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Methane oxidation over Pt/Al_2O_3 and Pd/Al_2O_3 catalysts under transient conditions

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Abstract

We communicate experimental results for the oxidation of methane by oxygen over alumina supported Pd and Pt monolith catalysts under transient conditions. Temperature programmed reaction (TPReaction) and reactant pulse-response (PR) experiments have been performed, using a continuous gas-flow reactor equipped with a downstream mass spectrometer for gas phase analysis. Special attention was paid to the influence of gas composition changes, i.e. O_2 and H_2 pulsing, respectively, on the methane conversion. For Pt/Al_2O_3 oxygen pulsing can significantly increase the methane conversion which can be even further improved by pulsing hydrogen instead. Such transient effects are not observed for the Pd/Al_2O_3 catalyst for which instead constantly lean conditions is beneficial. Our results suggest that under lean conditions

Pd and Pt crystallites may undergo bulk- and partial (surface oxide formation) oxidation, respectively, which for Pd results in more active surfaces, while for Pt the activity is reduced. The latter seems to connect to a lowering of the ability to dissociate methane.

Key words: Catalytic methane oxidation; Pulse-response experiments; Periodic operation; Platinum oxide; Palladium oxide; Pt/Al_2O_3; Pd/Al_2O_3

Introduction

The huge world reserve of natural gas, which essentially is methane (CH_4), appears as an attractive source of energy for heat and power production, and propulsion. The low amounts of sulphur- and nitrogen containing constituents in natural gas are beneficial and give low emission levels of sulphur and nitrogen oxides (SO_x and NO_x) during combustion. For efficient and environmentally sustainable conversion of methane, catalytic combustion offers an attractive alternative to conventional combustion, since the energy is released at moderate temperatures and the emission levels of carbon monoxide and nitrogen oxides are relatively low. Since methane is a greenhouse gas, such processes demand controlled methane handling with low methane slip. Moreover, the interest in natural gas fuelled vehicles (NGVs) to solve transportation issues in cities is growing since, compared to diesel engines, NGV engines produce lower amounts of NO_x and particulates. Natural gas engines can operate under lean conditions keeping the fuel consumption low compared to ordinary (otto) engines running close to stoichiometric conditions. However, the methane conversion is not complete in the combustion chambers (cylinders) and thus catalytic exhaust aftertreatment of methane is an important step in such applications.

Methane is generally considered as the most difficult hydrocarbon to oxidise where the rate limiting step is the abstraction of the first hydrogen atom [1, 2]. The most active catalysts for oxidation of saturated hydrocarbons, including CH_4, are the noble metals platinum and palladium where the latter in most cases is considered superior. Often the light-off temperature (T_{50}), i.e., the inlet gas temperature at which 50% conversion is achieved [3], for oxidation of methane by oxygen over typical Pt/Al_2O_3 catalysts is in the range 625-725 K [4, 5]. The corresponding temperatures for alumina supported Pd is about 50-75 K lower [6]. Although oxidation of methane has been studied for decades, the underlying mechanism, and thus the active state of the catalyst, is still under debate. For Pt catalysts neither a completely reduced nor a fully oxidised surface is optimal for methane oxidation. Instead, partially oxidised metal surfaces where the concentrations of adsorbed oxygen and methane are well balanced seem to be the most active [7]. Such surfaces can, probably, more effectively polarise the methane molecule and thereby also more efficiently break the C-H bond [1, 2]. In the case of palladium based catalysts, i.e. Pd/Al_2O_3, the oxidised form, PdO, is the most active state for methane oxidation [7]. Comparison between Pt/Al_2O_3 and Pd/Al_2O_3 catalysts show that Pd is the most appropriate choice for lean reaction conditions and at low conversions under stoichiometric or rich conditions whereas Pt/Al_2O_3 is more efficient at higher conversions with stoichiometric or rich conditions [7].

Previously, Pt-based catalysts have been used to study transient effects in the oxidation of CO [8, 9] and C_3H_6 [8], so-called self-poisoned systems, and C_3H_8 [10]. For the latter, interesting results indicating i) the existence of an optimum catalyst state for high propane conversion and ii) that this optimum could be approached by periodic operation of the gas composition, i.e., introducing rich periods to otherwise lean conditions, were shown. It is valuable to complement this work with studies of methane oxidation at transient conditions, since, for

example, methane is chemically very different compared to higher alkanes. It is also interesting to broaden such studies by including also other catalysts.

The aim with this letter is to study transient effects in the methane oxidation over Pd/Al_2O_3 and Pt/Al_2O_3 model catalysts. Special attention was paid to i) the influence of gas composition changes (periodic operation) on the methane conversion and the state of the catalysts, and ii) possible benefits of using periodic operation as a means for high overall CH_4 conversion.

Experimental section

Catalyst preparation and characterisation

Monolith samples (L=15 mm, Ø=12 mm, 69 channels) were cut out from a commercial honeycomb structure of cordierite with 400 cpsi. The samples were coated with 200 mg γ-alumina by repeating the cycle; first immersing the sample into a dilute ammonia solution (pH=11) and then into an aqueous γ-alumina slurry consisting of 13 wt% γ-alumina, 3 wt% bohemite and 1 wt% nitric acid (excess slurry was gently removed by blowing air through the channels) followed by gentle drying at 365 K in air and calcination at 825 K for 2 min, also in air. The samples were then calcined at 850 K in stationary air for 90 min.

Catalysts with 10 mg of either Pt or Pd were prepared by impregnating the samples with an aqueous solution of platinum(II)nitrate and palladium(II)nitrate, respectively, as the precursor for the active component. The samples were dried and calcined in stationary air at 365 K for 5h and 850 K for 90 min, respectively, and reduced in 4% H_2 at 725 K for 60 min followed by exposure to a net-oxidising mixture consisting of 1.0 vol.-% CO, 0.15 vol.-% C_3H_6 and 1.4

vol.-% O_2 (N_2 as balance) at 825 K for 90 min at a total flow rate of 3000 ml/min. In the following vol.-% will be noted by %.

