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Chemical modelling and measurements of the catalytic combustion of CH_4/air mixtures on platinum and palladium catalysts

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Abstract

This work reports experimental measurements and a modelling study carried out on palladium and platinum based catalytic monoliths used as methane combustors for heating purposes. It concentrates on the effects of operating conditions on combustion, heat transfer efficiency and pollutant formation. The development of a detailed homogeneous/heterogeneous chemical kinetics model for methane–air combustion over palladium using literature data was undertaken to model the behaviour of one of the experimental catalytic heaters. In addition, a published detailed chemical mechanism for methane combustion over platinum was used in the platinum catalyst model. The fuel–air equivalence ratios ranged from 0.3 to 0.6 and the space velocities used were between 24 000 and 72 000 h^{-1}. Although the model assumed perfectly stirred reactor (PSR) conditions and was applied to localised regions of the monoliths where little radial gradients of temperature and concentrations were measured, it predicted the surface temperature, methane slippage, CO and NO_x at the downstream face of the monolith with reasonable accuracy in some cases, but also highlighted the shortcomings of the PSR assumption in other cases. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: CH_4; Catalytic; Combustion; Platinum; Palladium

1. Introduction

Catalytic combustion of natural gas is an alternative way to conventional gas-phase combustion which produces hot gases at a lower temperature but also lower (or near zero) pollutant emissions. Due to the lower activation energies involved in the catalytic surface reactions, the attraction of catalytic combustion is its ability to occur outside gas-phase flammability limits of the fuel in air. This effect is to reduce the ignition temperature thereby offering greater range of fuel–air equivalence ratios and increased stability of operation. The lower temperatures achieved prevent nitric oxide formation whereas the fuel and carbon monoxide oxidation is completed by the catalytic reactions. Platinum group metals and particularly palladium and platinum have been found to be the best catalysts of methane oxidation to date [1]. These metals are used in very small concentration dispersed over ceramic washcoats deposited on supports that can be ceramic or metallic in nature. On-going research is oriented towards synthesising composite materials that would display the desired catalytic properties in high temperature environments [2]. In this work, honeycomb monoliths with palladium and with pla-

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tinum containing coatings on cordierite supports are studied experimentally and theoretically below the flammability limit of methane/air combustion with the aim of producing hot exhaust gases containing negligible concentrations of NO_x, CO and unburned hydrocarbons with applications to domestic heating appliances.

2. Experimental set-up

A schematic diagram of the experimental set-up is given in Fig. 1. A controlled flow of air was fed at the bottom of a cylindrical stainless steel reactor through four equidistant injectors. The air flow was electrically preheated to 400°C by a coil encased in a ceramic housing at the beginning of each run to activate the monolith. Once the mixture was ignited, the preheater was switched off. Methane was fed to a fuel injector consisting of a perforated spiral tube positioned just above the preheater. A swirler located above the fuel injector provoked turbulence in the flow to improve mixing of the fuel and air upstream of the monolith. A section or the duct between the swirler and the monolith allowed the mixing to take effect and two stainless steel gauzes placed before the monolith evened out the flow velocity field. Insulating fibre 4 cm thick surrounded the whole length of the reactor.

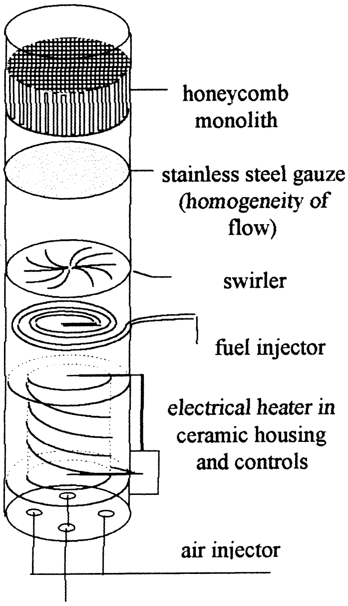

Fig. 1. Schematic diagram of the catalytic reactor.

A quartz probe translatable in the horizontal plane was inserted in the top part of the duct that enclosed the monolith and was followed by a heated PTFE line connected to a NO_x chemiluminescence analyser. Samples were also taken from the line and analysed by gas chromatography for unburned hydrocarbons, O_2, H_2, N_2, CO and CO_2 analysis. The radiative emission of the downstream face of the monolith was measured by a Land radiometer type RAD/P and the surface temperature was monitored with a Thermospot infra-red thermometer.

