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Spatially-Resolved Investigation of the Water Inhibition of Methane Oxidation over Palladium

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The Development of a Novel Dual-Site Kinetic Model of Water-Inhibited Methane Oxidation based on Spatially-Resolved Experimental Data

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Abstract

Pd/Al₂O₃ catalysts are known to be active for the low temperature methane oxidation reactions, however it has been shown that a number of gases normally associated with methane gas streams (H₂O, CO₂, H₂S) can have an inhibitory effect on the total oxidation reaction. This work focuses on the effect of H₂O on the complete oxidation of methane on a 3%Pd/Al₂O₃ wash-coated monolith, with a view to understanding the reaction and inhibition mechanisms and their interplay with heat and mass transport phenomena in the monolith. Steady state furnace temperatures of 400°C, 425°C and 450°C, in conjunction with a spatially resolved capillary inlet mass spectrometry (SpaciMS) approach, were employed to test the spatial effect of 0-10% H₂O feed concentrations and temperature on complete methane oxidation reactions. 12 sets of experimental intra-catalyst axially resolved gas temperature and concentration profiles were obtained in a central monolith channel and were used to screen a number of postulated global kinetic models, utilising an in house parameter estimation routine developed using Athena Visual Studio v.14.2. A 1D heterogeneous single channel reactor model has been incorporated into the model imposing a gaseous temperature spline to improve the confidence in parameter estimation. The Akaike information criterion (AIC) was used to discriminate between a number of hypothesised global kinetic models, with a newly derived 2 site model demonstrating the best statistical fit.

Introduction

Methane or natural gas is considered a relatively clean, cheap and abundant fuel^{1,2} compared to conventional sources (oil and coal), thus it has become attractive for combined heat and power plants (CHP) and natural gas vehicles (NGVs).³ The major drawback of utilising CH₄ gas as a fuel comes from its relatively large contribution to the greenhouse effect, originating from its Global Warming Potential (GWP) of 28 and 84 over 100 and 20 years respectively.⁴ Accordingly, an increasing focus is being placed on combating global warming and improving global air quality.

Conventionally, emissions from NGVs (CO, CO₂, H₂O, CH₄, NO_x, phosphates and sulphurous compounds) are abated via catalytic converters positioned in the exhaust stream of the vehicle. Typically, unreacted CH₄ (500-1000 ppm) represents the most challenging component⁵, requiring temperatures of 500-550 °C to bring about complete oxidation, therefore various supported noble metal catalysts have been investigated for low temperature CH₄ oxidation.^{1,2,6,7} Catalysts consisting of Pd supported on alumina have generally been found to be the most active.⁸⁻²² In most applications the active Pd/Al₂O₃ phase is wash coated on an inert cordierite or metallic honeycomb monolith substrate to: maximise the geometrical surface area of the catalyst; optimise the heat and mass transfer properties; minimise the pressure drop of the exhaust system.

Although useful information regarding the effectiveness of monolithic catalytic systems can be attained via conventional end-pipe testing approaches²³, important intra-monolith information will not be observed. Spatially resolved reaction profiles, temperature evolution, intermediates formation/removal, deactivation and reaction sequences are all unobtainable via end-pipe approach. To access such intra-catalyst information from structured monolithic catalysts, a number of spatially resolved analytical techniques have been developed.²⁴⁻³³ Spatially resolved capillary inlet mass spectrometry (SpaciMS) has proved a useful analysis technique for monolithic systems, utilising a series of minimally invasive physical probes²⁹, consisting of open ended capillaries and thermocouples to map the gaseous concentration and temperature profiles occurring inside of the monolith channels. Commonly, SpaciMS is used to assess the activity of structured catalysts with respect to conversion, selectivity, deactivation etc.²³, however the exploitation of vast quantities of spatially resolved data via kinetic modelling remains relatively scarce in literature. The complexity of modelling spatial systems may go some way to explaining this, as accurate predictive simulations rely on the use of an appropriate kinetic model (micro kinetic or global

kinetic); representative kinetic parameters (literature or experimentally estimated); and a suitable reactor model (1D, 2D or 3D) and scale (micro, meso or macro).

Numerous global kinetic models can be found in literature which account for various important physico-chemical factors such as temperature effects, surface species coverage, sulphur poisoning and deactivation.³⁴⁻⁴⁵ The use of power law models to represent the complete methane oxidation reaction under wet conditions are prevalent in literature. Multiple sources suggest that under lean reaction conditions, the reaction orders with respect to the reactants CH₄ and O₂ are 1 and 0 respectively.^{10,14,46,47} However under realistic operating conditions, Pd/Al₂O₃ catalysts are subjected to high concentrations of H₂O and CO₂ which have both been demonstrated to inhibit the CH₄ oxidation reaction.^{6,8-10,19,46-54} Some authors have hypothesised Pd(OH)₂ as the inhibitory surface species⁴⁸, preventing access of CH₄ to the active PdO sites, however this is still a topic of debate. In terms of the kinetics, Ribeiro *et al.* and van Giezen *et al.* have used power law models to estimate the activation energy of lean CH₄ oxidation reaction occurring on Pd/Al₂O₃ based catalysts, yielding apparent activation energies of 85 kJmol⁻¹ (dry)¹⁰ and 151 kJmol⁻¹ (wet).⁵¹ Although no kinetic analysis was reported in the work of Burch *et al.*, water inhibition was found to be temperature dependent, with lower inhibitory effects observed at higher temperatures.⁴⁶ Ciuparu and Pfefferle⁵² demonstrated that the reaction order with respect to water, varies with both temperature and water concentration under pulsed experimental conditions, thus suggesting that a more detailed kinetic model is required to accurately capture the reaction profile. Langmuir-Hinshelwood mechanisms have been proposed by Firth and Holland⁵⁵ and Groppi⁵⁶, an Eley-Rideal mechanism has been suggested by Seimanides and Stoukides⁵⁷ whilst a Mars van Krevelen mechanism has been proposed from the results of tests carried out by Garbowski *et al.*⁵⁸ and Ordóñez *et al.*⁵⁹, however no consensus has been reached with regards to a global reaction mechanism.

The complexity of coupling kinetic models with a suitable reactor model forms a crucial step in modelling gaseous reactions in monolithic supported catalysts⁶⁰. Various modelling approaches exist in literature, in which supported monolith reactors have been modelled using discrete and continuum models of varying degrees of dimensionality 1D^{61,62}, 2D^{63,64}, and 3D.⁶⁵⁻⁶⁷ 1D single channel models are relatively simple to formulate, generally making the assumptions that gaseous temperature and species concentrations vary only in the axial direction and that radial heat and mass transfer between the gas and solid phase can be captured by global heat and mass transfer correlations.⁶⁸⁻⁷⁵ Thus the solid and gas heat and

mass balance equations can generally be rectified by solving a combination of ordinary differential and algebraic equations.⁷⁶⁻⁷⁹

Internal and external heat and mass transfer⁸⁰ are phenomena that can have a marked effect on the observed rates of reaction, particularly affecting species diffusion rates in the bulk and within the pore network of the wash coat.⁸¹⁻⁹³ Internal pore diffusion limitations are generally accounted for via the inclusion of an effectiveness factor in both the energy and species transport equations, assuming two discrete phases i.e. solid and gas. The majority of research groups have estimated the effectiveness factor via the Thiele Modulus approach⁸¹⁻⁸⁵ however the Weisz-Prater criterion⁸⁹⁻⁹¹ and internal mass transfer coefficient^{92,93} approaches have also been utilised in numerous works. External diffusion is generally allowed for via lumped parameter models, distributed models and empirically derived correlations.⁹⁴ In many instances, empirical correlations have been found to adequately capture the external mass transfer behaviour of two-phase, 1D single channel models, therefore their use is widespread in literature.