Flow-reactor measurements

The methane oxidation experiments were performed in a continuous gas-flow reactor consisting of a quartz tube (L= 400 mm, Ø=15 mm) wherein the sample was positioned. Heating of inlet gas and the sample occurred via resistive heating of a metal coil surrounding the tube. Both the inlet gas and the catalyst temperature were measured by separate thermocouples (type K). Gases were introduced via individual mass flow controllers. The product stream was continuously analysed with a mass spectrometer (Balzers Quadstar 422) following the *m/e* ratios 2 (H_2), 15 (CH_4), 18 (H_2O), 28 (CO), 32 (O_2) 40 (Ar) and 44 (CO_2). The H_2O signal, however, is not shown due to low accuracy connected to lag time with our reactor set-up. Different temperature programmed reaction (TPReaction) and pulse-response (PR) experiments were performed as summarised in Table 1. In all experiments a total gas flow of 200 ml (NTP)/min, corresponding to a space velocity of 7000 h^{-1} was used (Ar as balance).

Results

Figure 1 and 2 show the TPReaction results for the Pd/Al_2O_3 and Pt/Al_2O_3 catalysts, respectively, at both net-oxidising (lean) and net-reducing (rich) conditions. For the Pd sample, the CH_4 concentration starts to decrease slowly at about 500 K for both lean and rich conditions and at 560 K a more rapid decrease is seen. A corresponding increase and decrease in the CO_2 and oxygen concentrations, respectively, can also be observed. For lean conditions, the T_{50} is about 620 K, which is about 25 K lower than the corresponding temperature at rich

conditions, and complete conversion of CH_4 into CO_2 is achieved at around 700 K. An interesting observation is the minimum in the O_2 response at this temperature. Although during conditions with oxygen deficiency all oxygen is consumed at around 670 K, complete CH_4 conversion is nevertheless observed at about 700 K due to changing reaction selectivity, i.e., formation of H_2 in this case. Also for the Pt/Al_2O_3 catalyst, the CH_4 conversion starts at about the same temperature for lean and rich conditions, however, contrary to the results for the Pd catalyst, the T_{50} is lower for rich compared to lean conditions, about 690 K compared to 705 K. For rich conditions, complete CH_4 conversion is reached at lower temperatures compared to lean conditions. A change in reaction selectivity towards H_2 formation as previously observed for the Pd sample can be seen also in this case.

The results from the oxygen PR experiments for the Pd/Al_2O_3 and Pt/Al_2O_3 catalyst, respectively, are shown in Figure 3 and 4. The outlet concentrations of O_2 and H_2 (top panel), CH_4 and CO (middle panel), and CO_2 with the addition of the carbon balance (bottom panel) are shown as a function of time for periods with repeatable responses.

For the Pd/Al_2O_3 sample (see Figure 3), during the initial phase of the introduction of a 1250 ppm oxygen pulse at t=26 min, a temporary minimum in the CH_4 concentration and a corresponding temporary maximum in the CO_2 concentration are clearly visible. The responses in CH_4 and CO_2 concentrations are seen slightly before any observable change in oxygen concentration. Upon further oxygen exposure then, t=26-31 min, both the CH_4 and O_2 concentration decrease continuously with a corresponding increase of CO_2 concentration. The carbon balance is steady at 500 ppm C during this period. At t=31 min, the oxygen feed is switched off and the oxygen concentration drops quickly to zero. The CO_2 concentration passes a small concentration maximum, drops then for about 1 min and finally decreases more

slowly for the next 4 min. Both the CH_4 concentration and the carbon balance pass through individual minima. The CH_4 concentration increases then slowly towards 500 ppm, however, reaches only 450 ppm since a new oxygen pulse is introduced at t=36 min. During the oxygen-free period, H_2 and minor amounts of CO are formed.

The introduction of an oxygen pulse to the Pt/Al_2O_3 sample (Figure 4) at t=36 min, results in a huge and relatively broad minimum in CH_4 concentration, reaching an almost complete CH_4 conversion for a short period. A corresponding maximum in the CO_2 concentration and a somewhat lower maximum in the carbon balance also occur. These responses are observed before any major change can be seen in the O_2 concentration. However, the transient responses are more pronounced and the observed maximum in methane conversion during this switch is considerably higher for the Pt/Al_2O_3 sample. Contrary to the previous results for Pd/Al_2O_3, a stationary CH_4 concentration is reached during continuous oxygen exposure. Considering the O_2 switch-off at t=41 min, a minimum in CH_4 concentration is passed again where after the CH_4 concentration approaches 300 ppm. The carbon balance passes a minimum. During this switch a considerable amount of H_2 is formed while CO starts to be produced. While the H_2 concentration decreases from about 1100 to 500 ppm, the CO concentration increases monotonically towards 100 ppm.

The results from the PR experiments where H_2 pulses were introduced to a slightly oxidising $CH_4/O_2/Ar$ mixture for the Pd/Al_2O_3 and Pt/Al_2O_3 catalysts are shown in Figure 5 and 6, respectively. For the Pd/Al_2O_3 sample, the results are similar to the oxygen PR experiments described above. During the introduction of a 0.5% H_2 pulse at t=37 min results in a temporary minimum both in the CH_4 concentration and in the carbon balance while the CO_2 concentration drops to about zero. However, for the Pt sample a broad and deep minimum in

the CH_4 concentration is seen when the hydrogen is switched off at t=36 min. The CH_4 concentration minimum corresponds with a broad and high maximum in CO_2 production.

