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Modelling of Phosphorus Poisoning Using Computational Fluid Dynamics and its Effect on Automotive Catalyst Performance

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ABSTRACT

Accumulation of phosphorus in an automotive catalyst is detrimental to catalyst performance, leading to partial or total deactivation. The deactivation model described in this paper utilises CFD to derive a one-dimensional mathematical solution to obtain phosphorus accumulation profiles down the length of a catalyst. The early work of Oh and Cavendish [1] is the basis for this study. A model output, θ , represents the fraction of catalytic surface area that is deactivated. This poisoned fraction is shown to build up locally depending on exposure time to phosphoric acid (H_3PO_4) in the exhaust flow.

Having obtained the poisoned fraction from the model as a function of poison exposure time, θ is used to predict light off times and conversion efficiencies during the deactivation process through incorporation of a kinetic reaction scheme. The model provides a good representation of the phenomena noted in real catalysts; i.e. delayed light off times. The model can be readily adapted to 3D catalyst systems.

BACKGROUND

The Environmental Protection Agency now requires that any form of emission control equipment be reliable and functional for up to 150,000 miles of usage. Coupled with the fact that the actual amount of tail pipe emissions will have to be reduced also, this puts a huge demand on exhaust after treatment systems. Consequently automotive manufacturers have adopted an over-performing catalyst system which usually consists of an over-sized converter.

The catalytic converter is widely regarded as the main emissions treatment component in gasoline automobiles today, and its performance is substantially decreased by compounds found in the oil of internal combustion engines. ZDDP (zinc dialkyldithiophosphate) added to engine oil as an anti-wear additive has been shown to contribute to the majority of deactivation by depositing phosphates onto the catalysts' surface and increasing

the diffusive resistance. [2 - 6] To quantify the amount of phosphorus on a typical used catalyst would be difficult due to the different oil leakage rates of different engines. A catalyst that had been exposed to contaminants may be expected to perform less well during warm up and light off because it has been shown that the poisons mainly accumulate around the inlet section of the monolith [6]. Thermal deactivation would be linked to a reduced steady state conversion due to the agglomeration of precious metal particles over the length of the catalyst [7].

INTRODUCTION

Diagnosing catalyst poisoning is an expensive and time consuming task, and the results are obtained usually by destructive means, i.e. destroying the aged catalysts to analyse them for contaminants. Increasingly, mathematical models have provided an extra tool for analysis and investigation of the parameters that hinder or accelerate the deactivation process of TWCs.

Numerical kinetic schemes for chemical reactions have been investigated extensively, and have provided good agreement with experimental results. As early as 1973, kinetic schemes were proposed for chemical reactions [8]. Voltz et al. provided one of these early studies, and the results from this work are still used as the basis for kinetic schemes today. Voltz used kinetic parameters, experimentally derived from CO and C_3H_6 oxidation on platinum-alumina catalysts, in a set of Arrhenius equations to describe the rate of change of a reaction with temperature. This format of describing chemical kinetics has been adopted by many other authors right up to modern day schemes. The source of the kinetic scheme used in this paper was the work of Baba et al. [9] and is based on the oxidation kinetics of Voltz et al. with a reduction reaction incorporated into the oxidation scheme.

Oh et al. [1] developed a one-dimensional single channel adiabatic model that simulates the build up of phosphorus on the catalyst surface with exposure time to toxins in the exhaust. The phosphorus profiles were

mapped down the catalyst's length as well as the penetration into the wash coat via diffusion. There are sources that contradict this mechanism, saying the phosphorus layer is a glassy impermeable surface on top of the wash coat [10].

This paper uses the poison accumulation theory proposed by Oh et al. [1] and combines it with a three-way kinetic scheme proposed by Baba et al. [9]. The simulations are conducted using a commercially available CFD code.

POISON ACCUMULATION MODEL

The poison accumulation model of Oh and Cavendish is based on a one-dimensional approach incorporating mass transfer and a poisoning reaction for adiabatic conditions at 838K. The model described here is effectively the same, but with updated parameters to reflect modern engines. Using a commercially available CFD code to describe the model, will allow for the eventual description of poisoning in 3D systems.

