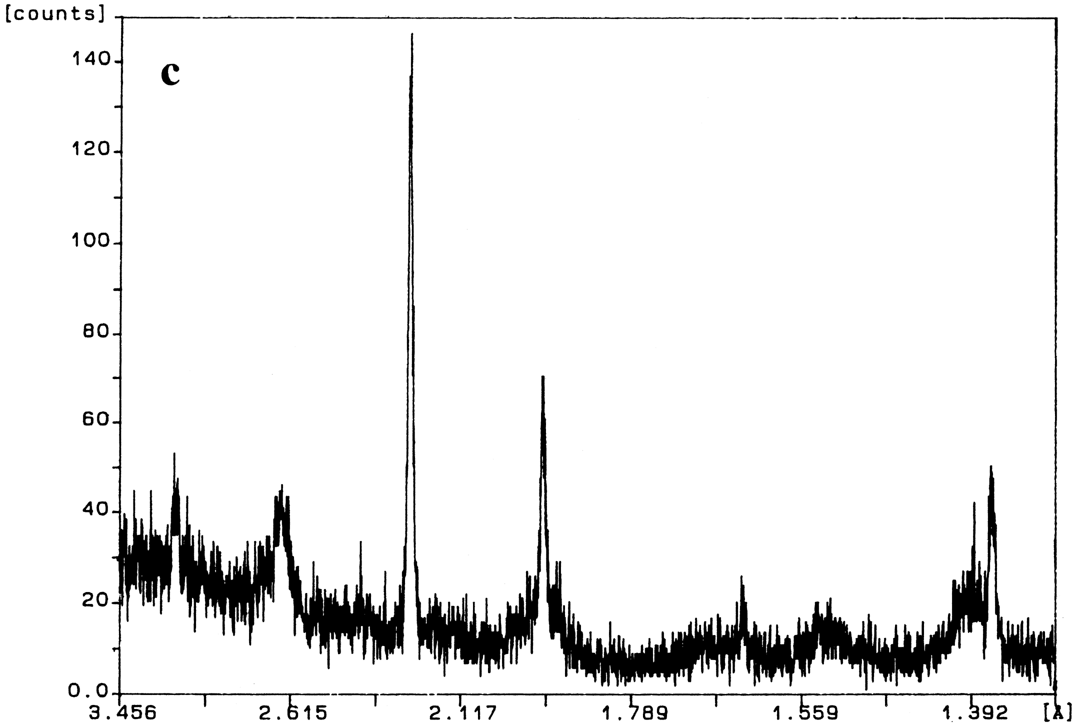

Fig. 1. (*Continued*)

Pd/Al_2O_3 and at ca. 270°C for $Pd–Pt/Al_2O_3$ and $Pd/Al_2O_3–CeO_2$. At low temperatures (<320°C), the activity of Pd/Al_2O_3 was higher than that of $Pd/Al_2O_3–CeO_2$ and considerably higher than that of $Pd–Pt/Al_2O_3$. At 490°C methane was almost completely converted to CO_2 for all three catalysts. When the temperature had reached 510–520°C, the reactor was allowed to cool with the flow of reactants maintained, and methane oxidation with temperature decreasing was carried out. Quite different changes in catalytic activity were observed, particularly in the temperature range 450–300°C. Respectively moderate and strong counterclockwise hysteresis in activity was observed for Pd/Al_2O_3 (Fig. 2(a)), and $Pd–Pt/Al_2O_3$ (Fig. 2(b)). For $Pd/Al_2O_3–CeO_2$, however, the activity trace, (Fig. 2(c)), was almost the same as that obtained as temperature was increased, i.e. there was almost no hysteresis.