Discussion

Palladium and platinum are precious metals with very different ability to incorporate oxygen into the atomic metal structure, i.e., form oxides [11]. Depending on the reaction conditions, Pd is known to form PdO in supported catalysts during reaction conditions [12]. The oxidation of a Pd crystallite is not restricted to just the surface region of the metal particles but can reach several atomic layers [13], thus relatively large amounts of oxygen can be incorporated into the Pd structure. For Pt, no evidence for such bulk oxidation has been found, however, neither the oxide stoichiometry nor the stability of the oxides is well known. The oxide phase of Pt is usually referred to as “surface oxide” or “subsurface oxide”, terms which are often used interchangeably. In the results presented here it is clear that the influence of the gas composition on the activity for methane oxidation as well as the transient response to gas composition changes are considerable different for Pd and Pt based catalysts respectively. Since no spectroscopic methods were used in the present study, we can not unambiguously discuss the catalyst state. However, guided by the cited references and previous results for Pt/Al_2O_3 [14], showing that Pt can be partially oxidised during CO oxidation at oxygen excess, we may draw a number of conclusions. In the following, we thus focus on the influence of the gas composition on methane conversion and state of the catalysts and how these are linked together. We follow up with commenting on potential benefits using periodic operation for high overall methane conversion.

Comparing Figure 1 and 2, it is clear that the oxygen level has significantly different influence on the methane conversion for the Pd and Pt catalysts, respectively. For the Pd catalyst, the oxidation of methane is governed by oxygen excess, the T_{50} is lower for lean compared to rich conditions, whilst for Pt, excess oxygen clearly suppress the reaction as reflected by the higher T_{50} in this case. Likely, see discussion above, both samples form oxides during oxygen excess conditions. The drop in the oxygen concentration for the Pd sample after light-off and the transition via a concentration minimum strongly suggests that the Pd sample stores a considerable amount of oxygen, i.e., bulk oxidation of the Pd crystallites, which governs the oxidation of methane. The corresponding results for the Pt catalyst show only a moderate decrease in O_2 concentration indicating no such bulk oxidation. Instead, the Pt crystallites may only be partially oxidised (surface oxide formation). However, the formation of surface oxide significantly lowers the activity of the catalyst, probably by decreasing the methane adsorption rate, i.e., reducing the ability to dissociate CH_4. This is motivated by comparing the results for rich and lean conditions (Figure 2) where during rich conditions complete CH_4 conversion into CO_2, CO and H_2 is observed at the higher temperatures while under lean conditions the CH_4 conversion is incomplete with no formation of CO or H_2. Contrary, no such behaviour is observed for the Pd catalyst (Figure 1).

The different roles of oxide formation are further emphasised in the PR experiments presented in Figure 3 and 4, respectively. For Pd, the introduction of an oxygen pulse initially results in a temporary over-production of CO_2. This is partly due to a transition from a mainly CH_4 covered to an almost O covered surface, as evidenced by the positive peak in the carbon balance, and partly due to the passage of a surface composition, i.e. certain CH_4 and O coverages, which is beneficial for the activity as indicated by the temporary minimum in the CH_4 concentration. After passing this transient regime with high activity, the system reaches a

state with almost no conversion of methane (t=27.6 min). We believe that this state corresponds to a Pd surface being either covered with a monolayer of O atoms or partially oxidised. Upon further oxygen exposure the catalyst regains activity, increasing methane conversion, which probably correlates to bulk oxidation of the Pd particles becoming more active. From our data, the construction of an oxygen balance is scarce due to experimental difficulties following the water signals. However, from Figure 3 one may observe that the oxygen concentration decreases slightly more than expected from the corresponding CO_2 production supporting the idea of a Pd bulk oxidation process. The temporary minimum in the CH_4 response occurring for the O_2 switch-off at t=31 min is mostly due to re-adsorption of methane as clearly supported by the simultaneous minimum in the carbon balance. While metal oxidation seems to be beneficial for Pd the contrary is, again, true for Pt. In Figure 4, the introduction of oxygen at t=36 min results in an initial huge temporary minimum in CH_4 concentration as the catalyst surface composition switches from being mainly CH_4 covered to almost O covered (maximum in carbon balance) similar to the Pd case. However, as a function of time on stream the methane conversion quickly decays towards a stationary state with a relatively low CH_4 conversion, i.e., the formation of a surface oxide layer reduces the activity for methane oxidation considerably. The negative influence of oxygen excess is further supported by the temporary high activity (maximum in CO_2 concentration) as the oxygen is switched off at t=41 min. The simultaneous passage through a concentration minimum for CH_4 is mainly due to a temporary high adsorption of CH_4 (minimum in carbon balance).

To lower the effect of accumulated methane on the metal surface and thereby more clearly study the effect of oxide formation on the methane oxidation one may use constant concentration levels of methane and oxygen and dose hydrogen (instead of oxygen) as shown

in Figure 5 and 6 for the Pd and Pt sample, respectively. For the Pd sample it is again clear that a certain surface composition on a metal like Pd is highly active. The hydrogen shut off at t=31 min results in a temporary minimum in CH_4 concentration and a corresponding temporary maximum in CO_2 concentration. The maximum in the carbon balance reveals a certain change in surface coverage from partly CH_4 to more or less O covered, however, contrary to the analogous oxygen pulsing experiment (Figure 3) the present maximum reaches a top level of 625 vol.-ppm instead of 800 vol.-ppm indicating less amounts of adsorbed CH_4 in this case and thus the high activity is mainly due to a beneficial surface composition. During further oxygen exposure, the methane conversion increases continuously analogous to previous results. However, the most interesting response to hydrogen pulsing is seen for the Pt sample. When hydrogen is switched off, a huge and relatively broad minimum in CH_4 concentration is seen together with the corresponding CO_2 production. The carbon balance is more or less constant for this period and thus the high CO_2 production is solely due to high activity. The enhanced methane oxidation kinetics is probably a result of hydrogen acting as a clean-up molecule preventing the surface from being deactivated by surface oxide formation.