The model incorporates three regions – a gas phase (exhaust gas), a solid phase (wash-coat pores) and a poisoning build up within the wash-coat itself. A poison precursor, H_3PO_4 (phosphoric acid) enters the system via the gas phase of the model, and via mass transfer, enters the pores of the wash-coat. The poisoning reaction rate then takes phosphoric acid from the pore to create a build-up of the poisoned fraction; θ . The parameter, θ , is a measure of how much active surface area has been poisoned, $\theta=0$ for fresh, $\theta=1$ for total local saturation. Fig 1. shows a schematic diagram of these regions.

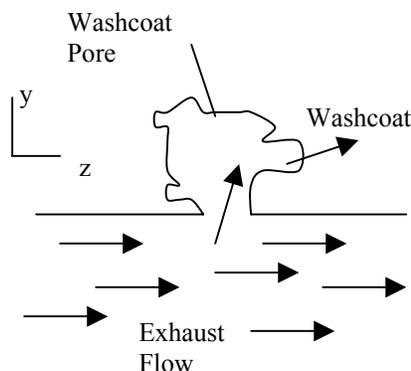


Fig.1. Regions Modelled by poisoning equations

In the poison accumulation model, diffusion has been suppressed in the axial (z) direction. Diffusion is simulated in the perpendicular direction (y) by specifying a mass transfer coefficient to take the precursor from the gas phase, and deliver it to the pores of the wash coat. Species in the solid phase (pores) react and disappear from the pore at the poisoning reaction rate, R_p , thus building up the poisoned fraction θ .

Equation (1) describes the conservation of the poison precursor in the gas phase:

$$\rho_g \frac{\partial c_{gp}}{\partial t} + \frac{\partial}{\partial z} (\rho_g w c_{gp}) = k_{mp} A_v \rho_g (c_{sp} - c_{gp}) \quad (1)$$

Equation (2) describes the conservation of the poison in the pores of the wash-coat:

$$\rho_g \frac{\partial c_{sp}}{\partial t} = k_{mp} A_v \rho_g (c_{gp} - c_{sp}) - R_p \quad (2)$$

where:

$$R_p = k_p c_{sp} (1 - \theta) \quad (3)$$

The governing equation for the build up of θ with time can be expressed as:

$$\frac{\partial \theta}{\partial t} = \frac{k_p c_{sp} (1 - \theta)}{c_{s,\infty}} \quad (4)$$

The model assumes an initial θ value of zero for all z. The poisoning reaction is assumed to be independent of temperature.

Oh et al stated an inlet concentration of H_3PO_4 of $1E-12$ mol P / cm^3 , which translates into a mass fraction of $8.17E-8$ kg H_3PO_4 / kg air. Oh et al have derived this from an oil consumption rate of 0.95 l / 8000km and a phosphorus content of 1.2g / l oil. These values were taken from 1983; therefore a revision of these parameters was necessary. Typical performance characteristics of modern day engines reveal a consumption rate of 1l / 20000km and phosphorus content of 0.86 g P / l oil. These translate into an inlet concentration of $2.47E-8$ kg H_3PO_4 / kg air.

Another key aspect of the poison accumulation model is the poison saturation concentration. This is one of the main parameters that will have a large influence on the poison accumulation rate. It too was based on 1983 technology, and will need modification as more experimental data becomes available. Oh et al state their poison saturation concentration as $3.65E-09$ mol P/ cm^2 BET, equivalent to 9.71 kg P/ m^3 reactor. This value will be seen to provide reasonable poisoning profiles. A larger poison saturation would slow the build up of θ , and vice versa.

The output of this model is the poisoned fraction, θ . When the catalyst is fresh, θ is zero at all axial positions. With time, θ then starts to increase locally, until a desired poisoning interval is reached, at which time the value of θ for all axial positions can then be extracted from the model. When local saturation is reached, when $\theta=1.0$, it is then assumed all local active surface area is covered by toxins and is 100% inactive.