Both Pd and Pt containing monoliths were 10.16 cm in diameter and 5.08 cm in length, with square shaped cells at 400 cpi^2 (cells per inch square) and were provided by Johnson Matthey. The monoliths contained a total of 1.0181 g Pt and 0.582 g Pd, respectively, deposited on approximately 6250 m^2 of washcoat supported on cordierite. No reduction or oxidation treatment were imposed on the monoliths prior to the experiments and both were new when the experiments began.

3. Modelling study

For a preliminary model study of the monoliths behaviour, the approximation of the monolith to a group of adjacent segments of perfectly stirred reactors with a detailed homogeneous and heterogeneous chemistry description was made. An illustration of discretisation of the monolith into segments is given in Fig. 2.

The code SURFACE PSR [3] was used on which a few modifications concerning the sites definition and the radiation heat losses description were performed. We refer the reader to the code's manual for the theory and solution techniques of the program and will only present here the changes that were implemented to it.

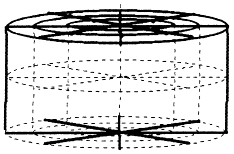

Fig. 2. Segmentation of the monolith into PSRs.

The gas-phase reactions and kinetic data were those of the GRI2.11 mechanism [4]. Surface PSR predicts the steady-state temperature and species composition in a perfectly stirred reactor. The data used as inputs are:

1. For the *flow characteristics*: pressure, volume flow rate (STP), composition and assumed temperature (subsequently calculated by solving the energy conservation equation), the flow is perfectly well mixed and isothermal following the PSR assumptions.
2. For the *reactor characteristics*: reactor volume, surface area-to-volume ratio, and heat losses. Here the code was modified to allow radiation heat losses depending on the temperature and emissivity of the downstream monolith surface. In order to model the behaviour of the catalytic monoliths, it was assumed that the dominant heat loss was via thermal radiation from the open end. The heat losses were defined as described by the following equation:

   $$Q = F\pi R^2 \epsilon\sigma(T^4 - T_a^4), \quad (1)$$

   where Q is the radiative heat loss; F is a view factor that takes into account the radiation reabsorbed by the part of the stainless steel tube which extended above the open surface, F was between 0.81 and 0.85; R is the monolith's radius; ϵ is the emissivity of the washcoat (0.5); σ is the Stefan–Boltzmann constant; T is the surface temperature and T_a is the ambient temperature.
3. For the *catalytic characteristics*: gas, site and bulk phases definitions. Surface site densities, estimated surface site fractions, allowance for conservation of sites. In this model, the "open site" formalism was used, i.e. $2O(S) \Rightarrow O_2 + 2Pd(S)$, Pd(S) being the open site, rather than $2O(S) + 2Pd(B) \Rightarrow O_2 + 2Pd(S)$, where Pd(B) is the bulk species. The open site formalism means that a molecular weight of 0 for all open sites has to be imposed in the code to be able to respect the energy conservation equation.

3.1. *Platinum mechanism*

The catalytic oxidation of methane/air mixtures on platinum is now sufficiently documented so as to be able to be reproduced by mathematical modelling. The mechanism used here is that proposed by Deutschmann et al. [5,6]. This mechanism has been able to predict the surface temperature corresponding to the gas-phase ignition of nitrogen-diluted methane–air mixtures impinging on an electrically heated platinum foil. In addition it was recently successfully used by Bond et al. [7] to model methane combustion in a Pt/alumina washcoated cordierite monolith in gas turbine conditions. The same mechanism was also used to explain the inhibitory effects of water desorption on the ignition temperature of H_2/air mixtures at low equivalence ratios by Bui et al. [8].