In this work, the **known** inhibitory effect of water on the steady-state, lean methane oxidation activity^{46,52,95} of a commercial 3%Pd/Al₂O₃ monolith catalyst, has been axially profiled using the SpaciMS technique. The resulting reaction profiles have been utilised in screening a number of hypothesised global kinetic models via a built in parameter estimation routine developed using Athena Visual Studios, coupled with a 1D heterogeneous single channel model. Potential mass transfer limitations have been assessed locally within the channel via spatially resolved determination of the Weisz-Prater criterion, which has been used to pre-filter multiple spatially resolved datasets, selectively identifying non-mass transfer limited regions suitable for the process of kinetic parameter estimation. By applying the Weisz-Prater criterion approach it was possible to utilise the observed reaction rate, calculated by taking the differential of the mathematically fitted CH₄ concentration profile with respect to time thereby eliminating the need to iteratively calculate the intrinsic reaction rate; a prerequisite for the conventionally applied Thiele Modulus approach. The temperature differences existing between the gas and solid phases have been assessed by considering a combination of convective and conductive heat transport at all axially probed positions, culminating in the calculation of a criterion that denotes the likelihood of significant gas-solid temperature differences existing. The utilisation of data sets consisting of non-mass transfer limited data exhibiting insignificant gas-solid temperature differences, increased confidence in the estimation of kinetic parameters. Model discrimination was subsequently exploited at

this point, making use of the Akaike Information Criterion (AIC) to identify the most representative global kinetic model of those screened.

Experimental

Fig. 1 Spatially resolved capillary inlet mass spectrometry experimental setup

In this work, the SpaciMS previously approach adopted by Queen's University Belfast (QUB)^{25, 29, 96} is summarised in Fig. 1. Specific to this study, a stainless steel reactor (I.D. mm, length 102 mm) positioned centrally inside a 1 m split tube Carbolite furnace, was used to house the 3%Pd/Al₂O₃ monolith core. The monolith core was wrapped in 2 mm of insulation, preventing flow bypassing and ensuring all gas flow was directed through the parallel channels. Gas temperature was measured via a 250 µm O.D. type K thermocouple (Omega) located inside a central monolith channel, and recorded by a TC-08 Thermocouple Data Logger. Gas composition was sampled via a 220 µm O.D. open ended fused silica capillary (Polymicro Technologies) located inside a central monolith channel and detected by a quartz inert capillary (QIC) quadrupole mass spectrometer (Hiden HPR20). The thermocouple and capillary are located in adjacent monolith channels to minimise invasiveness as shown in Fig. 2 (a) and (b). As with previous work using this experimental setup, the invasiveness of the probes was minimised by reducing parameters known to be crucial to invasiveness, including probe diameter, channel flow rate and capillary suction rate²⁹ as well as positioning the probes in the corners of the channels, demonstrated computationally to be the least invasive configuration. The probes were translated axially inside the monolith channels via a movable z-motion linear stage controlled by a Thorlabs APT Microstepping Controller (BSC101), automated with an in house Matlab program. Water vapour was supplied via a controlled evaporation and mixing system (Bronkhorst

CEM, Model W-101A), allowing the delivery of precise quantities of water vapour to the reactor.

Fig. 2 (a) Actual radial distribution of measurements probes at inlet face of monolith core (b) Representative radial distribution of measurements probes at inlet face of monolith core (c) Axial positions scanned

Initially steady state spatially resolved analysis was carried out on complete methane oxidation reactions, in the presence and absence of water. A total gaseous flow of 2 Lmin^{-1} was applied to the monolith core at a pressure of 1 atm, with the feed consisting of 0.4 v/v % CH_4 , 12 v/v % O_2 , 0, 1, 5 and 10 v/v % H_2O , balanced with Ar. Three steady state furnace temperatures of 400°C , 425°C and 450°C were selected to assess the effect of temperature on water inhibition on the methane oxidation reaction, culminating in twelve tested conditions.

Fig. 3 Flow diagram describing the process of experimental data gathering culminating in the final estimation of kinetic parameters

Axial positions of between 0-60 mm were scanned as represented by Fig. 2 (c).

Prior to each experimental test, the monolith core was pre-treated for two hours using a 2 L.min⁻¹ gas stream containing 20 v/v % O₂ in Ar, utilising a furnace temperature of 450°C. Following pre-treatment, a three hour baseline period was allowed to develop utilising a 2 L.min⁻¹ flow of 100 v/v % Ar, ensuring the development of a stable mass spectrometer background signal. Succeeding baseline development, steady state reaction conditions are (summarised in Table S1) were set up with the remainder of the gas flow being made up of CH₄, O₂ and Ar. Probes were translated axially inside the monolith channels, scanning positions between 0-60 mm, with an axial resolution of 3 mm (see ESI for more detailed experimental method).

A description of the modelling procedure is summarised in Fig. 3, in which heat and mass transfer processes were assessed initially, discarding any data found likely to have a significant T_s-T_g ($\delta_s > 0.1$), or experience mass transfer limitation (WP < 0.3). Kinetic parameters were then estimated based on data within the kinetically controlled regime, via a combination of crude Non-linear least squares (NLLS), followed by refined Bayesian Estimation. Models were ranked based on statistics, with the highest ranking model reintroduced to the mass transfer limited and significant ΔT data, and subsequently employed to estimate one final set of kinetic parameters. The final comparison of statistics, goodness of fit and chemical relevance of kinetic parameters, was used to determine whether this approach was suitable in fitting multiple, mass transfer and temperature corrected data sets, ultimately yielding a single, representative set of kinetic parameters. A more comprehensive description of the methodology will be detailed in the subsequent Results and Discussion section.