Via equation (5), θ is converted to a deterioration factor, which is incorporated into the reaction kinetics described below.

$$DF_{\text{twc}} = (1.0 - \theta) \quad (5)$$

THREE-WAY LIGHT-OFF MODEL

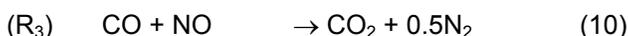
Equation (6) describes the conservation of the gas phase chemical scalars where j can be CO_g , C_3H_{6g} , NO_g or O_{2g} .

$$\rho_g \frac{\partial c_{gj}}{\partial t} + \frac{\partial}{\partial z} (\rho_g w c_{gj}) = k_{mj} A_v \rho_g (c_{sj} - c_{gj}) \quad (6)$$

Equation (7) describes the conservation of solid phase chemical scalars, where j can be CO_s , C_3H_{6s} , NO_s or O_{2s} . The i refers to the reaction scheme. Depending on the chemical scheme R_i will differ as follows: For CO , R_i will be $(R_1 + R_3)$. For C_3H_6 , R_i will be R_2 . For NO R_i will be R_3 . For O_2 , R_i will be $(0.5R_1 + 4.5R_2)$ as indicated by equations 8 –10.

$$\rho_g \frac{\partial c_{sj}}{\partial t} = k_{mj} A_v \rho_g (c_{gj} - c_{sj}) - M_j R_i \quad (7)$$

The chemical reaction scheme has been proposed by Baba et al and includes the reduction reaction chemistry as well as the oxidation of C_3H_6 and CO . There are three main reactions modelled:



The reaction rates of the above three reactions are given below:

$$R1 = DF_{\text{twc}} \cdot k_1 \cdot C_{s,\text{CO}} \cdot C_{s,\text{O}_2} / G1 \quad (11)$$

$$R2 = DF_{\text{twc}} \cdot k_2 \cdot C_{s,\text{C}_3\text{H}_6} \cdot C_{s,\text{O}_2} / G2 \quad (12)$$

$$R3 = DF_{\text{twc}} \cdot k_3 \cdot C_{s,\text{CO}} \cdot C_{s,\text{NO}} / G3 \quad (13)$$

Where:

$$G1 = (1+K_{1,\text{CO}} \times C_{s,\text{CO}})^2 \times (1+K_{1,\text{NO}} \times C_{s,\text{NO}})^2 \times (1+K_{1,\text{C}_3\text{H}_6} \times C_{s,\text{C}_3\text{H}_6})^2 \quad (14)$$

$$G2 = (1+K_{2,\text{CO}} \times C_{s,\text{CO}})^2 \times (1+K_{2,\text{NO}} \times C_{s,\text{NO}})^2 \times (1+K_{2,\text{C}_3\text{H}_6} \times C_{s,\text{C}_3\text{H}_6})^2 \quad (15)$$

$$G3 = (1+K_{3,\text{CO}} \times C_{s,\text{CO}})^2 \times (1+K_{3,\text{NO}} \times C_{s,\text{NO}})^2 \times (1+K_{3,\text{C}_3\text{H}_6} \times C_{s,\text{C}_3\text{H}_6})^2 \quad (16)$$

The rate constants (k_i) and adsorption equilibrium constants ($K_{i,\text{CO}}$, $K_{i,\text{NO}}$ and $K_{i,\text{C}_3\text{H}_6}$) are shown in the appendices in the form of a set of Arrhenius equations.

The solid phase temperature dictates the reaction rates' activity. The inlet temperature was ramped for the first 5 seconds, from 300K at $t=0s$ to 900K at $t=5s$. A linear ramp was used for simplicity. For $5s < t < 40s$, $T=900K$. This is typical of a close-coupled catalyst temperature ramp. Under floor catalysts could be modelled by changing this temperature ramp to suit.

The solid phase and gas phase temperatures were solved using the standard energy equation. The accuracy of CFD for predicting temperature is of the order of +/- 5%. Full details of monolith warm-up modelling are given in references [11, 12].

CFD SIMULATION

The CFD code employed for the simulation was the commercial CFD code Star-CD, produced by Computational Dynamics™. The simulations were performed on an SGI Octane Work station with 512 Mb of RAM and an R12000 processor.

Transient simulations were performed for both models, allowing data to be obtained at discrete time intervals. It is necessary to run the poison accumulation model for a real time of 1500 hours. For the CFD run, the time-steps were incrementally increased, as shown below.

1200 time-steps @0.05s/ time-step (60s)

800 time-steps @4.425s/ time-step (59 mins)

6000 time-steps @900s/ time-step (1500 hours)

The Courant number (time step / cell residence time) was 54 during the first 60 seconds of the simulation. After this time, the flow was established and larger time-steps were acceptable. The CFD run that simulated 1500 hours of aging took approximately 6 hours of computation time.