Similar experiments involving temperature-programmed methane oxidation under reaction conditions as employed above but with gas mixtures of O_2/CH_4=1.7–1.8. The general trends of activity vs. temperature were almost independent of gas composition near this range and are shown, for the three catalysts, in Fig. 3. As the temperature was increased, the activities increased smoothly. After almost all oxygen was used (ca. 395°C for Pd/Al_2O_3, 410°C $Pd/Al_2O_3–CeO_2$ and 430°C $Pd–Pt/Al_2O_3$), the formation of CO_2 increased only slightly. When catalysts were allowed to cool from ca. 520°C with the flow of reactant mixture maintained, considerable differences in activity behaviour were observed. With Pd/Al_2O_3 (Fig. 3(a)), the activity decreased in an irregular way relative to the upward activity trace and an increased trend in activity was shown over 370–320°C. Also, the temperature of the catalyst bed fluctuated correspondingly, indicating time-dependent variations in reaction rate. With $Pd–Pt/Al_2O_3$, a similar fluctuation was also observed at an early stage of cooling (high temperature, Fig. 3(b)), but at ca. 420°C the activity collapsed suddenly and could not be recovered (except by heating in air again). Thus, a clockwise loop in activity was formed, which was reversed in comparison with oxygen-rich conditions.

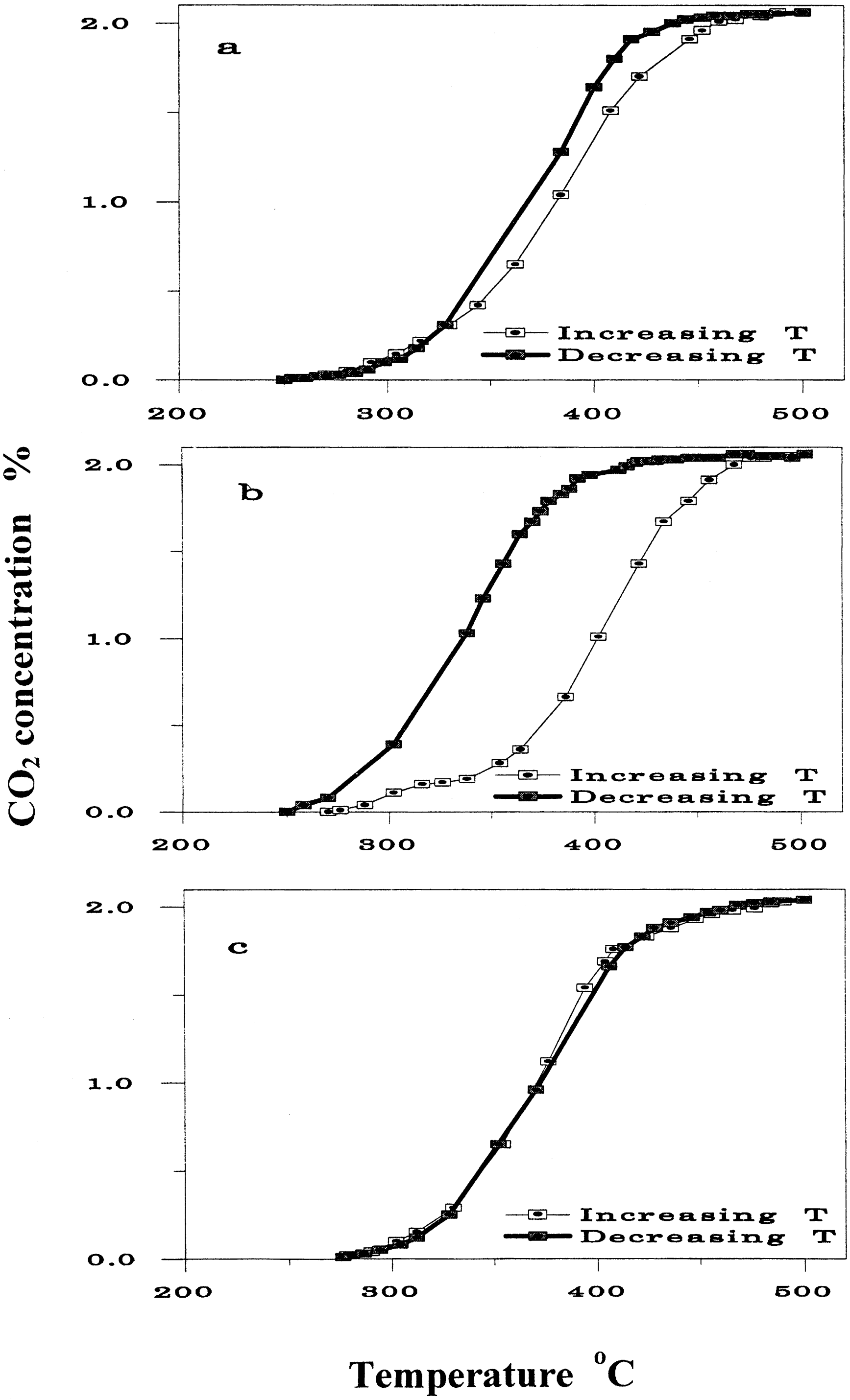

Fig. 2. Evolution of CO_2 over a temperature loop during temperature-programmed methane oxidation. Reaction conditions: 2% methane in air. The rate of increasing temperature: 2.5 K/min and the rate of decreasing temperature: ca. 10 K/min: (a) Pd/Al_2O_3; (b) $Pd–Pt/Al_2O_3$; (c) $Pd/Al_2O_3–CeO_2$.