Results & Discussion

Fig. 4 (a), (c) and (e) display the CH_{4(g)} conversion profiles as a function of axial position for feeds containing between 0 - 10 v/v % H₂O, exposed to steady state furnace temperatures ranging from 400 - 450°C. Measured gaseous temperature profiles inside the monolith channels exceeded that of the furnace set point as detailed in Fig. 4 (b), (d) and (f). This can be explained by the exothermic nature of the methane oxidation reaction, typically exhibiting an enthalpy of reaction ($-\Delta H_r$) at standard temperature and pressure of 890.16 - 890.7 kJ mol⁻¹^{97,98}, although higher values have been reported elsewhere⁹⁹. In this work, the inhibitory effect of water on the complete methane combustion is readily apparent from the plots in Fig. 4, where feeds consisting of 5 v/v % and 10 v/v % H₂O exhibit a notable

reduction in the catalytic activity over the range of axial positions scanned for all furnace temperatures. Such inhibitory effects have been observed by many research groups^{6-10,33,46-54}, with the majority of groups reaching the consensus that Pd supported on alumina can form a Pd(OH)_x species in the presence of H₂O, which subsequently demonstrates a slow H₂O desorption rate which is hypothesised to be the rate determining step. With the higher concentration of H₂O in the gas phase, a larger surface concentration of H₂O or OH is adsorbed on the Pd or PdO sites, thus a greater amount of energy is required to desorb or break down the inhibiting species, limiting the rate of methane oxidation. Both theories are verified to some extent by Fig. 4 (a), (c) and (e), exemplifying lower levels of inhibition at a furnace temperature of 450 °C compared to 400 °C.

In the interest of establishing a meaningful global reaction mechanism, a number of hypothesised global rate expressions have been fitted to the spatially resolved profiles and assessed statistically. Hypothesised rate expressions employed in this work are detailed in Table 1, with models 1-8 previously summarised by Shahrestani¹⁹, whilst model 9 has been derived during this work. All model assumptions associated with derivations can be found in the Electronic Supplementary Information (ESI). Based on observations made during previous studies on CO oxidation in the presence of H₂O²⁵, carried out on a 3%Pd/Al₂O₃ catalyst, a further model has been derived as part of this work (model 9). Under rich conditions, H₂O was found to promote the CO oxidation reaction occurring on a 3%Pd/Al₂O₃ monolith core, contributing a perceived additional oxygen storage-like component (OSC). The additional OSC was hypothesised to originate from the formation of a Pd(OH)_x species, forming in the presence of H₂O, therefore it would be prudent to expect the formation of the same species under the conditions explored in this study. In contrast to the previously observed promotional effect of H₂O on Pd catalysed CO oxidation reactions, an inhibitory effect is realised during CH₄ oxidation under lean conditions, as shown by Fig. 4.

Fig. 4 Methane conversion as a function of axial position in the central channel of a 3%Pd/Al₂O₃ monolith catalyst performed at (a) 400°C (c) 425°C (e) 450°C. Gas temperature as a function of axial position in the central channel of a 3%Pd/Al₂O₃ monolith catalyst performed at (b) 400°C (d) 425°C (f) 450°C.

Low gas phase temperatures and high gas phase H₂O concentrations correlate with larger inhibitory effects, however CH₄ conversion is still achieved at the lowest temperature and highest H₂O concentration employed during this investigation, suggesting that potentially two active sites are contributing to the overall CH₄ conversion. Therefore Model 9 makes the assumption that two active sites exist for CH₄ oxidation, site one (S₁) representing oxidised Pd (PdO) and site two (S₂) representing a hypothesised Pd(OH)_x species. S₂ is thought to form from the conversion of S₁ (PdO) to Pd(OH)_x in the presence of H₂O, represented by Eqn S83 in the ESI. In this situation, S₁ is surmised to be a more active site than S₂, with respect to the CH₄ oxidation, therefore $r_{S1} \gg r_{S2}$. A detailed derivation of Model 9 can be found in the ESI, Eqns. S83-S93.

Table 1 Hypothesised rate expressions

Model	Rate Expression	Model Mechanism
1	$r_m = \frac{k_r C_{CH_4}}{C_{H_2O}}$	Power Law
2	$r_m = \frac{k_r C_{CH_4}}{1 + K_{H_2O} C_{H_2O}}$	Eley-Rideal
3	$r_m = \frac{k_r C_{CH_4}}{(1 + K_{H_2O} C_{H_2O})^2}$	Langmuir-Hinshelwood
4	$r_m = \frac{k_r C_{CH_4}}{(1 + K_{CH_4} C_{CH_4} + K_{H_2O} C_{H_2O})^2}$	Langmuir-Hinshelwood
5	$r_m = \frac{k_r C_{CH_4}}{1 + K_{CO_2} C_{CO_2} + K_{H_2O} C_{H_2O}}$	Eley-Rideal
6	$r_m = \frac{k_r C_{CH_4}}{(1 + K_{CO_2} C_{CO_2} + K_{H_2O} C_{H_2O})^2}$	Langmuir-Hinshelwood
7	$r_m = \frac{k_r C_{CH_4} k_{O_2} C_{O_2}}{k_{O_2} C_{O_2} + 2k_r C_{CH_4} (1 + K_{H_2O} C_{H_2O})}$	Mars van Krevelen
8	$r_m = \frac{k_r C_{CH_4} k_{O_2} C_{O_2}}{k_{O_2} C_{O_2} (1 + K_{H_2O} C_{H_2O}) + 2k_r C_{CH_4}}$	Mars van Krevelen
9	$r_m = \frac{k_1 C_{CH_4} + K_{Eq} k_2 C_{CH_4} C_{H_2O}^x}{(1 + K_{Eq} C_{H_2O}^x)}$	Dual site

Mass Transfer

Localised internal mass transfer limitation was assessed via pre-screening of experimental data using the Weisz-Prater criterion^{100,101} (Eqn. 1). The Weisz-Prater criterion assesses the contribution of pore diffusion on the reaction rate of the limiting reactant, where it is generally accepted that a negligible decrease in concentration gradient between the catalyst particle surface and inner pore network, corresponds to a negligible decrease in reaction rate. Consequently a criterion is applied, at which a maximum allowable concentration gradient corresponding to negligible mass diffusion limitation ($\eta \geq 0.95$) is assigned, allowing the determination of conditions where mass transfer limitation is likely to exist. Assuming a spherical particle experiencing Knudsen diffusion under isothermal and steady state conditions, it has been demonstrated via mathematical derivation that a dimensionless Weisz-Prater criterion of less than 0.3, 0.6 and 6 corresponds to kinetically controlled regimes for 2nd, 1st and zero order reactions, respectively.⁸⁹ The main advantage of using the Weisz-Prater Criterion over conventional internal mass transfer criteria, such as Thiele Modulus, revolves around the ability to calculate the Weisz-Prater Criterion using only observable parameters which can be easily measured or calculated, whereas intrinsic kinetic rate parameters are required in the application of the Thiele Modulus.