For the three-way chemistry model, the time scale was several orders of magnitude less. The runs last for 40s, which is split up into 2000 time-steps of 0.02 seconds each. The Courant number for this run was 21.6. The simulation took roughly half an hour to run to completion.

Both models discussed in this paper used an inlet mass flow rate of 30g/s. This value was taken from the Oh and Cavendish case and is typical of exhaust flows.

Fig 2 shows the mesh employed for the poison accumulation model. The mesh shows 68 cells, comprised of 60 porous cells, (middle block) and 4 fluid cells attached at each end of the mesh.

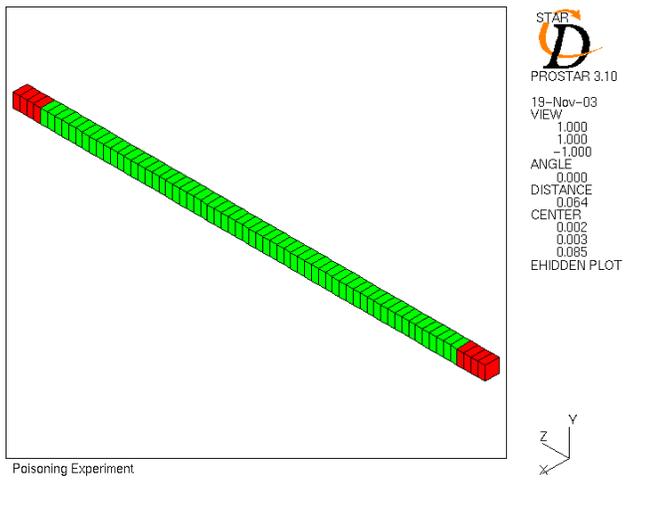


Fig. 2 – Mesh for Poison Accumulation model.

The poison accumulation mesh is simply modelling a block of porous medium, with an overall pressure drop equal to the pressure drop for the monolith geometry described by Oh et al.

Fig.3 displays the mesh employed for the 3 way light off model. The lower block of cells is identical to those of the poison accumulation model. In this case however, there is an extra bank of cells to account for the solid phase temperature, see [11, 12] for details. Solid phase scalars are modelled in the gas phase cells, but with the advection solver turned off, as modelled in equation (7).

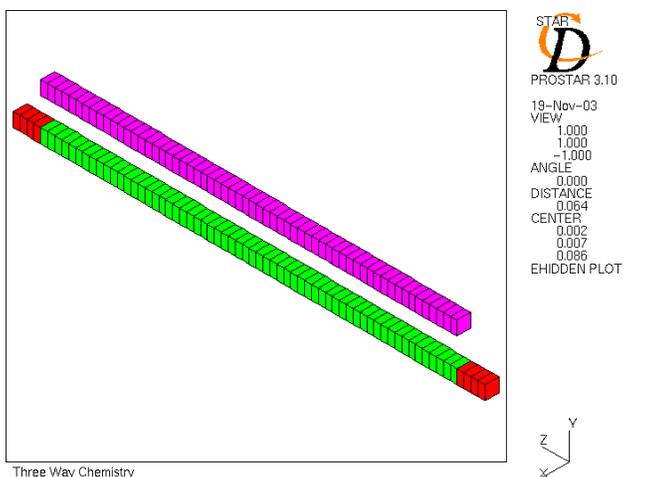


Fig.3 – Mesh for Three Way light off model.

RESULTS AND DISCUSSION

Fig. 4 shows the results from the poison accumulation model. These results are similar to the profiles noted in Oh et al. [1], but with reference to equation (4), the poisoning rate is slower than the original case due to a reduced inlet concentration. It is worthy of note, that an increase of the poison saturation concentration would have a similar effect.

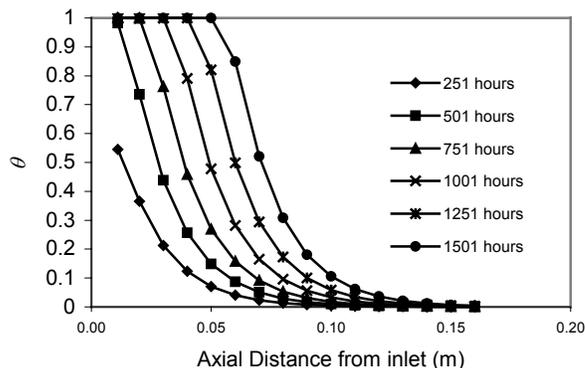


Fig. 4 – Poison Accumulation in the monolith for poison exposure times of 251-1501 hours.