Conclusions

Our results show that for methane oxidation with oxygen under lean conditions Pd/Al_2O_3 is superior to Pt/Al_2O_3. Under these conditions both metals undergoes oxidation, however, the degree of oxidation and the impact on the methane oxidation differs considerably between the two metals. While the Pd crystallites may form bulk oxides resulting in highly active surfaces the Pt crystallites seem to be only partially oxidised (surface oxide formation) resulting in surfaces with low catalytic activity. The latter seems to connect to a lowering of the ability to dissociate methane. The results also suggest that for both catalysts optimal surface

compositions, i.e., CH_4 and O coverages, may exist for which the methane oxidation activity is high.

During periodic operation (oxygen pulsing) of the Pt/Al_2O_3 catalyst an increased activity was observed while switching from rich to lean conditions as compared to stationary conditions analogous to previous results for oxidation of CO [8, 9], C_3H_6 [8] and C_3H_8 [10]. The activity improvement was even more pronounced when periodic operation with hydrogen pulses, i.e., switching between hydrogen and CH_4 oxidation, was used.

References

[1] R. Burch and M.J. Hayes, J. Mol. Catal. A: Chem. 100 (1997) 13.

[2] R. Burch, D.J. Crittle and M.J. Hayes, Catal. Today 47 (1999) 229.

[3] J.T. Kummer, Prog. Energy Combust. Sci. 6 (1980) 177.

[4] R. Burch and P.K. Loader, Appl. Catal. B: Environ. 5 (1994) 149.

[5] T.P. Garetto and C.R. Apesteguia, Catal. Today 62 (2000) 189.

[6] P. Gélin and M. Primet, Appl. Catal. B. 39 (2002) 1.

[7] R. Burch, P.K. Loader and F.J. Urbano, Catal. Today 27 (1996) 243.

[8] P.-A. Carlsson, P. Thormählen, M. Skoglundh, H. Persson, E. Fridell, E. Jobson, and B. Andersson, Top. Catal. 16/17(1-4) (2001) 343.

[9] P.-A. Carlsson, M. Skoglundh, E. Fridell, E. Jobson and B. Andersson, Catal. Today 73 (2002) 307.

[10] P.-A. Carlsson, S. Mollner, K. Arnby and M. Skoglundh, Chem. Eng. Sci. 59 (2004) 4313.

[11] C. Cullis and B. Willatt, J. Catal. 83 (1983) 267.

[12] O. Demoulin, M. Navez, E. Gaigneaux, P. Ruiz, A.-S. Mamede, P. Granger and E. Payen, Phys. Chem. Chem. Phys. 5 (2003) 4394.

[13] D. Ciuparu, M. Lyubovsky, E. Altman, L. Pfefferle and A. Datye, Catal. Rev. 44 (2002) 593.

[14] P.-A. Carlsson, L. Österlund, P. Thormählen, A. Palmqvist, E. Fridell, J. Jansson and M. Skoglundh, J. Catal. 226 (2004) 422.

Table 1. Summary of the experimental conditions for the flow-reactor measurements.

Type of experiment	**Sample**	**Temperature [K]**	**Gas composition**		
			CH_4 conc. [ppm]	**O_2 conc. [ppm]/ (duration [min])**	**H_2 conc. [ppm]/ (duration [min])**
TPReaction (rich)	Pd/Al_2O_3 Pt/Al_2O_3	303 =>773 (20K/min)	500	750	--
TPReaction (lean)	Pd/Al_2O_3 Pt/Al_2O_3	303 =>773 (20K/min)	500	1250	--
PR (lean-rich)	Pd/Al_2O_3	623	500	1250(5)/0(5)	--
PR (rich-lean)	Pd/Al_2O_3	623	500	1250	5000(5)/0(5)
PR (lean-rich)	Pt/Al_2O_3	673	500	1250(5)/0(5)	--
PR (rich-lean)	Pt/Al_2O_3	673	500	1250	5000(5)/0(5)