Fig. 5 Double exponential fit of CH₄ concentration as a function of axial position for inlet H₂O concentrations of (a) 0% H₂O (b) 1% H₂O (c) 5% H₂O (d) 10% H₂O at a steady state furnace temperature of 425 °C.

$$\varphi' = \frac{L^2 r'_p}{D_{eff,A} C_{s,A}} = \eta_{su} \varphi^2 \quad (1)$$

Characteristic length L was estimated via the average wash coat thickness taken from SEM images, Fig S6 (see ESI). Effective diffusivity $D_{e,A}$ was calculated from a correlation derived by Fuller, Giddings, Ensley & Schettler.¹⁰² External diffusion limitations were not observed during this work, indicated by the spatial Mears number plots reported in the ESI, thus the assumption that $C_{A,g} = C_{s,A}$ can be validated. Kinetic parameters contained within the observed rate expression r'_p (k_r , K_i , E_a , ΔH_i) were estimated as part of the model routine, thus were not available during the mass transfer pre-screening process without adding an additional iterative process to the model routine. An alternative method was utilised to calculate the observed rate r'_p , employing a purely mathematical expression in the form of a linear combination of decaying exponential functions, to capture the change in concentration with residence time (Eqn. 2).

$$C_{CH_4} = a_0 + a_1 e^{-a_2 t} + a_3 e^{-a_4 t} \quad (2)$$

Parameters a_0 , a_1 , a_2 , a_3 and a_4 were estimated via Bayesian estimation using Athena Visual Studios. The first derivative (dC_{CH_4}/dt) was calculated analytically to give Eqn. 3:

$$\frac{dC_{CH_4}}{dt} = -a_1 a_2 e^{-a_2 t} - a_3 a_4 e^{-a_4 t} \quad (3)$$

Fig. 6 Localised Weisz-Prater criterion as a function of axial position for 0% H₂O, 1% H₂O, 5% H₂O, 10% H₂O at steady state furnace temperatures of (a) 400 °C (b) 425 °C (c) 450 °C

An example of the double exponential fitting of the CH₄ concentration evolution obtained at a steady state furnace temperature of 425 °C, is highlighted in Fig. 5. The proximity of the predicted values to the experimental values as well as the large r^2 values, indicates that the double exponential expressions characterise the experimentally measured data with suitable accuracy in this specific case. The additional mathematical fits for steady state temperatures of 400 °C and 450 °C, (see supplementary Figs. S8 and S9 in the ESI),

also show good agreement between the predicted and experimental values. By fitting the data with decaying exponential functions, it was possible to remove any noise associated with the experimental data, therefore changes in gradient attributed to noise can be eliminated from the solutions of Eqn. 3. By employing this approach it was possible to ascertain values for observed reaction rates at the respective axial positions, without having to rely on intrinsic kinetic parameters estimated in literature which exhibit a large variation.

The results of the internal mass transfer screening process are displayed in Fig. 6, presenting the calculated Weisz-Prater criteria as a function of axial position for steady state furnace temperatures of 400 °C, 425 °C and 450 °C employing feeds of 0%, 1%, 5% and 10% H₂O with 4000 ppm CH₄ and 12% O₂. It is apparent from Fig. 6 (a-c) that feeds consisting of 5% and 10% H₂O do not exhibit internal mass transfer limitation at any of the axial positions probed within the steady state furnace range tested i.e. 400-450 °C. It should be noted that the actual gas temperature range experienced within the monolith channel ranges from 390-540 °C due to the exothermic nature of the methane oxidation reaction coupled with the apparent cooling effect of the fresh incoming gas under high H₂O feed concentrations, highlighted by Figs. 3 (b), (d) and (f).

Heat Transfer

Using the SpaciMS approach it is possible to attain the gaseous temperature and composition profiles along the axial axis of the monolith channel. However the corresponding solid phase temperature profiles are not attainable using this technique. This provides a complication when it comes to modelling heterogeneous reactions as the solid phase characteristics dictate the rate of reaction. Various methods exist in which it is possible to approximate both the solid phase concentration and temperature via semi-empirical correlations.¹⁰³⁻¹⁰⁸ One such approach utilised an adapted version of the heat transfer correlation based on Mears criteria.¹⁰⁹ Using this approach, it is possible to use Eqn. 4 to predict the solid state temperature from the gaseous temperature profile, as well as utilising Eqn. 7 to estimate the likely relative temperature difference between the solid and gas phase. Eqn. 7 consists of a dimensionless heat transfer component (α_c) detailing the ratio of conductive heat transfer to convective heat transfer; and a dimensionless mass transfer component (f_{ex}) detailing the ratio of apparent reaction rate to diffusion rate. The numerator $k_{D,A}C_{A,g}(-\Delta H)$ in Eqn. 5 represents the heat generated by the reaction at the surface of the catalyst, whilst the denominator represents the heat transferred to the gas phase via

convective heat transfer. The greater ratio of heat generated by the chemical reaction to convective heat transfer, corresponds to a larger δ_s and therefore a more significant temperature difference between the gas and solids phases. An analogous theory applies to the dimensionless mass transfer component (f_{ex}) in Eqn. 6, where a larger ratio of apparent reaction rate to diffusional mass transfer, results in a higher likelihood of mass transfer limitation occurring and therefore a greater value of δ_s . To calculate δ_s , the activation energy is required as an input in Eqn. 7, however prior to the parameter estimation routine a value for the activation energy has not yet been estimated. To circumvent this problem, a practical range for the methane oxidation activation energy occurring over Pd/Al₂O₃ based catalysts has been selected based on typical values found in literature, ranging from 50-200 kJ.mol⁻¹, and the δ_s value has been assessed as a function of this activation energy range and axial position.

$$\frac{T_s - T_g}{T_g} = \frac{r'_p L}{k_{m,A} C_{g,A}} \cdot \frac{k_{m,A} C_{g,A} (-\Delta H)}{h T_g} = \frac{r'_p L (-\Delta H)}{h T_g} \quad (4)$$

$$\alpha_e = \frac{k_{m,A} C_{g,A} (-\Delta H)}{h T_g} \quad (5)$$

$$f_{ex} = \frac{r'_p L}{k_{m,A} C_{g,A}} \quad (6)$$

$$\delta_s = \frac{E_a}{R T_g} \cdot \frac{\alpha_e f_{ex}}{1 + \alpha_e f_{ex}} \quad (7)$$

Fig. 7 Plot of δ_s as a function of axial position and activation energy for (a) 0% H_2O (b) 1% H_2O (c) 5% H_2O (d) 10% H_2O at a steady state furnace temperature of 450°C

Fig. 7 displays how δ_s varies with axial position and activation energies between 50-200 kJ.mol⁻¹. δ_s represents the relative likelihood that the solid and gas temperature difference is significant, with any value above the threshold value of 0.1 representing a region where a significant temperature difference is observed. These regions are highlighted in red in Fig. 7 signifying areas in which it is not possible to directly utilise the gaseous temperature as an input into the model. In the regions where δ_s is less than 0.1, the difference between the gas and solid temperature is considered negligible therefore the gaseous temperature can be applied as a direct input into the model, via the Arrhenius and van 't Hoff equations. For the axial regions where the δ_s value is above the threshold value of 0.1, the solid temperature can be estimated using the Eqn. 8.

$$T_s = \frac{r'_p L(-\Delta H)}{h T_g} + T_g \quad (8)$$

The heat and mass transfer screening processes made it apparent that the experimental data sets produced under 5% and 10% H₂O feed conditions, at all temperatures investigated in this work, lay within the kinetically controlled regime where it was likely that a negligible temperature difference between the catalyst gas and solid temperatures would be present. Based on these results, six experimental data sets, 5 v/v % H₂O 400 – 450 °C and 10 v/v % H₂O 400 – 450 °C, were selected to screen models 1-9, with the view of identifying the global kinetic model which best describes the water inhibited system. The global kinetic rate expressions attributed to each model were applied independently, estimating a single set of kinetic parameters for the six experimental data sets via NLLS and Bayesian estimation. Each simulated model was simultaneously fitted to experimentally measured CH_{4(g)}, O_{2(g)}, H₂O_(g) and CO_{2(g)} concentrations, applying a cubic spline to the experimental gas temperatures for each set of conditions, to aid in the accuracy of kinetic parameter estimation. Between 2 and 6 kinetic parameters were estimated for each model, over the total range of screened global kinetic models, detailed in Table 2. Initial parameter estimates were provided based on values obtained in literature^{110,111}, refined using Non-Linear Least Square (NLLS) regression and subsequently used as inputs to the final Bayesian estimation refinement.

