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Phosphorus Accumulation in Automotive Catalysts

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Steady-state, accelerated phosphorus accumulation experiments were conducted using a multistage integral reactor which was mounted on an engine dynamometer system. Electron microprobe studies showed that the phosphorus accumulation process is controlled by pore diffusion and that the phosphorus tends to form a monolayer over the pore surfaces of the poisoned band in the catalyst pellets. Excellent agreement was found between the experimental results and a progressive shell-type poison accumulation model.

INTRODUCTION

The durability of automobile emission control catalysts depends on a number of complicated events which include poisoning of the catalyst by traces of phosphorus in the exhaust.

The aim of this work was to conduct carefully controlled poisoning experiments and to analyze the results by an appropriate mathematical model, for the purpose of elucidating the mechanism of the poison accumulation process and of determining the parameters which influence its rate.

Although automotive catalysts operate under transient conditions, steady-state experiments at a set of typical average operating conditions were chosen for this study to make the problem more tractable. A fuel with elevated phosphorus level was used in order to accelerate the time scale of the experiments. Because of these modified experimental conditions, care has to be used when extrapolating the results to actual automotive converters. However, as we will see, these idealized experiments allowed a considerable insight into the process of poison accumulation over the catalyst. This, in turn, was found to be helpful in the design of more poison-resistant catalysts (*5*).

PRELIMINARY EXPERIMENTS

Figure 1 shows an electron microprobe photograph of a phosphorus-poisoned catalyst pellet which was cut in half to expose its inner cross section. This catalyst had been exposed to experimental conditions which are discussed later on in this paper. As the picture shows, the phosphorus penetrates the catalyst pellet in form of a well-defined band, indicative of a diffusion-limited poisoning process. Phosphorus concentration scans along the pellet radius (Fig. 2) indicate that the poison profiles can be well approximated by a step function.

Inspecting Fig. 2 it also appears that the phosphorus level of the inward progressing shell has reached saturation such that as the phosphorus-containing poison precursor (presumably H_3PO_4) enters the pores of the catalyst, it prefers to diffuse past the already poisoned layer to react with the support (and with the active component) at the front of the poisoned

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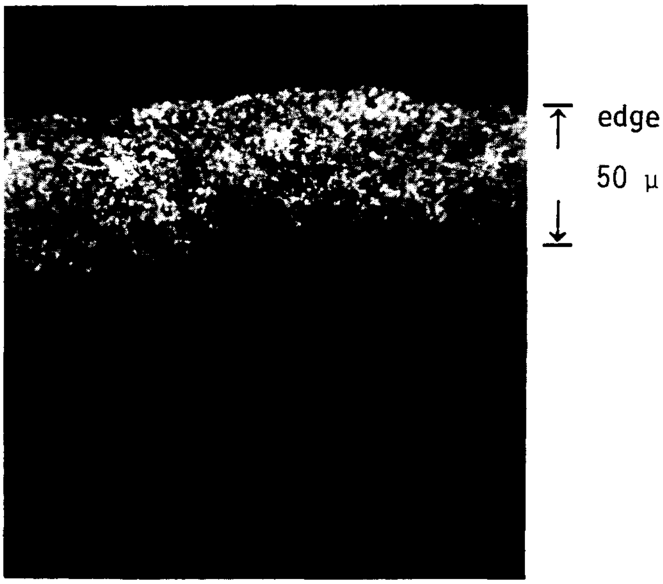

FIG. 1. Electron microprobe photograph of the cross section of a phosphorus-poisoned catalyst pellet (high P fuel, T = 566°C).

and unpoisoned sections. This observation suggests that the interaction between the poison precursor and the catalyst is chemical rather than physical. Further proof was supplied by additional experiments which showed that the phosphorus accumulation process is irreversible and is essentially independent of the presence of an active metal component over the alumina support.

The electron microprobe studies, then, suggest that the poison accumulation process is of the "progressive shell" type in which the saturation concentration of the poison in the poisoned shell and the effective diffusivity of the poison precursor across this shell play an important role. To explore this further, catalyst pellets with varying surface areas were phosphorus poisoned under similar experimental conditions (T^1 = 566°C, high P fuel). The heights of the saturation plateaus were expressed in saturation phosphorus concentrations and were plotted against the N_2 BET surface areas of the catalyst pellets in Fig. 3.

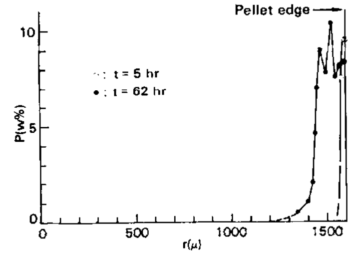

FIG. 2. Phosphorus concentration profiles along the radius of a poisoned catalyst pellet (by electron microprobe).