To assess the quality of the reaction kinetics of Baba et al, a lambda sweep was performed by varying the inlet concentrations. The sweep was performed using a fresh monolith, and by allowing the conversion to reach a steady state for a temperature of 800K. The sweep can be seen in Fig. 5.

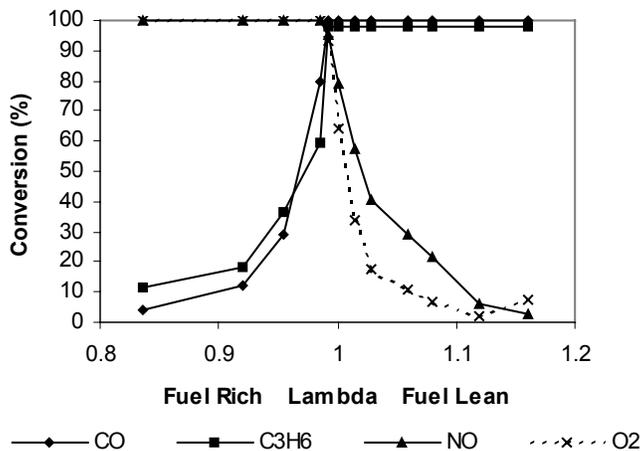


Fig. 5 – Lambda Sweep on Fresh Catalyst

The results of the temperature inlet ramp for the three way chemistry model are shown in figs 6 a, b and c. This series of graphs describe the differences in warm-up characteristics for differently aged catalysts. The brick and the exhaust gas temperatures have been shown.

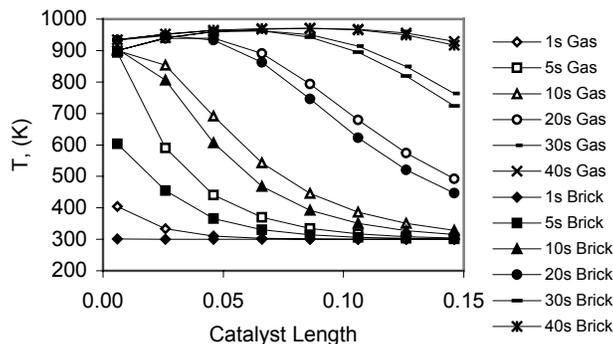


Fig. 6a – Predicted fresh catalyst warm-up.

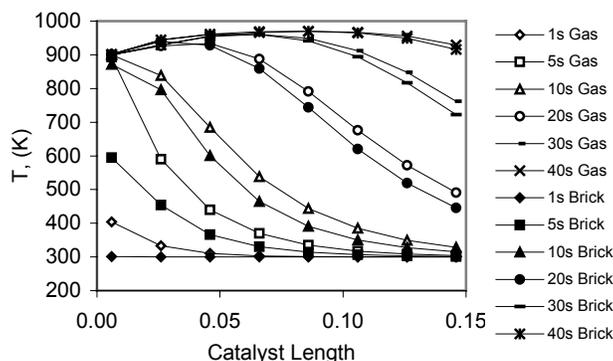


Fig. 6b – Predicted catalyst warm-up of a 751 hours aged catalyst.

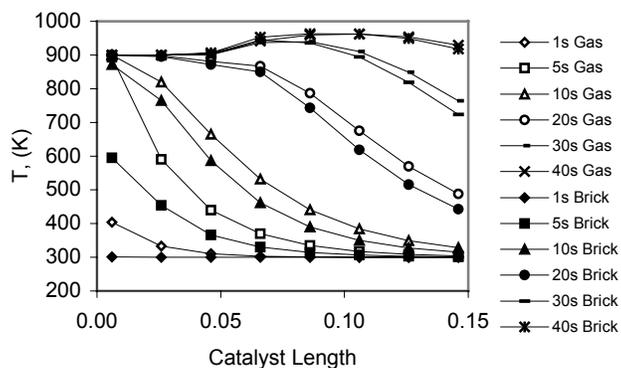


Fig. 6c – Predicted catalyst warm-up of a 1501 hours aged catalyst.