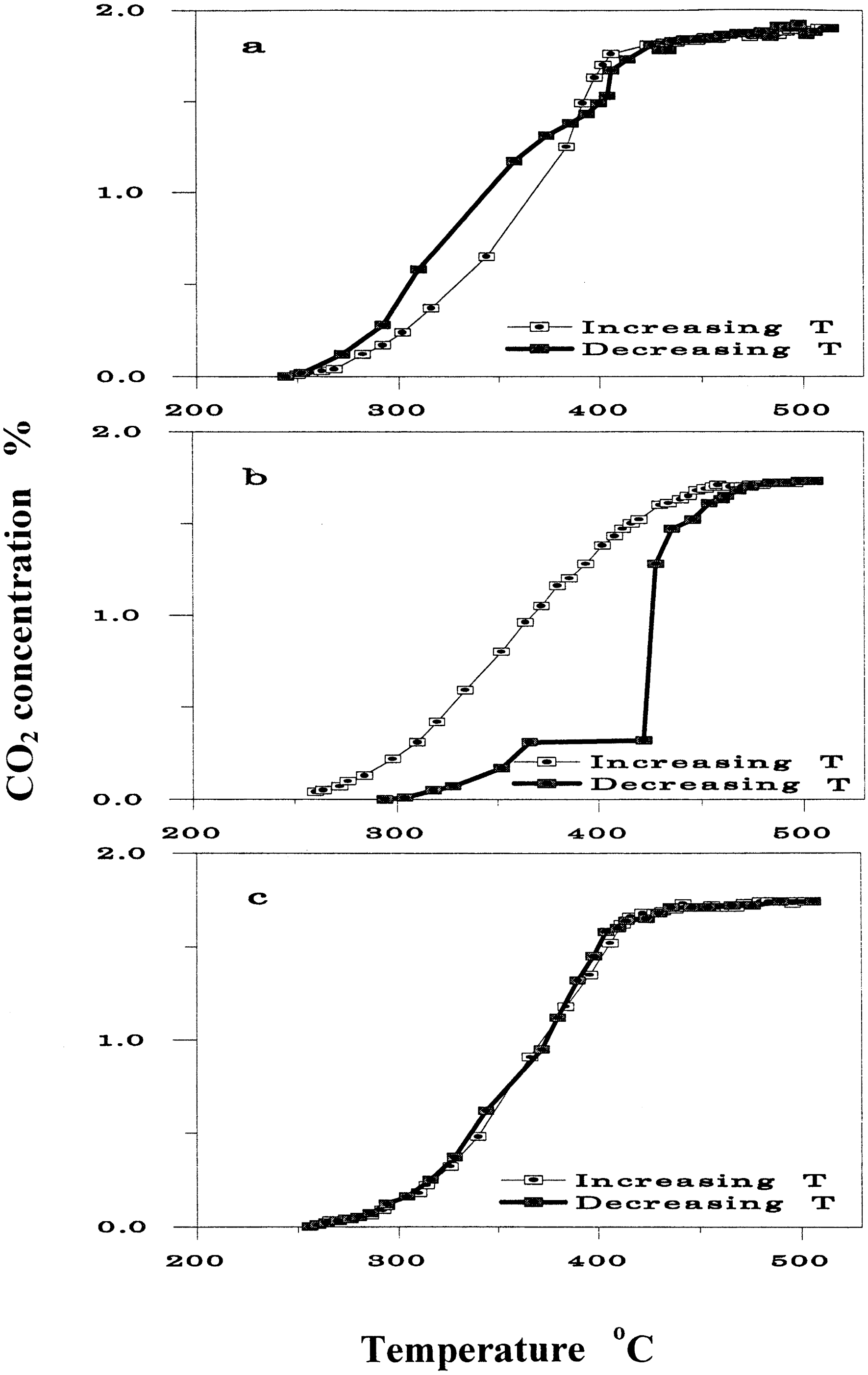

Fig. 3. Evolution of CO_2 over a temperature loop during temperature-programmed methane oxidation. Reaction conditions: $O_2/CH_4<2.0$, N_2 balance. The rate of increasing temperature: 2.5 K/min and the rate of decreasing temperature: ca. 10 K/min: (a) Pd/Al_2O_3, $O_2/CH_4=1.8$; (b) $Pd–Pt/Al_2O_3$, $O_2/CH_4=1.7$; (c) $Pd/Al_2O_3–CeO_2$, $O_2/CH_4=1.7$.

By contrast, for Pd/Al_2O_3–CeO_2 (Fig. 3(c)), there was almost no difference between the upward and downward activity traces, although very small fluctuations in catalyst bed temperature were observed during the temperature decreasing stage.

When the O_2/CH_4 ratio was decreased further (e.g. O_2/CH_4=1.0), similar behaviour but with reduced fluctuation was observed for Pd/Al_2O_3 and the reduction in activity for Pd–Pt/Al_2O_3 when the temperature was reduced was less marked. For Pd/Al_2O_3–CeO_2, there was a small difference in activity over 270–360°C with activity being slightly lower on the downward stage of the cycle.

Under methane-rich conditions and at higher temperatures, CO was formed over all three catalysts. The amounts of CO formation were small and much dependent on the O_2/CH_4 ratio but independent of the catalysts (e.g. ca. 0.08% at 500°C with O_2/CH_4 ratio=1.7 and 0.3% at 500°C with O_2/CH_4 ratio=1.0). The evolution of CO over the three catalysts with temperature increasing and decreasing showed no difference, and there were also no detectable differences between the three catalysts in the temperatures at which CO formed and disappeared.

3.3. *Oscillation of methane oxidation over a packed bed of Pd/Al_2O_3*

Since, from the results of temperature-programmed methane oxidation, sustained and strong fluctuations in activity were displayed over Pd/Al_2O_3 with the methane-rich mixture during the temperature-decreasing stage, possible oscillatory behaviour was looked for under similar conditions. The temperature of the catalyst was initially adjusted and stabilised at between 280°C and 330°C under flowing air and then the reactant gas mixture was introduced (O_2/CH_4= 1.7).