TPReaction=temperature programmed reaction, PR=pulse-response

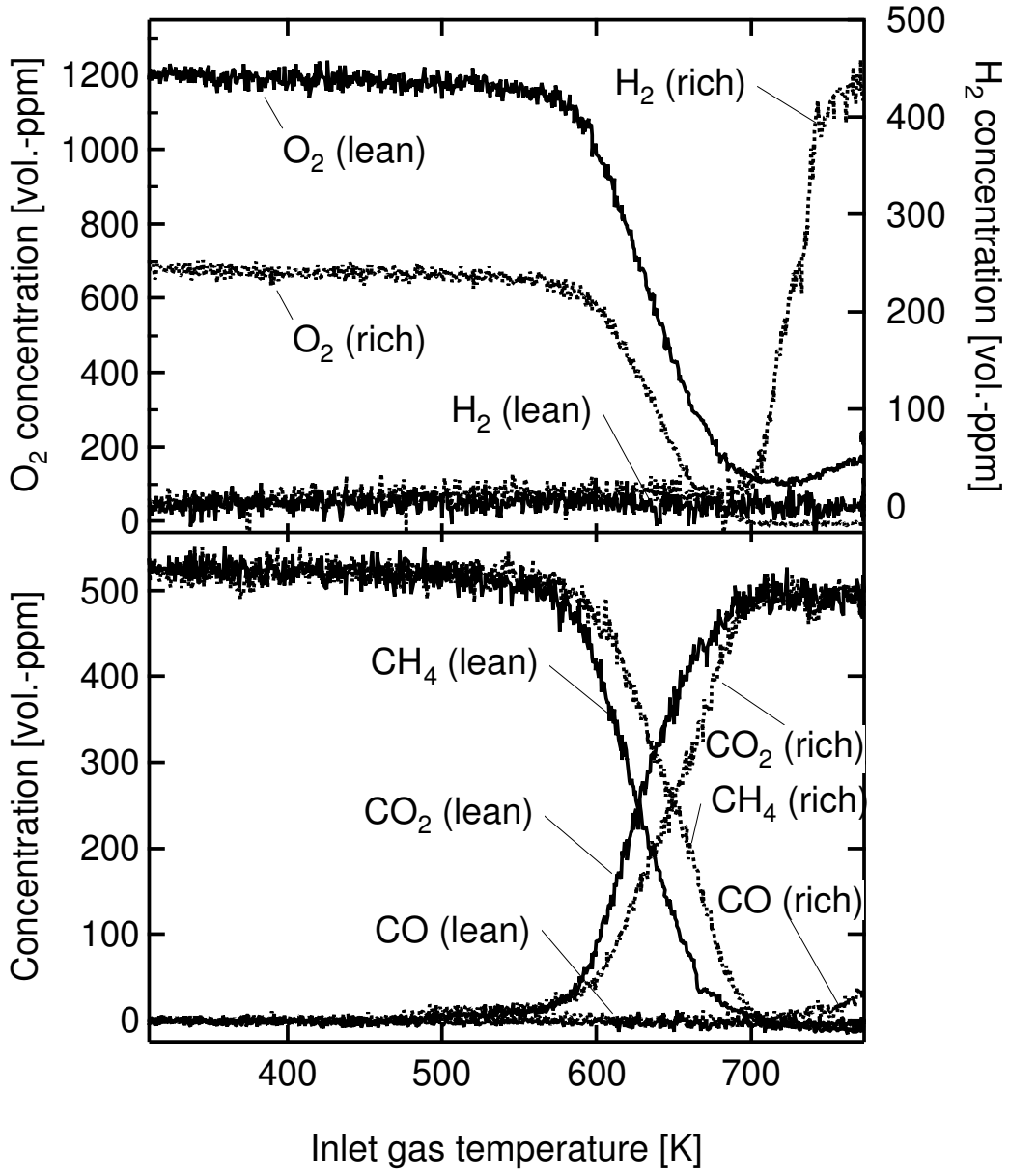

FIG. 1: Temperature programmed oxidation of 500 vol.-ppm CH_4 at net-reducing (rich, 750 vol.-ppm O_2, dotted line) and net-oxidising (lean, 1250 vol.-ppm O_2, solid line) conditions, respectively, over a 5%Pd/Al_2O_3 catalyst. Methane was preadsorbed and the heating ramp was 20 K/min.

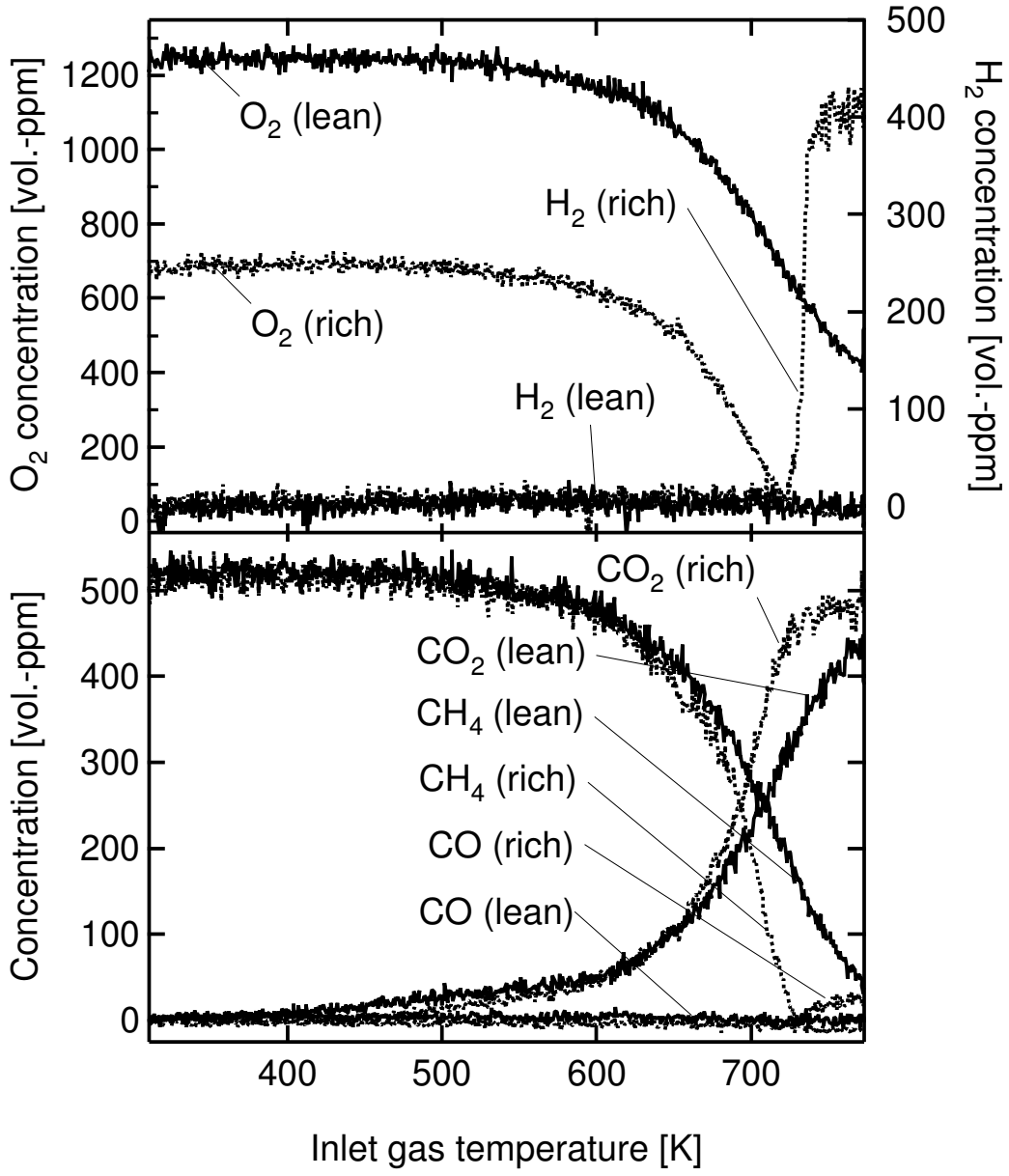

FIG. 2: Temperature programmed oxidation of 500 vol.-ppm CH_4 at net-reducing (rich, 750 vol.-ppm O_2, dotted line) and net-oxidising (lean, 1250 vol.-ppm O_2, solid line) conditions, respectively, over a 5%Pt/Al_2O_3 catalyst. Methane was preadsorbed and the heating ramp was 20 K/min.