From observation of figures 6a, 6b and 6c, the deactivated zone can clearly be seen to be gradually suppressing the heats of reactions. Fig 6c shows this effect most significantly.

The active surface area (θ) for each of the light-off simulations was obtained from the poison accumulation model described earlier.

Figures 7, 8 and 9 show the predicted conversion of CO, C₃H₆ and NO respectively, through the light off stage as a function of time for varying ageing severities.

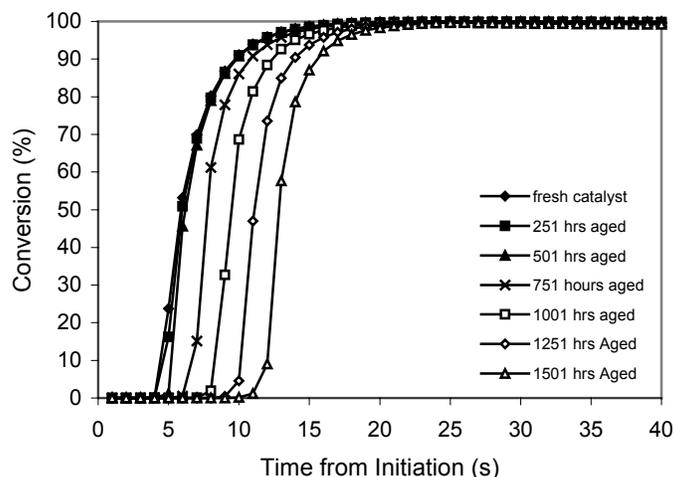


Fig. 7 – Predicted conversion of CO through light off as a function of time for varying ageing severities.

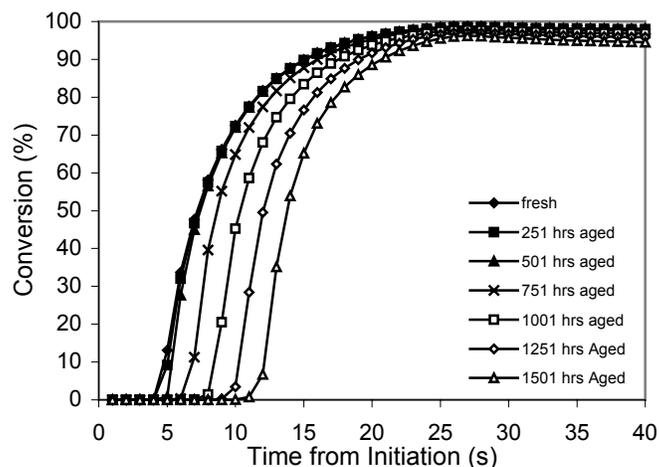


Fig. 8 – Predicted conversion of C₃H₆ through light off as a function of time, for varying ageing severities.

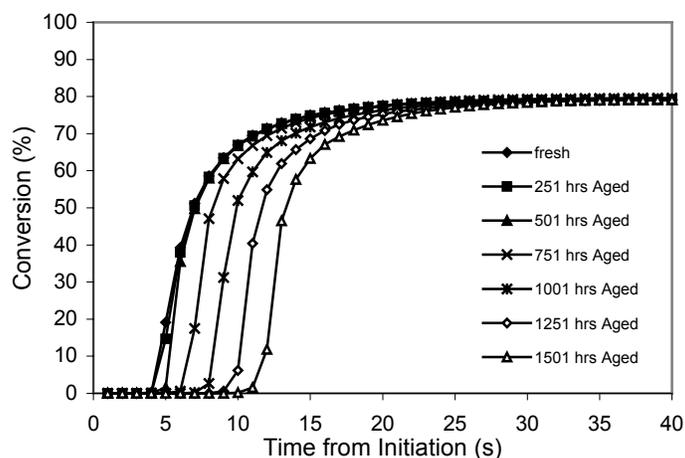


Fig. 9 – Predicted conversion of NO through light off as a function of time, for varying ageing severities.