3.2. *Palladium mechanism*

The mechanisms involved in the oxidation of hydrogen, carbon monoxide and methane on palladium surfaces are still very much a matter of debate especially in the case of methane. Whereas the platinum mechanism involves with certainly the metallic Pt as active site, it is still discussed whether in the case of palladium, the formation of PdO deposited on metallic Pd in oxidising conditions at temperatures higher than 400°C and its nature as a site for adsorption of CO and methane is a path more likely to occur than that involving a metallic Pd site. A number of publications tend to support the former theory [9–11], while others favour the latter [12,13]. In their modelling of H_2/air mixtures ignition on palladium, Deutschmann et al. [6] used Pd as the active site in a similar manner as Pt is used. In the postulation of one or the other mechanism under the form of elementary reactions of adsorption of reactants/surface reaction/desorption of products, many kinetic data are unsure or unknown. In this study, the approach was taken of using metallic Pd to be the active site for CO and CH_4 oxidation on the washcoat, making use of the H_2/air data from [6] and of the CO oxidation on Pd from [14]. This approach was taken for various reasons. Firstly, at the high temperatures used here, it is likely that PdO is at the limit of reverting back to Pd state; secondly, there is a lack of kinetic data on the individual steps involved in the adsorption, surface reaction and desorption of CH_4 and CO on an active PdO site. Thirdly, although it is possible that an active form of PdO still existed at these high temperatures, we believe its participation in the methane combustion would be inferior to that of an active metallic Pd site. Table 1 summarises the kinetic data used and their origin, together with comments on their implementation.

Table 1
List of surface reactions for CH_4/air mixtures combustion on Pd surfaces

			A		*n*	*E*
1	$H_2+2Pd(S)\Rightarrow 2H(S)$	S	0.70		0.0	0.0
2	$H+Pd(S)\Rightarrow H(S)$	S	1.0		0.0	0.0
3	$O_2+2Pd(S)\Rightarrow 2O(S)$	S	0.4		0.0	0.0
4	$O+Pd(S)\Rightarrow O(S)$	S	1.0		0.0	0.0
5	$H_2O+Pd(S)\Rightarrow H_2O(S)$	S	0.75		0.0	0.0
6	$OH+Pd(S)\Rightarrow OH(S)$	S	1.0		0.0	0.0
7	$2H(S)\Rightarrow H_2+2Pd(S)$		4.8E21		0.0	84.0
8	COV/H(S) 0.0 0.0–15.0/					
9	$2O(S)\Rightarrow O_2+2Pd(S)$		7.1E21		0.0	230.0
10	$H_2O(S)\Rightarrow H_2O+Pd(S)$		1.3E13		0.0	44.0
11	$OH(S)\Rightarrow OH+Pd(S)$		1.3E13		0.0	213.0
12	$O(S)+H(S)\Leftrightarrow Pd(S)+OH(S)$		6.5E21		0.0	11.5
13	$H(S)+OH(S)\Leftrightarrow H_2O(S)+Pd(S)$		6.5E21		0.0	17.4
14	$OH(S)+OH(S)\Leftrightarrow H_2O(S)+O(S)$		6.5E21		0.0	48.2

The above desorption and reversible reactions are also taken from [6]. The five following CH_4 reactions are inspired from the Pt mechanisim of Deutschmann et al. [5] with the 6.5E21 figures altered to take account of the different site density for Pd. Also the CH_4 adsorption sticking parameter given as in the range 0.01–0.19 in the text of Deutschmann et al. [5] Pt mechanism is kept for the Pd mechanism. We found that the highest value gave most realistic results.

15	$CH_4+2Pd(S)\Rightarrow CH_3(S)+H(S)$	S	0.19		0.0	0.0
16	$CH_3+Pd(S)\Rightarrow CH_2(S)+H(S)$		6.5E21		0.0	20.0
17	$CH_2(S)+Pd(S)\Rightarrow CH(S)+H(S)$		6.5E21		0.0	20.0
18	$CH(S)+Pd(S)\Rightarrow C(S)+H(S)$		6.5E21		0.0	20.0
19	$C(S)+O(S)\Rightarrow CO(S)+Pd(S)$		6.5E21		0.0	62.8

The activation energy for the reaction below is as given by Engel and Ertl [14].

20	$CO(S)+O(S)\Rightarrow CO_2+2Pd(S)$		6.5E21		0.0	104.6

The two reactions below have been postulated by Eagel and Ertl [14]. According to these authors, the sticking coefficient for the adsorption of CO is temperature dependent and after peaking at 0.96 at 470 K decreases down to 0.2 at 700 K, this trend suggests a zero sticking coefficient at temperatures above 1000 K. Hence the two values of 0.96 and 0 were used in the simulations. The activation energy of desorption of CO is also found in [14] as 32 kcal/mol.