[1] Abbreviations used: A (cm^2), reactor frontal area; Bi, Biot number; Da, Damköhler number; c_0 (mol/cm^3), inlet concentration of poison precursor; c_s (mol/cm^3 of pellet), saturation concentration of poison; D (cm^2/sec), diffusivity of poison precursor; D_{eff} (cm^2/sec), effective diffusivity of poison precursor; k_c (cm/sec), chemical rate constant; k_m (cm/sec), mass transfer coefficient; L (cm), reactor length; Q (cm^3/sec), exhaust gas flow rate; R (cm), radius of the catalyst pellet; s (cm^2/g), BET surface area (N_2); t (sec), time; T (K), temperature; v (cm/sec), superficial gas velocity; x (cm), reactor length coordinate; α (sec), constant, see text; ϵ, void fraction of catalyst bed; Θ, fraction of catalyst pellet volume poisoned; ζ, dimensionless reactor length coordinate; τ, dimensionless time, see text; Φ, poisoning function, see text; Ψ, dimensionless gas phase concentration of poison precursor.

The slope of the saturation concentration–surface area line is about 2.2×10^{15} P atoms per cm^2 of support surface. This number is quite close to the number of atoms per square centimeter of solid surfaces (generally on the order of 10^{15}), and thus it indicates a monolayer-equivalent coverage of the alumina surfaces by phosphorus. (Similar results were found for lead poisoning under isothermal conditions. However, temperature fluctuations in actual catalytic converters tend to disperse the lead bands, while they leave the phosphorus bands intact.) The fact that the poisons tend to deposit in a monolayer-like concentration over the surfaces of the poisoned shell explains the results of diffusivity measurements which showed very little change in the effective diffusivity upon poisoning, at least for the mode of catalyst poisoning discussed here (*3*). While the pores of the catalyst can indeed be obstructed by poisonous deposits in certain instances (*4*), such a process apparently did not occur in the experiments reported here, and thus the simple pore-mouth-poisoning mechanism was adapted.

MATHEMATICAL ANALYSIS

The accumulation of a poison in an isothermal plug flow reactor is described by the following conservation equations (*2, 6*):

$$\frac{\partial \Psi}{\partial \zeta} + \frac{\partial \Theta}{\partial \tau} = 0 \tag{1}$$

$$\frac{\partial \Theta}{\partial \tau} - \Phi(\Theta)\Psi = 0 \tag{2}$$

$$\Psi(0, \tau) = 1 \tag{3}$$

$$\Theta(\zeta, 0) = 0, \tag{4}$$

where $\Phi(\Theta)$ reflects the mechanism by which the poison accumulates within the individual catalyst particles. For the progressive shell-type poison accumulation in spherical catalyst pellets, $\Phi(\Theta)$ was derived by Olson (*6*):

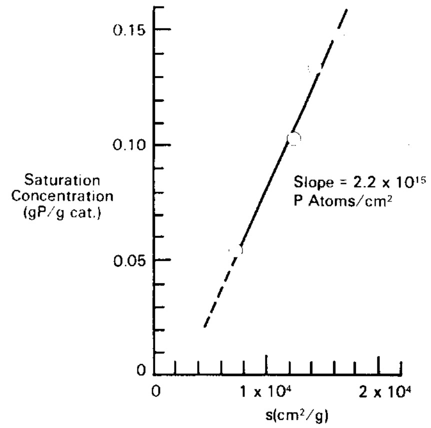

FIG. 3. Phosphorus saturation concentration as a function of the BET (N_2) surface area of the supported catalyst (from electron microprobe experiments).

$$\Phi[\Theta(\zeta, \tau)] = \frac{\alpha}{\dfrac{1}{\mathrm{Bi}} + \dfrac{1-(1-\Theta)^{\frac{1}{3}}}{(1-\Theta)^{\frac{1}{3}}} + \dfrac{1}{\mathrm{Da}(1-\Theta)^{\frac{2}{3}}}}, \tag{5}$$

where

$$\alpha = (1-\epsilon)\frac{3D_{\mathrm{eff}}L}{R^2 v} \tag{6}$$

$$\mathrm{Bi} = \frac{k_m R}{D_{\mathrm{eff}}} \text{ (Biot number)}, \tag{7}$$

and

$$\mathrm{Da} = \frac{k_c R}{D_{\mathrm{eff}}} \text{ (Damköhler number)}. \tag{8}$$

The time scale of the process is

$$\tau = t\left(\frac{1}{1-\epsilon}\frac{c_0}{c_s}\frac{v}{L}\right). \tag{9}$$

Equations (1) to (5) were solved numerically by Olson (*6*) and in a generalized, quasianalytical fashion by Bischoff (*2*). In our application, Bischoff's integrals were evaluated numerically, and the implicit, simultaneous equations were solved for the poison distribution in the bed, $\Theta(\zeta, \tau)$,