During the model fitting procedure, a pre-built parameter estimation routine constructed in Athena Visual Studios, was adapted to deal with multiple spatially resolved data sets and utilised to estimate a number of kinetic parameters, consisting of pre-exponential factors (k_r) and activation energies (E_a) for the reaction; pre-exponential factors (k_i) and heat of adsorptions (ΔH_i) for particular reactants, inhibitors and promoters. To achieve meaningful estimates for the kinetic parameters, it was important to consider the

reactor configuration via a suitable reactor model, whilst ensuring initial and resultant parameter estimates fall within chemically feasible ranges.

Reactor Model and Parameter Estimation

The reactor model was based on the one dimensional pseudo-continuous heterogeneous model developed by Hinrichsen *et al.*¹¹² Simultaneous solution of gas and solid phase heat and mass balance (Eqns. 9-12) were used to describe the reactor system of a single channel within the monolith.

Solid phase energy balance

$$\left(k_s \frac{d^2 T_s}{dz^2}\right) - \frac{4Dh(T_s - T_g)}{(D_{wc}^2 - D^2)} - \frac{\eta(\Delta H_r)(-r_A)(D_{wc}^2 - D^2)}{(D_s^2 - D^2)} = 0 \quad (9)$$

Fluid phase energy balance

$$k_g \frac{d^2 T_g}{dz^2} - v_m(\rho_f C_{pf}) \frac{dT_g}{dz} + \frac{4h(T_s - T_g)}{D} = 0 \quad (10)$$

Solid phase mass balance

$$\frac{4D}{(D_{wc}^2 - D^2)} k_m \rho_g (w_{g,A} - w_{s,A}) = \eta(-r_A) \quad (11)$$

Fluid phase mass balance

$$\frac{\partial}{\partial z} \left(D_{eff,A} \rho_g \frac{\partial w_{g,A}}{\partial z} \right) - (\rho_g v_m) \frac{\partial w_{g,A}}{\partial z} - k_m \rho_g (w_{g,A} - w_{s,A}) \left(\frac{4}{D_H} \right) = 0 \quad (12)$$

Eqns. 11 and 12 have been combined to produce a combined mass balance (Eqn. 13) thus removing the need to calculate the mass transfer coefficient via correlations. To increase the confidence of the estimated kinetic parameters, Eqns. 9 and 10 have been replaced by the recorded experimental temperature spline, creating a semi empirical approach. By imposing the experimental temperature spline on the model, the complexity of the model was decreased, the need for prediction of the axial solid and gaseous temperature profiles has been removed, and calculation of a correlation derived heat transfer coefficient is no longer needed, provided $T_s - T_g$ is insignificant.

Combined mass balance

$$-\left(v_m \rho_g \frac{dw_{g,A}}{dz}\right) - \left(\frac{\eta(-r_A)(D_{wc}^2 - D^2)}{D_H D_r}\right) = 0 \quad (13)$$

The combined mass balance and imposed temperature spline were used to form the framework of the reactor model, into which the various rate expressions, stated in Table 2, were inserted. Rate constant (k_r) and equilibrium constants (K_i) are incorporated into rate

expressions via re-parameterised Arrhenius and van 't Hoff Eqns. 14 and 15 respectively. The subscript *i* in Equation 15 denotes the inhibiting species CO₂, H₂O or CH₄.

$$k_r = k_0 e^{\left(\frac{-E_a}{RT_{ref}}\right)} e^{\left(\frac{-E_a}{RT_{ref}}\left(\frac{T_{ref}}{T}-1\right)\right)} \quad (14)$$

$$K_i = K_0 e^{\left(\frac{-\Delta H_r}{RT_{ref}}\right)} e^{\left(\frac{-\Delta H_r}{RT_{ref}}\left(\frac{T_{ref}}{T}-1\right)\right)} \quad (15)$$

For each respective global kinetic model, the relevant kinetic parameters were estimated via a parameter estimation routine developed using Athena Visual Studios software. NLLS regression was used to provide initial parameter estimates, by fitting each model to multiple axially resolved gaseous concentration profiles produced under various inlet conditions. Multi data set fitting was carried out in a simultaneous manner, yielding one set of kinetic parameters per model, encompassing all inlet conditions. Initial parameter values derived from NLLS regression, were then used as the starting inputs for a more refined multi data set Bayesian estimation approach, in which parameter estimates were fine-tuned to a point where the confidence limits of each solution was maximised. Each hypothesised global model was assessed in terms of chemical significance (meaningful reaction mechanism and conceivable parameter estimates) as well as statistical significance (goodness of model fit and relative static applicability).

Tables 2 and 3 report the kinetic parameters estimated as a result of Bayesian Estimation routine, highlighting the HPD confidence limits of each parameter in brackets.

Table 2 Estimated global kinetic parameters (*k_c*, *E_a*, *k₀₂*, *E_{a,02}*) from Bayesian estimation model fitting routine

Model	<i>k_c</i> (s ⁻¹)	<i>E_a</i> (J.mol ⁻¹)	<i>k₀₂</i> or [KCO ₂]	<i>E_{a,02}</i> or [Δ <i>H</i> CO ₂] (J.mol ⁻¹)
1	2.09x10 ⁸ (±5.15%)	95,500 (±6.76%)	-	-
2	8.79x10 ⁹ (±3.81%)	96,026 (±8.94%)	-	-
3	4.66x10 ⁹ (±43.62%)	97,897 (±48.63%)	-	-
4	3.85x10 ¹⁰ (±42.96%)	121,180 (±53.34%)	-	-
7	1.46x10 ⁹ (±47.12%)	95,403 (±74.24%)	9.6x10 ⁶ (±9.13%)	62,167 (±116.56%)
8	7.36x10 ¹¹ (±4.03%)	119,646 (±5.25%)	4.88x10 ⁷¹ (±3.74%)	932,631 (±29.08%)
9 (x=2)	4.19x10 ¹⁰ (± 0.08%)	85,932 (± 0.00%)	4.17x10 ⁸ a (± 0.04%)	101,520b (± 0.00%)

Table 3 Estimated global kinetic parameters (K_{H_2O} , ΔH_{H_2O} , K_{CH_4} , ΔH_{CH_4}) from Bayesian estimation model fitting routine