21	$CO+Pd(S)\Rightarrow CO(S)$	S	0.96–0		0.0	0.0
22	$CO(S)\Rightarrow CO+Pd(S)$		1.3E13	0.0	133.9	

The symbol S indicates that the kinetic data are given with the sticking coefficient formulation. The units are kJ/mol for *E*, the activation energy and in mol, cm, s for *A*, the preexponential factor. *n* is the exponential order of the temperature dependent term. COV is a parameter depending on the relevant species surface coverage that affects the reaction rate.

4. Results and discussion

4.1. Experimental

The errors expected from the measurements for CO_2 and O_2 were less than ±3% (relative), ±2 ppm for CH_4 and ±1 ppm for NO_x. Errors on the surface temperatures were estimated at ±50 K. Gas temperatures were also measured with a type K thermocouple and although not shown here because of necessitating a complex correction factor accounting for radiation losses, the values found let us to believe they would be lower than the surface temperature by approximately 100 K. The main results for the Pt and for the Pd

Table 2
Experimental average values and local extrema of surface temperature and species concentrations for the Pt and for the Pd monoliths at the total flow rates 40 and 100 l/min

Flow (l/min)	T_S av (K)		T_S max (K)		CO_2 av (%)		CO_2 max (%)		CH_4 max (ppm)		NO_x max (ppm)	
			T_S max–T_S min				CO_2 max–CO_2 min		CH_4 av		NO_x av	
	Pt	Pd	Pt	Pd	Pt	Pd	Pt	Pd	Pt	Pd	Pt	Pd
40	1219	1276	1286	1333	4.65	4.06	5.86	5.44	1239	1208	0.3	0.9
			142	130			2.2	2.23	83	188	0.2	0.5
100	1382	1438	1418	1473	4.00	4.20	4.43	4.92	39	2018	1.5	3.3
			98	80			0.96	1.23	7	161	0.9	1.4

monoliths are shown in Table 2. The averages were taken from 17 equidistant points over the downstream surface of the monolith, the location of these points can be seen in Fig. 2. The CO_2 contours revealed a maldistribution of the fuel that did not exceed 25% of the average. It can be seen from the CO_2 results in Table 2 that this fuel maldistribution decreased with increasing flow rates, this being attributed to a better mixing induced by the larger velocities through the swirler. Fig. 3. shows the contours of surface temperature obtained for the Pt monolith at a total input flow rate of 40 l/min.

It can be seen from Table 2 that the surface temperatures for similar input fuel concentrations are higher for Pd than for Pt, also the higher flow rates yield higher surface temperatures. No NO nor CO formation was found for all cases, whereas methane slippages showed large variations with both catalysts

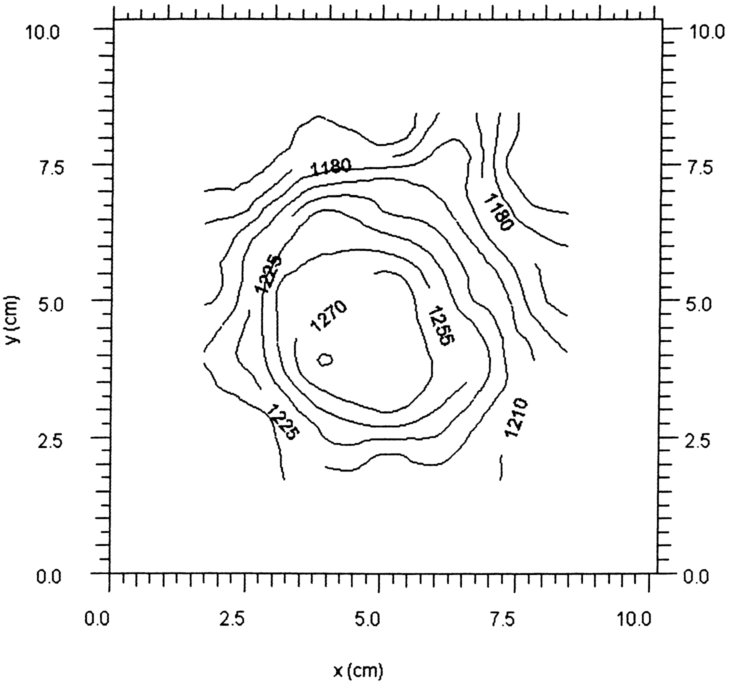

Fig. 3. Contours of measured surface temperature (K) for the Pt monolith at 40 l/min.