Figs 7-9 show that light off occurs at about 5 seconds for the fresh catalyst. Fig 6a shows that the temperature at the front of the brick has reached 600K at this time. Figs 6b and 6c for the aged catalysts show that even though this temperature is also reached, light off has not occurred, (see figs 7-9) as this region lies within the deactivated zone of the catalyst. It is not until the active part of the catalyst reaches 600K that light off occurs. For the 751 and 1501 hours aged catalysts this is at approximately 7 and 12 seconds respectively, as shown in figs 6b and c. The experimental work of Zhenfu, [13] qualitatively shows this effect in real aged and fresh catalysts.

It can also be deduced from Figs 7, 8 and 9 that the steady state conversion is minimally altered from the fresh case. This is due to the fact that the model used here considered only poisoning as the deactivation mechanism so that a sufficient part of the catalyst remains active. It is sintering that will degrade the steady state conversion as this phenomenon occurs at all axial positions.

CONCLUSIONS

1. A model of catalyst poisoning has been developed using a commercially available CFD code.
2. A three-way catalytic model has been developed which incorporates poison profiles deduced from the poisoning model.
3. Model predictions show poison profiles qualitatively consistent with experimental data.
4. It is shown that light-off is delayed as the catalyst is aged, although steady state emissions were predicted to be largely unaffected under the conditions modelled.
5. The CFD model can readily be extended to simulate 3D systems.

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NOMENCLATURE

A_v	Wetted Surface Area (m^2/m^3)
C_{gp}	Gas Phase Concentration of H_3PO_4 (kg/kg)
C_{sp}	Pore Phase Concentration of H_3PO_4 (kg/kg)
$C_{s,\infty}$	Poison Saturation Concentration ($kg H_3PO_4/m^3$ of reactor)
$C_{s,j}$	Solid Phase Concentration of Species j ($kg j/kg$ air)
DF_{twc}	Deterioration Factor (No Units)
G_i	Rate Inhibitor For Reaction i.

K_{ij}	Adsorption Equilibrium Constant For Reaction i and Species j
k_m	Mass Transfer Coefficient (m/s)
k_p	Rate Constant for Poisoning Reaction (m/s)
k_i	Rate Constant for Reaction i
M_i	Molecular Weight of species i
R_p	Poisoning Rate ($\text{kg}/\text{m}^3/\text{s}$)
T_s	Solid Phase Temperature (K)
t	Time (s)
w	Gas Velocity (m/s)
x	Spatial Coordinate (m)
y	Spatial Coordinate (m)
z	Spatial Coordinate (m)
ρ_g	Gas Density (kg/m^3)
θ	Poisoned Fraction (No Units)
Subscript	g Denotes gas phase
Subscript	j Denotes chemical species
Subscript	i Denotes reaction number
Subscript	p Denotes poison precursor
Subscript	s Denotes solid phase

ACCRONYMS AND ABBREVIATIONS

BET	Brunauer-Emmett-Teller surface area
CFD	Computational Fluid Dynamics
TWC	Three Way Catalyst

APPENDIX

Adsorption Equilibrium and Rate Constants for the three-way chemistry model [9]:

$$k_1 = 1.0 \times 10^{16} \exp(-13652/T_s)$$

$$k_2 = 2.0 \times 10^{16} \exp(-15562/T_s)$$

$$k_3 = 3.0 \times 10^{16} \exp(-15163/T_s)$$

$$K_{1,\text{CO}} = 6.019 \times 10 \exp(-403.4/T_s)$$

$$K_{1,\text{NO}} = 9.846 \times 10 \exp(-244.9/T_s)$$

$$K_{1,\text{C}_3\text{H}_6} = 1.809 \times 10^3 \exp(-2334.0/T_s)$$

$$K_{2,\text{CO}} = 1.504 \times 10 \exp(-415.0/T_s)$$

$$K_{2,\text{NO}} = 1.824 \times 10 \exp(52.9/T_s)$$

$$K_{2,\text{C}_3\text{H}_6} = 1.917 \times 10^2 \exp(-893.2/T_s)$$

$$K_{3,\text{CO}} = 4.836 \times 10 \exp(-727.0/T_s)$$

$$K_{3,\text{NO}} = 3.962 \times 10 \exp(-288.9/T_s)$$

$$K_{3,\text{C}_3\text{H}_6} = 1.848 \times 10 \exp(274.1/T_s)$$