Model	K_{H_2O}	ΔH_{H_2O} (J.mol ⁻¹)	K_{CH_4}	ΔH_{CH_4} (J.mol ⁻¹)	Model Applicability
1	-	-	-	-	Rejected due to lack of visual fit in Figure 8.
2	9.35 (±12.02%)	-8,147 (±70.30%)	-	-	Rejected due to lack of visual fit in Figure 8.
3	0.623 (±27.72%)	-9,227 (±330.42%)	-	-	Not rejected prior to AIC
4	0.645 (±27.59%)	-10,369 (±384.51%)	7.1×10^{-74} (±3914.96%)	957,154 (±264.33%)	Rejected as reduces to Model 3
7	8.24 (±3.80%)	-11,223 (±8.36%)	-	-	Not rejected prior to AIC
8	2.18 (±4621.59%)	19,082 (±361.74%)	-	-	Rejected due to lack of visual fit in Figure 8.
9 (x=2)	38.91 (± 0.02%)	-938 (± 0.17%)	-	-	Not rejected prior to AIC

Fig. 8 Experimental and simulated CH₄ concentration as a function of event number (EN) for feed conditions of 4000 ppm CH₄, 12% O₂, balance Ar and 5% H₂O at 400 °C (EN 1-20), 425 °C (EN 21-40), 450 °C (EN 41-60) and 10% H₂O at 400 °C (EN 61-80), 425 °C (EN 81-100), 450 °C (EN 101-120) for (a) Model 1 (b) Model 2 (c) Model 3 (d) Model 4 (e) Model 7 (f) Model 8 (g) Model 9. .

Model Discrimination

To discriminate between the models, a number of factors were considered including the physical and chemical significance of the parameter estimates, the quality of the parameter estimates i.e. 95% HPD intervals as well as the statistical relevance of the model. The Akaike Information Criterion (AIC), detailed in Eqn. 16, was employed as an additional metric for assessing the statistical relevance of each model fit.

$$AIC = N \ln \left(\frac{RSS}{N} \right) + 2(q + 1) \quad (16)$$

AIC essentially estimates the quality of a model fit via residual sum of squares (RSS) calculation, whilst introducing a penalizing term based on the number of parameters utilized by the model (q).¹¹³ The calculated AIC value represents a measure of the model fit relative to other models, with larger negative AIC values corresponding to a better statistical fit of the data. It should be noted that the AIC value does not equate to an absolute measure of the strength of the model, but merely provides a means of comparing the probability of one model representing a given dataset more accurately than another model, exemplified by Eqn. 17.

$$probability = \frac{e^{-0.5(AIC_1 - AIC_2)}}{1 + e^{-0.5(AIC_1 - AIC_2)}} \quad (17)$$

The AIC values for each model are detailed in Table 4, each employing an equal sample size of 120 experimental observations with a variable number of kinetic parameters dependent on the model. By employing Eqns. 16 and 17, it was possible to compare model pairs for goodness of fit, whilst accounting for the number of parameters available to fit the model, with the results detailed in Table 5. Each value displayed in Table 5 represents the relative probability of one model (AIC_1) representing the experimental data in a more meaningful way than a second comparison model (AIC_2), with a relative probability of 1.000 signifying a model that is certain to fit better than the compared model. For example, Model 2 is 0.011 times as probable of representing the experimental data more effectively than Model 1, as detailed by the value contained in row 2, column 1 in Table 5.

On initial inspection of the parameter estimates detailed in Tables 2 and 3, some candidate models can be removed based on non-practical values and low confidence limits of the estimated parameters. For example, Model 4 reveals a CH_4 pre-exponential factor of approximately zero (K_{0,CH_4}) as well as a large, positive heat of adsorption (ΔH_{CH_4}), resulting

in $K_{CH_4} \ll 1$. This signifies that CH_4 inhibition ($K_{CH_4}C_{CH_4}$) is insignificant, therefore Model 4 essentially reduces to Model 3, so can ultimately be disregarded. The lack of contribution of CH_4 towards reaction inhibition has also been demonstrated by carrying out various profile reactions utilizing different feed concentrations of CH_4 , highlighted by Fig. S1. A number of kinetic parameters estimated within Model 8 also fail to withstand chemical critique, demonstrating a positive heat of adsorption for H_2O (ΔH_{H_2O}) and extremely high activation energy for the lattice O reaction, both of which represent unrealistic kinetic descriptors under the tested conditions. Models 5 and 6 both assume that CO_2 plays a part in the inhibition process, however light-off tests carried out with different feed concentration of CO_2 , Fig. S3 (see ESI), have shown little CO_2 inhibitory effects, therefore Models 5 and 6 effectively simplify to Models 2 and 3. The remainder of the models yield realistic parameters estimated with reasonable confidences, based on cross referencing with empirical and simulated values established by other researchers.^{10,114-116}

The calculated AIC values coupled with the relative probability comparison were then used to distinguish between the remaining models. It is obvious from the relative probability comparisons in Table 6, that Models 3 and 9 represent the most likely fitting models, with Model 9 superior in comparison to Model 3. In terms of the statistical preeminence of Model 9, the strength originates from the relatively low total RSS value, demonstrated by the close fit of the six ‘wet’ datasets in Fig. 8. The low total RSS counteracts the penalty incurred by the relatively high number of parameters included in the model, whilst the relatively tight 95% HPD intervals increases the confidence in the estimated parameters.

With regards to the chemical significance of Model 9, the strength of the model is believed to come from the assumption that two active sites exist for the methane oxidation reaction; site one representing a relatively fast methane oxidation reaction (S1); and site two representing a relatively slow methane oxidation reaction (S2). It is widely accepted in the literature that under exposure to oxygen rich atmospheres at atmospheric pressure and temperatures below 1000K, a layer of PdO forms the stable phase on Pd/Al₂O₃ catalysts, contributing to the complete CH_4 oxidation reaction^{1,6,10,14,15} Thus site S1 in Model 9 embodies the active PdO phase. It has also been suggested in literature that the formation of hydrated PdO sites i.e. Pd(OH)_x species, is probable under humid, lean conditions, a phenomena observed by numerous authors.^{48,49,50,51} Although consensus has not yet been achieved regarding the exact identification of this inhibiting hydroxyl based species, Ribeiro *et al.* and Burch *et al.* have been able to demonstrate the reversible removal of the inhibiting species at temperatures exceeding 450 °C.^{10,51} The reversible nature of the inhibiting

hydroxyl species suggests the existence of an equilibrium relationship between hydrated and non-hydrated PdO sites, and this is embodied by Eqns. S83 and S89 detailing the equilibrium between sites S1 and S2.