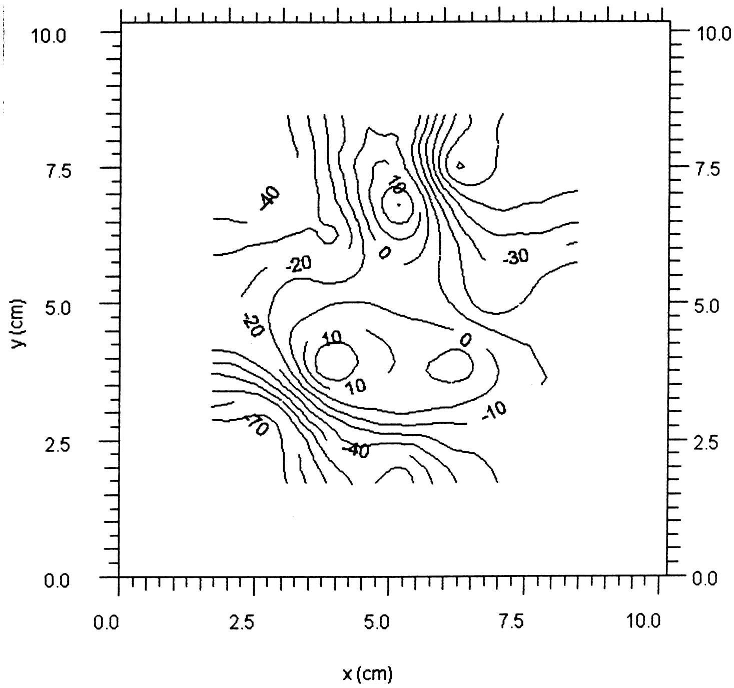

Fig. 4. Contours of predicted temperature minus measured surface temperature (K) for the Pt monolith at 40 l/min. The average difference is 30 K.

and flow rates. Few high methane concentrations were found very locally in a random way for all cases. The average methane slippages were mitigated by the low number of points measured over the whole surface (17 points). Nevertheless, it would seem that the Pd catalyst gave rise to higher methane slippages than the Pt catalyst. Ignition was more easily achieved with the Pd catalyst at lower flow rates, higher ones often being the cause of flashback during the ignition period.

4.2. Modelling

Fig. 4 shows the difference between the experimentally measured temperature contours from Fig. 3 with those calculated numerically for a flow rate of 40 l/min over the Pt monolith. In order to calculate the temperature distribution, it was assumed that the CO_2 distribution at the outlet was equal to that of the fuel at the input, the contribution of other carbon containing species being negligible. The modelling work using the code surface PSR was, at this early stage, based on some coarse approximations which will be discussed later. However, good agreement with the experimental temperature distribution was achieved for this case. Such a good correspondence between experimental and predicted temperatures was not obtained in the remaining experiments. Therefore subsequent model results were presented for the system as a whole. As mentioned, there was a great deal of uncertainty in the model of the Pd surface mechanism. In particular it was assumed that the adsorption of methane itself occurred via a mechanism equivalent to that used in the Pt reaction scheme [6]. The latter authors have quoted a range of values from 0.01 to 0.19 for the sticking coefficient of methane. Although we have followed their approach in taking the lowest value in this range for Pt, we found that, because of the increased O adsorption for Pd, described in the same paper, the highest value in this range was required to model combustion successfully over the range of concentrations and flow rates corresponding to our experiments.

Fig. 5 shows the variations of temperature and of site fraction occupied by surface oxygen over a range