Depending on the initial temperature, there was an increase in temperature of up to 100 K due to catalytic combustion, so that the temperature of the catalyst bed reached to 370–430°C. For most of this range, the catalyst remained at a constant temperature indicating a constant overall reaction rate. Reaction conditions for oscillations became very narrowly defined in this reaction system. A slightly higher or lower temperature would result in either too much or insufficient methane oxidation, and consequently, the oscillatory behaviour of methane oxidation was not observed. At ca. 400°C, however, a pronounced oscillation was observed after the reaction had proceeded for 8 min, Fig. 4. The amplitude was relatively weak, e.g. maximum fluctuation of temperature, ca. 13 K (stages (a) and (b) in Fig. 4) and the corresponding conversions of methane were 69% and 80%, respectively. The frequency was apparently low (ca. 6/h) in comparison with the oscillation of over individual pellets of similar catalysts observed using the microcalorimetric method [14]. In addition, the oscillatory behaviour over the packed bed was not maintained but became progressively weaker before ceasing completely after ca. 30 min.

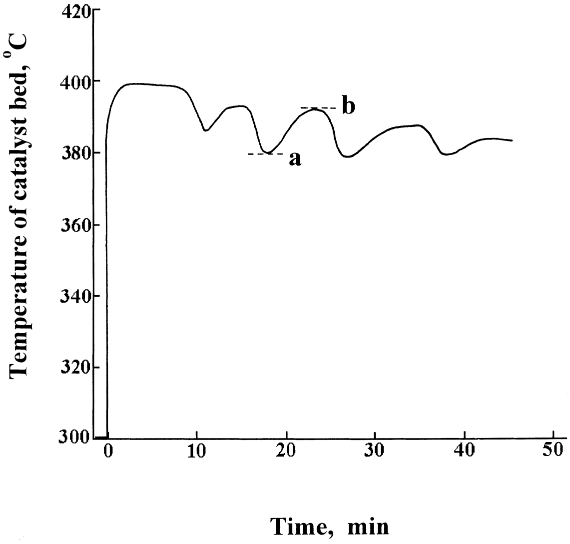

Fig. 4. Oscillation behaviour of methane oxidation over Pd/Al_2O_3 in packed-bed reactor. Reaction conditions: O_2/CH_4=1.7, N_2 balance; initial temperature of catalyst 300°C.

4. Discussion

From the experimental results, the complexities of the methane oxidation over supported Pd catalysts have been shown particularly for gas mixtures with the O_2/CH_4 ratio near or below the stoichiometric value and reaction temperatures in the range 400–500°C. Although the influence of heat transfer and diffusion cannot be neglected and a relatively high loading of Pd in the catalyst was employed in this work, the changes of Pd active phase modulated by both the reactant gas mixtures and Pt or CeO_2 play an important role.

The activity of Pd/Al_2O_3 catalyst modified with CeO_2 became insensitive to the reaction environment. This stabilisation effect may be due to the capability of CeO_2 for oxygen storage [17]. Thus the surface of the relatively small Pd particles may be maintained in an oxidised state. On the other hand, platinum has a higher ionisation potential [11] than Pd and the oxide is of lower stability. A solid solution of the metals may have been formed [18] and van der Oetelaar et al. [19] have reported that platinum–palladium particles on alumina are enriched in platinum at the surface after treatment under a reducing environment at elevated temperature. Since platinum on alumina is much less active than palladium for methane oxidation at temperatures below 500°C, the activity "collapse" could have followed "enrichment" of Pt on Pd at the surface, giving a much lower activity towards methane oxidation. Since it has been reported that the activities of reduced Pd on γ-Al_2O_3 and on α-Al_2O_3 could be greatly different [4,13], the formation of α-Al_2O_3 phase in Pd/Al_2O_3 and Pd–Pt/Al_2O_3 may also have some impact on the non-steady behaviour in their activities.

The oscillation behaviour of methane oxidation over the catalyst packed bed was very different from that found with a single small pellet (bead) of catalyst [14], even though the catalysts and other reaction conditions were very similar. This is to be expected since non-isothermal oscillation is very dependent on the reactor type and on the form of the catalyst [1]. It is also reasonable that the resultant frequency on oscillation from the packed bed is much lower (only ca. $6\,h^{-1}$ cf. ca. $90\,h^{-1}$ for the microcalorimetric bead system) because of the much larger thermal lag possessed by the packed bed.

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