Table 4 Residual sum of squares (RSS), sample size (N), number of parameters (q) and calculated AIC values

Model	RSS	N	q	AIC
1	1.96×10^{-3}	120	2	-1316
2	2.06×10^{-3}	120	4	-1307
3	1.08×10^{-3}	120	4	-1384
4	2.03×10^{-3}	120	4	-1309
7	2.32×10^{-3}	120	6	-1288
8	2.03×10^{-3}	120	6	-1304
9	7.98×10^{-4}	120	6	-1417

Table 5 Model pair probability comparison

		AIC ₂						
		M1	M2	M3	M4	M7	M8	M9
AIC ₁	M1	-	0.989	0.000	0.971	1.000	0.998	0.000
	M2	0.011	-	0.000	0.269	1.000	0.818	0.000
	M3	1.000	1.000	-	1.000	1.000	1.000	0.000
	M4	0.029	0.731	0.000	-	1.000	0.924	0.000
	M7	0.000	0.000	0.000	0.000	-	0.000	0.000
	M8	0.002	0.182	0.000	0.076	1.000	-	0.000
	M9	1.000	1.000	1.000	1.000	1.000	1.000	-

During the model discrimination process, the reaction order of H₂O with respect to Model 9, was fixed at a value of 2 i.e. $x = 2$. To identify if H₂O reaction order had an impact on model fit and subsequent kinetic parameter estimation, two additional values of x were tested. The parameter estimation routine was reapplied to Model 9, fixing the value of x at 1, 2 and 3 for Models 9 (a), (b) and (c) respectively. Six parameters were estimated i.e. pre-exponential factor and activation energy for fast and slow CH₄ oxidation rate, and equilibrium pre-exponential and enthalpy of adsorption for H₂O adsorption. The simulated fits for Models 9 (a-c) display almost identical goodness-of-fit in terms of R² values, however the values of the estimated parameters differ substantially as shown in Table 6. On inspection of the estimated parameters, it is apparent that Model 9 (a) can be ruled out as a potential candidate, as the estimated pre-exponential factor (k_2) yields a negative value, suggesting that CH₄ is being formed on the hydrated PdO sites (S₂), a phenomenon which is unfeasible. Model 9 (c) is also unlikely to be chemically reflective of the experimental data due to the

fact that the energy required to activate CH₄ on the Pd(OH)_x sites (S₂) is estimated to be lower than that of the PdO sites (S₁), contradicting the expected theory. Model 9 (b) avoids both of the issues demonstrated by Models 9 (a) and (c), exhibiting values of $E_{a,2} > E_{a,1}$ and a positive pre-exponential factor for the reaction of CH₄ on Pd(OH)_x. Considering the fact that the value of $E_{a,2}$ is greater than $E_{a,1}$ combined with the larger value of k_1 relative to k_2 , it can be concluded that Model 9 (b) validates the assumption that the PdO sites (S₁) exhibit a greater activity for CH₄ oxidation compared to Pd(OH)₂ sites (S₂). The negative ΔH_{H_2O} value represents the adsorption of H₂O, with the relatively large equilibrium constant K_{EQ} indicating that the position of equilibrium in Eqn. S83 favours the formation of Pd(OH)₂ sites in the presence of either fed or produced H₂O.

Table 6 Estimated global kinetic parameters (k_1 , $E_{a,1}$, k_2 , $E_{a,2}$, K_{EQ} , ΔH_{H_2O}) from Bayesian estimation model fitting routine

Model	k_1 ($\text{mol}^3\text{m}^{-3}\text{s}^{-1}$)	$E_{a,1}$ (J.mol^{-1})	k_2 (s^{-1})	$E_{a,2}$ (J.mol^{-1})	K_{EQ}	ΔH_{H_2O} (J.mol^{-1})
9 (a)	4.96×10^{10}	100,200	-2.67×10^{10}	103,361	29.02	-1,620
9 (b)	4.19×10^{10}	85,932	4.17×10^8	101,520	38.91	-938
9 (c)	1.52×10^{10}	100,053	5.58×10^9	99,692	24.59	-535

The most representative global kinetic Model 9 (b) was then applied to the twelve data sets in Table 1, inclusive of the six data sets that were shown to have high probabilities of exhibiting mass transfer limitations and gas-solid temperature difference in specific axial regions. As previously discussed, axial locations corresponding to $\phi' < 0.3$ are generally recognised to exhibit negligible internal mass transfer within the wash coat, corresponding to $\eta \geq 0.95$. In this work, CH₄ oxidation reactions proceeding in the presence of 5 v/v % and 10 v/v % H₂O in the feed, have satisfied the criteria describing internal non-mass transfer limited regions at all axial positions. However, CH₄ oxidation reactions carried out in the presence of 0 v/v % and 1 v/v % H₂O in the feed have not satisfied these conditions at all axial positions, as exemplified by Fig. 6. For the first and second axial measurement positions, $\phi' > 0.3$ under all furnace temperatures, therefore internal mass transfer limitation is highly probable. The ϕ' values corresponding to mass transfer limited regions range from 0.31-1.15, thus reside within an intermediate regime of diffusion limitation. It is generally accepted that in cases in which significant internal mass transfer limitation is at play i.e. $\phi' > 3$, the relationship between η and $1/\phi'$ becomes linear, thus Eqn. 18 can be applied to calculate values for the effectiveness factor⁹⁰.

$$\eta \sim \frac{1}{\phi'} \quad (18)$$

However, because the calculated mass transfer limited values of $\phi' < 3$, applying Eqn. 18 as part of the parameter estimation routine is likely to underestimate effectiveness factors in the mass transfer limited regions.

Under reaction conditions employing 0 v/v % and 1 v/v % H₂O in the feed, Fig 7 and S7 highlight that the existence of temperature differences between the solid and gas phases are highly likely to be realised at axial positions between 0-10 mm from the inlet. The origins of this expected temperature difference have already been discussed, and the effects on kinetic parameter estimation limited by considering only data in which negligible temperature difference is predicted. The estimated kinetic parameters summarised in Table 3 and 4, are based solely on ‘wet’ data sets i.e. 5 v/v % and 10 v/v % H₂O feed concentrations, however a truly predictive model is desired to simulate all practical conditions expected to be experienced by the catalyst under operating conditions, inclusive of dry oxidative conditions which are expected to experience mass and heat transfer limitations. To account for the temperature difference between gas and solid phases, Eqn. 11 has been adapted to allow calculation of the approximate catalyst surface temperature (T_s), via Eqn. 19.

$$T_s = T_g + \frac{r_p L (-\Delta H)}{h} \quad (19)$$

Eqn. 19 approximates the surface temperature of the catalyst by assuming that the heat generated by the exothermic CH₄ oxidation reaction, is transferred to the gas by convection, with low values of observed reaction rate (r_p), characteristic length (L), enthalpy of reaction (ΔH) and a value of large heat transfer coefficient (h) favouring smaller relative temperature differences between the gas and solid phases. The temperature difference is likely to be overestimated owing to the fact that axial heat conduction in the solid phase has been neglected as well as heat transfer to adjacent channels.

On reapplication of Model 9 (b) to the 12 full data sets (mass and non – mass transfer limited, significant and insignificant ΔT between solid and gas), the simulated plot reported in Fig. 9 (a) was produced. In this case, kinetic parameters estimated during the fitting of Model 9 (b) to non-limited data sets (Table 6), were fixed at constant values during the fitting process. Subsequently, mass and heat transfer limitations were considered by incorporating localized effectiveness factors and surface temperature corrections into the modelling routine. By eliminating optimization of kinetic parameter estimates during this modelling routine, the relative strength of the model fitting process could be assessed under application of the heat and mass transfer corrections. Fig. 9 (a) details the simulated fit of Model 9 (b), whilst Fig. 9

(b) represents the associated parity plot. From visual analysis of Figs. 9 (a) and (b), it appears that Model 9 (b) fits the experimental data relatively well with no appreciable systematic deviation released between simulated and experimental results. By applying the AIC approach as a means of relative comparison between heat and mass transfer corrected (Model 9(b-12)) and non-corrected (Model 9(b-6)) models, it is observed that Model 9(b-12) obtains a better statistical fit to the experimental data, as demonstrated in Table 7.