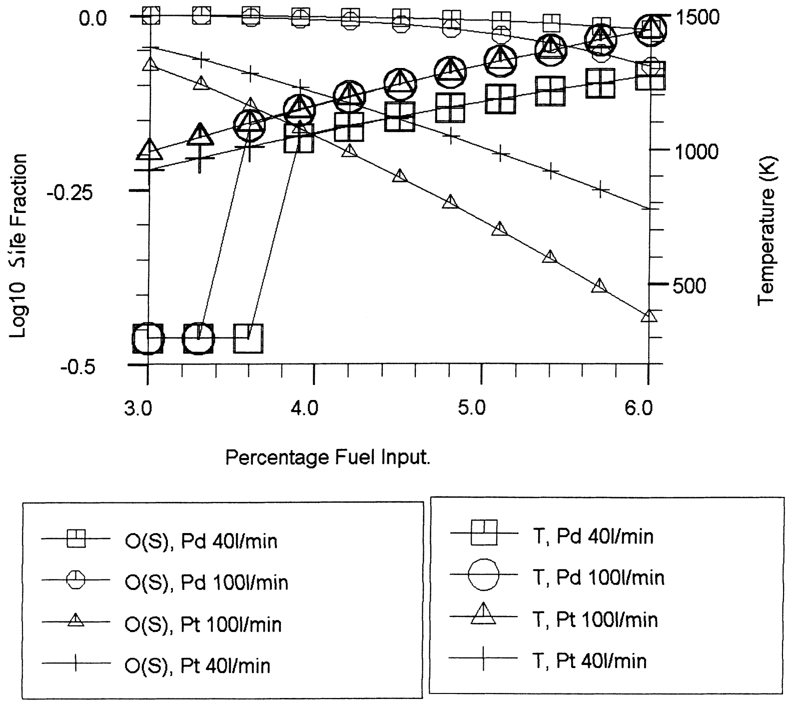

Fig. 5. Variations of site fraction of adsorbed O and of surface temperature with input fuel concentration for Pt, Pd, and the total flow rates 40 and 100 l/min.

of inlet fuel concentrations predicted by our model for the two flow rates 40 and 100 l/min. Even with the higher sticking coefficient, we were still unable to find steady burning solutions for Pd at lower concentrations due to the domination of surface sites by adsorbed O. Whilst it is possible that this effect was genuine, and that in the experiments combustion was supported at these lower concentrations by heat conduction from other parts of the catalyst, it is more likely that we have highlighted a limitation of the model. Comparison with the experimental results shows that the model underpredicts the surface temperatures for palladium by up to 200 K, but the gas temperatures (not shown here) are in fact lower than the measured surface temperatures by an estimated value of 100 K. It seems that the monolith must store considerable heat in order to raise the surface temperature to promote O desorption before ignition can take place.

Fig. 6 shows the of variation of temperature and site fraction occupied by surface oxygen with volumetric flow rate for CH_4 inlet concentrations of 4.5% and 6%. These values are well above the average experimental concentrations except for the 40 l/min Pt case, and the results show that steady combustion can be maintained over the whole range of flow rates shown (20–140 l/min). The temperatures show almost exact agreement between corresponding Pt and Pd models. This is to be expected, as predicted slippages and CO outlet concentrations are negligible for all our simulations. The single temperature prescribed for both gas and surface in our simple model is therefore solely determined by the inlet fuel concentration and the form of heat loss.

Negligible NO_x production was found from both experiment and numerical simulation due to the low temperatures.

Table 3 shows the minimum fractional consumption of methane by adsorption onto the surface over the flow rate range in Fig. 6. The two Pd values corresponded to flow rates which were only just sufficient for the exothermic reactions to overcome the heat losses and high O coverages. In fact when a