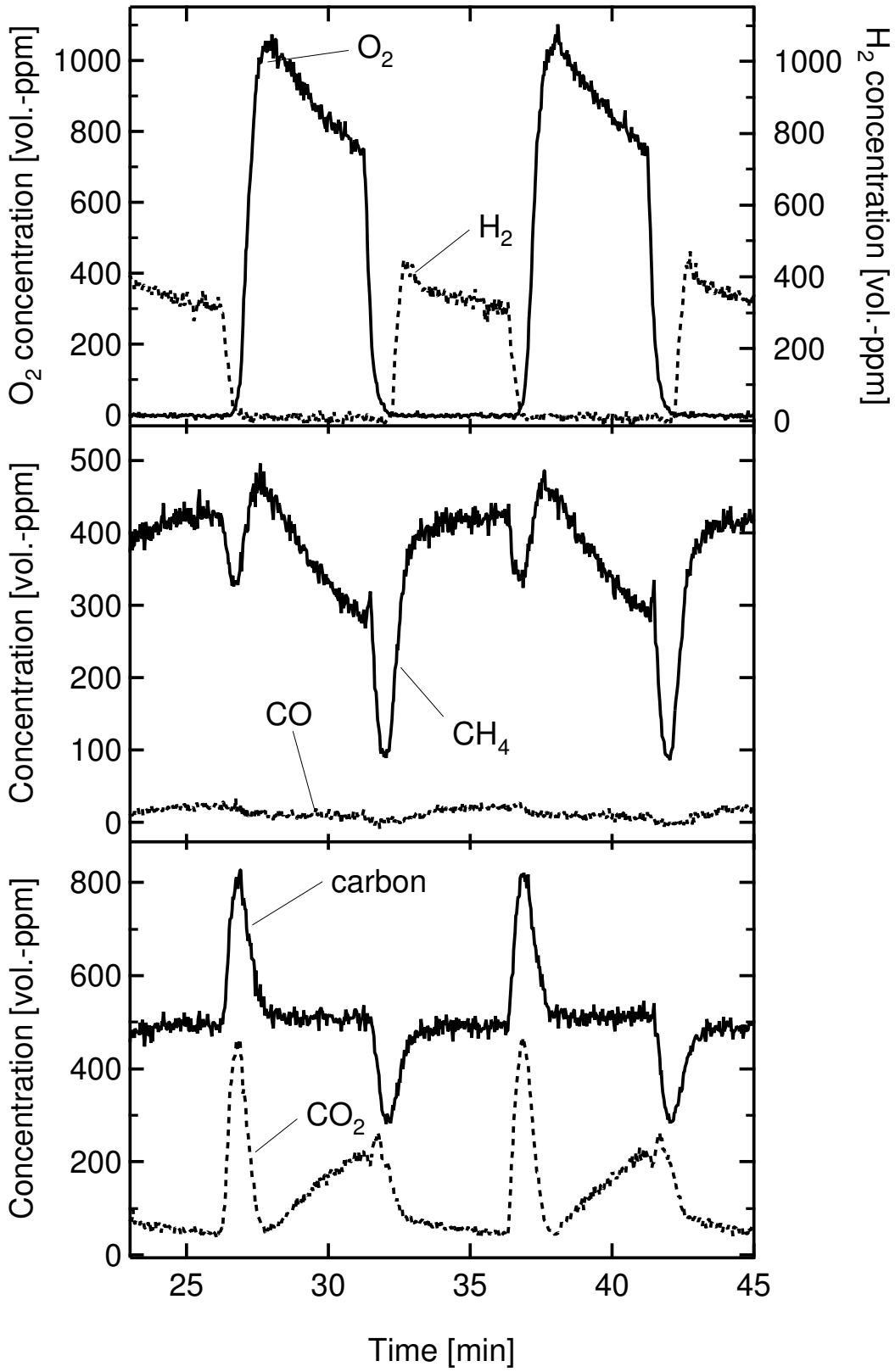

FIG. 3: Oxidation of 500 vol.-ppm CH_4 over a 5%Pd/Al_2O_3 catalyst while periodically varying the oxygen concentration between 0 vol.-ppm for 5 min and 1250 vol.-ppm also for 5 min at an inlet gas temperature of 623 K.