Fig. 9 (a) Experimental and simulated CH₄ concentration as a function of event number (EN) for Model 9, under feed conditions of 4000 ppm CH₄, 12% O₂, balance Ar and 0% H₂O at 400 °C (EN 1-15), 425 °C (EN 61-75), 450 °C (EN 121-135); 1% H₂O at 400 °C (EN 16-30), 425 °C (EN 76-90), 450 °C (EN 136-150); 5% H₂O at 400 °C (EN 31-45), 425 °C (EN 91-105), 450 °C (EN 151-165); 10% H₂O at 400 °C (EN 46-60), 425 °C (EN 106-120), 450 °C (EN 166-180). **(b)** Parity plot for Model 9.

Table 7 Model pair probability comparison

		AIC ₂	
		9 (b-6)	9 (b-12)
AIC ₁	9 (b - 6)	-	1.000
	9 (b-12)	0.000	-

Table 8 Residual sum of squares (RSS), sample size (N), number of parameters (k) and calculated AIC values

Model	RSS	N	k	AIC
9 (b-6)	7.98×10^{-4}	120	6	-1417
9 (b-12)	6.55×10^{-4}	120	6	-1440

Conclusions

H₂O inhibition for methane oxidation reactions has been shown to vary spatially and thermally, inside a commercial 3%Pd/Al₂O₃ monolith catalyst, with greater temperatures resulting in lower levels of inhibition. The H₂O inhibition process on 3%Pd/Al₂O₃ has been

shown to be partially reversible at temperatures $> 400\text{ }^{\circ}\text{C}$, with minimal levels of deactivation observed under exposure to H_2O feed concentrations of $0 - 10\text{ v/v}\%$. The reversible inhibitory effect of H_2O was ascribed to the formation of $\text{Pd}(\text{OH})_x$ species under humid conditions, based on the results of a global kinetic model screening routine. A parameter estimation procedure was developed, capable of pre-screening experimental data sets for spatial regions in which mass transfer limitations and significant gas – solid temperature differences were likely to exist. The identification and subsequent removal of such data, ensured kinetically controlled information was utilised during model fitting and parameter estimation, consequently increasing the confidence in estimated kinetic parameter values. Using this methodology, a two – site global kinetic model was identified as the best statistical fit with respect to minimisation of total residuals and optimisation of kinetic parameter quantities, as well as demonstrating chemical feasible kinetic parameter values. The model assumed $\text{CH}_3\text{-H}$ as the rate determining step, occurring on a combination of active (PdO) and less active ($\text{Pd}(\text{OH})_2$) reaction sites, existing in equilibrium with each other due to reaction of PdO with gaseous H_2O . The two – site model exhibited the lowest r^2 , lowest HPD limits and practical kinetic parameter estimates compared to all other screened global kinetic models, therefore was deemed the most reflective description of the reaction system under these conditions. A reaction order of *ca.* 2 with respect to H_2O , was found to be the most statistically relevant description of the system. On reintroduction of data containing mass transfer limitations and significant gas-solid temperature differences, mass transfer and surface temperature correction of the model resulted in a statistically better fit, yielding chemically feasible parameter estimates. It is anticipated that this advance in modelling the methane oxidation process will result in higher methane conversions by providing sufficient understanding to determine more optimum conditions which can be considered as part of the reactor design.

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Notation

$C_{i,s}$ – concentration of species i (mol.m^{-3})
 C_{pf} – specific heat capacity of fluid ($\text{J.kg}^{-1}.\text{K}^{-1}$)
 d – pore diameter (m)
 D – Combined hydraulic diameter of channel and wash coat (m)
 $D_{\text{eff},i}$ – effective diffusivity ($\text{m}^2.\text{s}^{-1}$)
 $D_{\text{Kn},i}$ – Knudsen diffusivity ($\text{m}^2.\text{s}^{-1}$)
 D_{wc} – washcoat diameter (m)
 D_s – Combined hydraulic diameter of channel, wash coat and substrate (m)
 E_a – activation energy (J.mol^{-1})
 h – heat transfer coefficient ($\text{W.m}^{-2}.\text{K}^{-1}$)
 ΔH_i – heat of adsorption for species i (J.mol^{-1})
 ΔH_r – Heat of reaction (J.mol^{-1})
 k_r – reaction rate constant
 k_j – adsorption rate pre-exponential factor for species i
 k_g – fluid phase thermal conductivity ($\text{W.m}^{-1}.\text{K}$)
 k_s – solid phase thermal conductivity ($\text{W.m}^{-1}.\text{K}$)
 K_{Eq} – equilibrium constant
 K_i – equilibrium constant of species i
 k_m – mass transfer coefficient (m.s^{-1})
 L – washcoat thickness (m)
 M – molecular mass (g.mol^{-1})
 N – size of data set
 Nu – Nusselt number
 p_i – partial pressure of species i
 Pr – Prandtl number $\frac{\mu_g C_{p,g}}{k_m}$
 q – number of kinetic parameters
 r_o – overall rate of reaction ($\text{mol.m}^{-3}.\text{s}^{-1}$)
 $r'_{p,i}$ – observed rate of reaction ($\text{mol.m}^{-3}.\text{s}^{-1}$)
 R – universal gas constant ($\text{m}^3.\text{atm.K}^{-1}.\text{mol}^{-1}$)
 Re – Reynolds number $\frac{\rho_g v_m D_h}{\mu_g}$
 $S_{1,2}$ – active site 1,2
 S_T – total sites
 Sc – Schmidt number $\frac{\mu_g}{\rho_g D_{\text{eff}}}$
 Sh – Sherwood number
 t – residence time (s)
 T – temperature (K)
 T_{ref} – reference temperature (K)
 ΔT – temperature difference between gas and solid (K)
 v_m – superficial velocity (m.s^{-1})
 w_i – mass fraction of component i
 X_i – conversion (%)
 z – axial position (m)

Symbols

$$\alpha_e = \frac{k_{D,A} C_{A,g} (-\Delta H)}{h T_g}$$

a_j – mathematical fitting parameters

A – species A

B – species B

ε – porosity

$$f_{ex} = \frac{r_p L}{k_{D,A} C_{A,g}}$$

o – overall

θ_1 – fraction of available sites

ϕ' – Weisz-Prater criteria

η – effectiveness factor

ρ – fluid density (kg.m^{-3})

μ – dynamic viscosity

γ – tortuosity

Subscripts and Superscripts

eff – effective

f – fluid phase

g – gas phase inside monolith channel

i – index of gaseous species

j – index of mathematical fitting parameters

mes – mesopores

ref – reference state

s – solid phase including washcoat and substrate

x – order of reaction

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