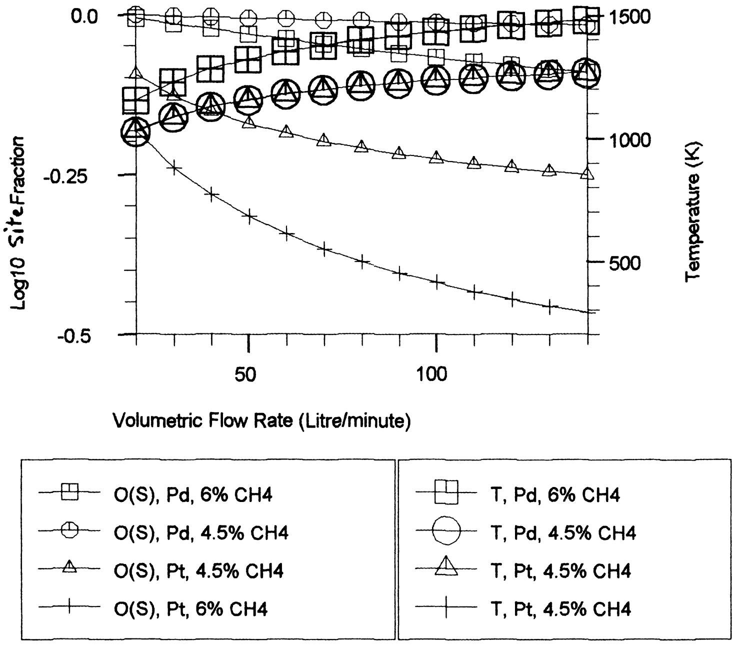

Fig. 6. Site fraction of O and surface temperature vs. flow rate for Pt, Pd, at 4.5% and 6% CH_4 input concentration.

corresponding simulation was tried with no catalytic surface, we could only find steadily burning solutions when the heat losses were removed.

Fig. 7 shows the variation in fractions of vacant sites and outlet gas-phase CH_4 concentration with input fuel concentration. The tendency of palladium to allow greater slippages is shown clearly as well as the decrease in the number of vacant sites. In fact, the ranges of values for slippage, 1–10 ppm for Pt, and 10–500 ppm for Pd correspond quite well with our experimental results.

5. Conclusion

Although it is difficult to draw firm conclusions as to the accuracy of our chemical schemes due to the limitations of our model, we have isolated reasonable mechanisms for some tendencies in our experimental results. In every case our arguments are connected with the behaviour of O with respect to the catalytic surfaces. In particular we have been able to explain the occurrence of higher methane slippages for Pd than for Pt in terms of the domination of surface sites by adsorbed O. It also seems that the greater sticking coefficient with the former is a possible explanation for the poorer agreement between our experimental and model results in that a greater temperature differential must be maintained between gas and surface phase for the overall reaction to proceed at a sufficient rate. The primary requirement for improving our model of catalytic monoliths seems to be a method to deal with the detailed thermodynamic exchange between the monolith and the gas flowing through it.

There are also issues concerning the surface chemistry which have not been addressed in the current work. In all our work so far, we have assumed that every metal atom within the washcoat is available as a catalytic site. It is likely that more accurate simulations will require detailed information on metal particle sizes in order to assess the latter assumption.

Table 3
Minimum fractional consumption of CH_4 by adsorption over flow range 20–120 l/min

CH_4 input (%)	Pt	Pd
4.5	1	0.991
6	0.999	0.994

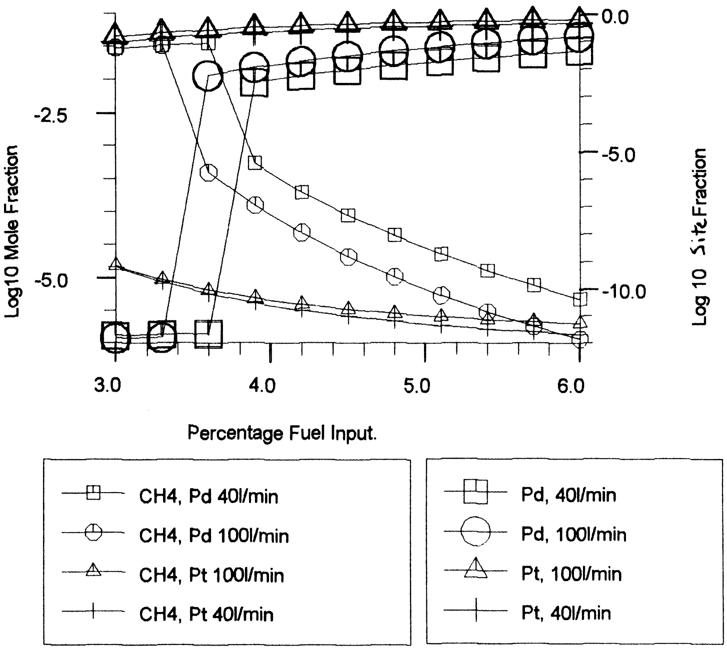

Fig. 7. CH_4 slippage and fraction of vacant sites vs. input fuel input concentration for Pt, Pd, at 40 and 100 l/min.

Also restricted site densities of oxygen, and variations in sticking coefficients for CO on both Pt and Pd referred to by Engel and Ertl [14] may be important, although the latter authors dealt with lower pressures and temperatures than we have in the current work.

Acknowledgements

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