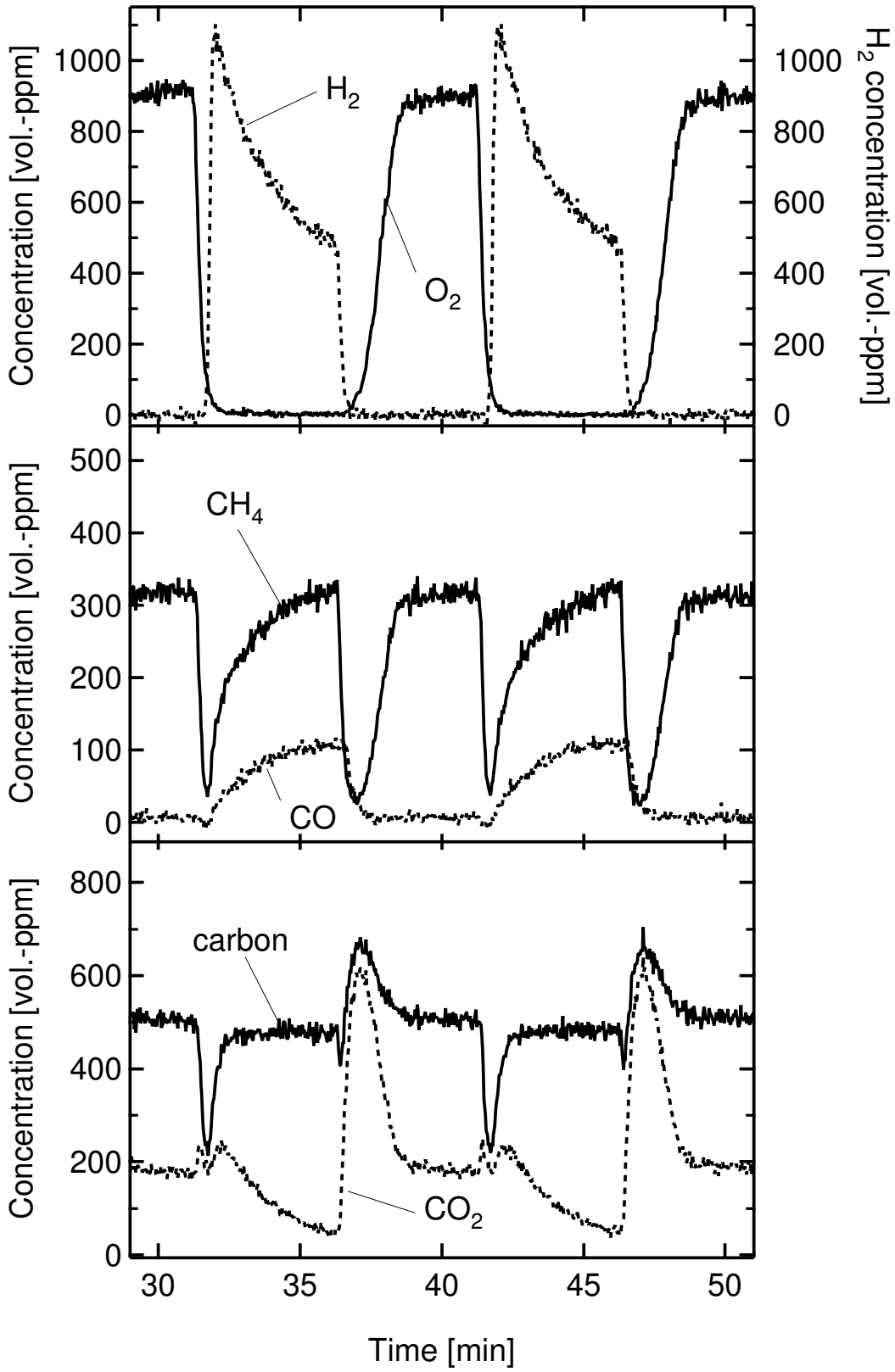

FIG. 4: Oxidation of 500 vol.-ppm CH_4 over a 5%Pt/Al_2O_3 catalyst while periodically varying the oxygen concentration between 0 vol.-ppm for 5 min and 1250 vol.-ppm also for 5 min at an inlet gas temperature of 673 K.

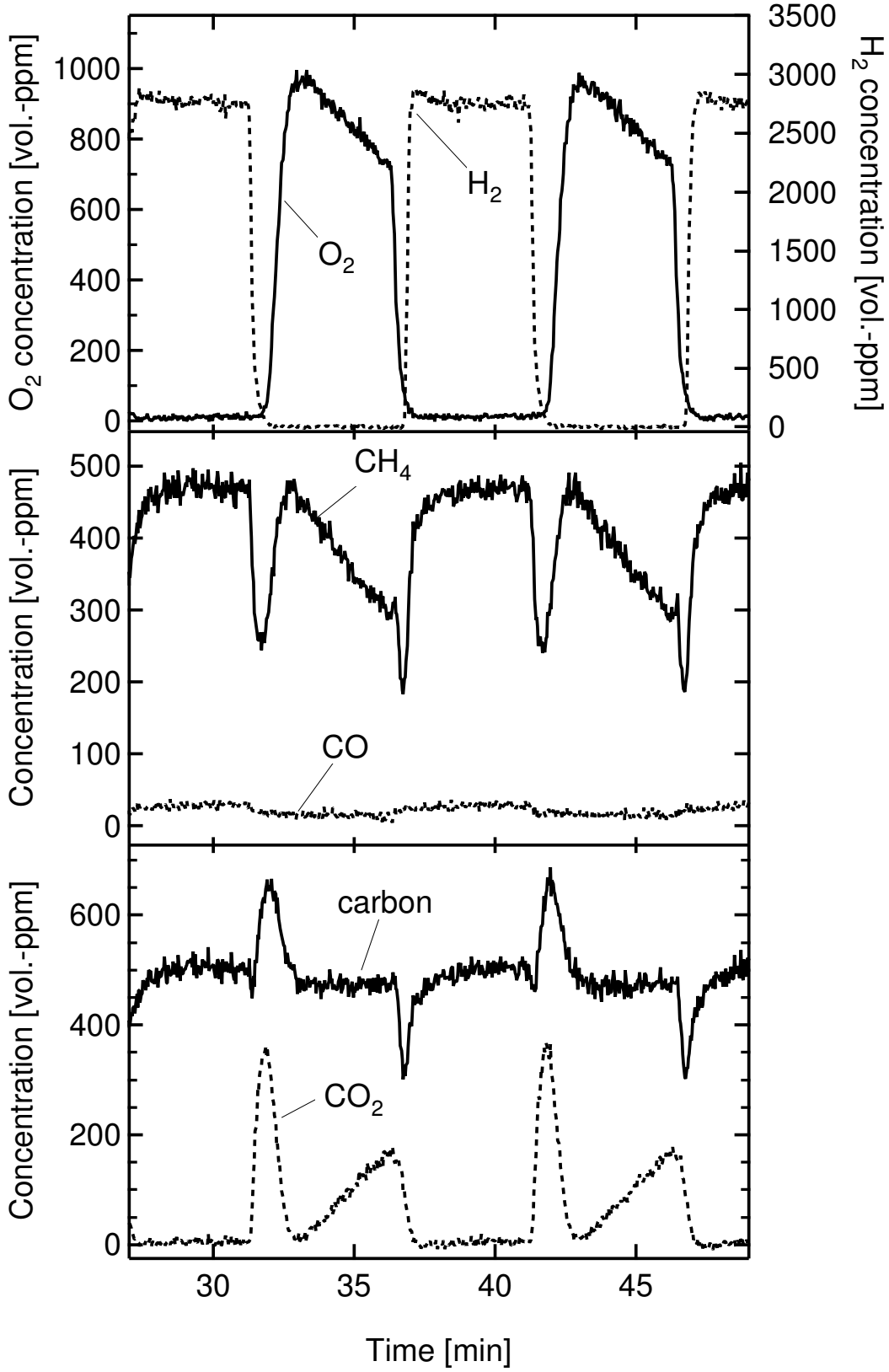

FIG. 5: Oxidation of 500 vol.-ppm CH_4 over a 5%Pd/Al_2O_3 catalyst at net-oxidising conditions (1250 vol.-ppm O_2) while periodically introducing 0.5 vol.-% H_2 for 5 min at an inlet gas temperature of 623 K.

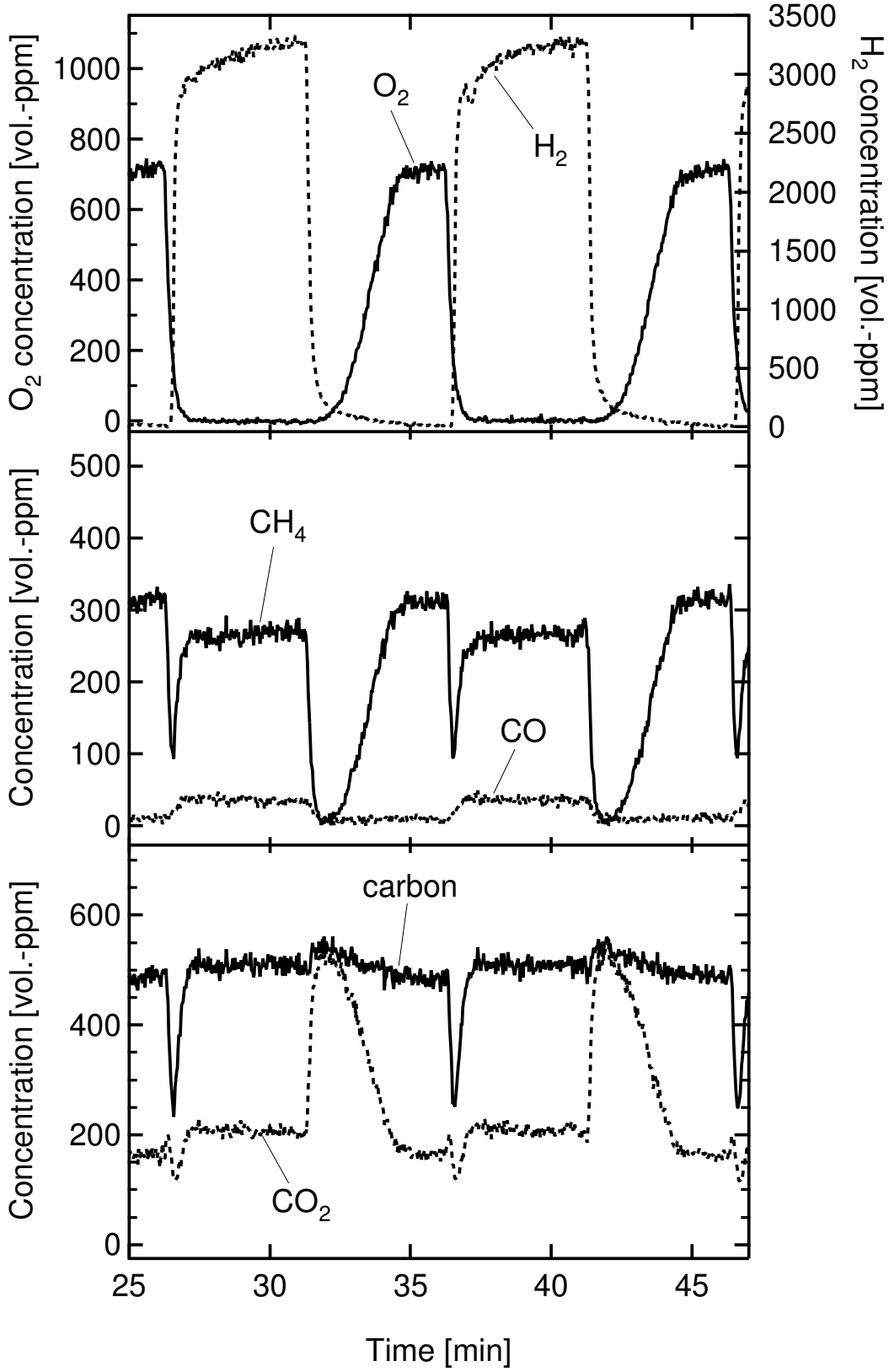

FIG. 6: Oxidation of 500 vol.-ppm CH_4 over a 5%Pt/Al_2O_3 catalyst at net-oxidising conditions (1250 vol.-ppm O_2) while periodically introducing 0.5 vol.-% H_2 for 5 min at an inlet gas temperature of 673 K.