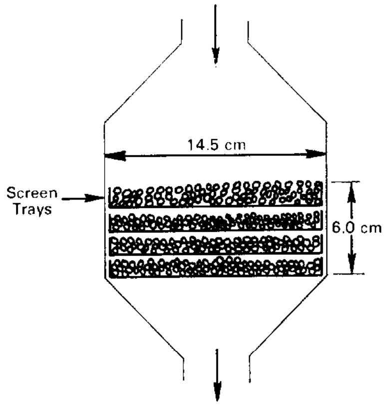

FIG. 4. Experimental four-stage reactor for catalyst poisoning studies. The reactor is fed by the exhaust of an engine dynamometer system.

using the Newton–Raphson root-finding technique. The total poison content of the bed could then be calculated from:

$$\bar{\Theta}(\tau) = \tau - \frac{\Theta(1, \tau)}{\alpha \mathrm{Bi}} + \frac{3}{2\alpha}\{[1 - \Theta(1, \tau)]^{\frac{3}{2}} - 1\} + \frac{\Theta(1, \tau)}{\alpha} + \frac{3}{\alpha \mathrm{Da}}\{[1 - \Theta(1, \tau)]^{\frac{1}{3}} - 1\}. \quad (10)$$

PHOSPHORUS POISONING EXPERIMENTS

To check the validity of the above diffusion-limited poison accumulation scheme for our phosphorus poisoning problem, experiments were carried out in a small integral reactor which was attached to the exhaust pipe of a dynamometer-mounted 5.7 1 V-8 engine. The engine provided an exhaust flow rate of 34,990 cm^3/sec (20°C, 760 Torr) and consumed 3.18 gal of fuel/hr at 1800 rpm and at the particular load selected for the studies.

The fuel (indolene clear) was artificially enriched in phosphorus (0.186 g of P/gal, by the addition of tricresyl phosphate) to accelerate the time scale of the poisoning process.

The reactor is depicted in Fig. 4. It has a catalyst volume of 1000 cm^3, distributed over four stainless-steel screen trays, such that the experiment could be interrupted from time to time and the four trays could be sampled for catalyst analysis.

The experiments employed a platinum–alumina catalyst (0.1 wt% Pt). The average radius of the spherical catalyst pellets was 0.159 cm. Temperature measurements showed that at the steady-state conditions of our experiments, the reactor was essentially isothermal (about 28°C difference between inlet and exit, at an inlet temperature of 566°C).

The parameters in Eqs. (6) to (9) were determined as follows:

The poison precursor was assumed to be H_3PO_4, the diffusivity of which was approximated from the Chapman–Enskog theory (*1*). The effective diffusivity of the poison precursor in the catalyst was calculated from the random pore diffusivity model of Wakao and Smith (*7, 8*). The pore size distribution data which are necessary for the random pore diffusivity model were determined by ultrahigh-pressure mercury porosimetry.

The exhaust gas flow rate was determined from air intake and fuel consumption measurements. The saturation concentration of the phosphorus in the poisoned catalyst pellets was determined by electron microprobe (Fig. 3). The electron microprobe observations also allowed us the measurement of phosphorus penetration depths into the catalyst pellets at various bed depths and poison exposure times.

The phosphorus concentration in the exhaust entering the reactor was calculated from fuel consumption, gas flow rate, and fuel chemical analysis for P. The engine and exhaust system were stabilized before the experiment to avoid transients in phosphorus emissions.

The phosphorus content of the catalyst pellets was determined by wet chemical analysis.

TABLE 1

Model Input Parameters for the Phosphorus Poisoning Studies[a]

$T = 839$ K
$Q = 100{,}193$ cm^3/sec (T, P)
$P = 761$ Torr
$A = 165.6$ cm^2
$L = 6.0$ cm
$R = 0.159$ cm
$\epsilon = 0.34$
$D = 0.503$ cm^2/sec (T, P)
$D_{\mathrm{eff}} = 0.0304$ cm^2/sec (T, P)
$c_s = 0.00457$ mol of P/cm^3 pellet
$c_0 = 5.29 \times 10^{-11}$ mol of P/cm^3 exhaust gas (T, P)

[a] For large values of Da, the results were insensitive to its magnitude.

COMPARISON OF MODEL WITH EXPERIMENT

For the phosphorus poisoning experiment discussed here, Table 1 lists the input parameters which were used to calculate poison profiles and accumulations.

Figure 5 compares the measured and calculated phosphorus profiles in the reactor at four different exposure times. The agreement between the calculations and the experiment is rather satisfactory, especially if one considers the complexity of the experimental system and the fact that no adjustable parameters were employed to fit the data.

Despite some statistical scatter which usually accompanies electron microprobe experiments, the model was also reasonably successful in predicting the penetration depth of phosphorus into the catalyst pellets on the four catalyst trays, as a function of elapsed poison exposure time.

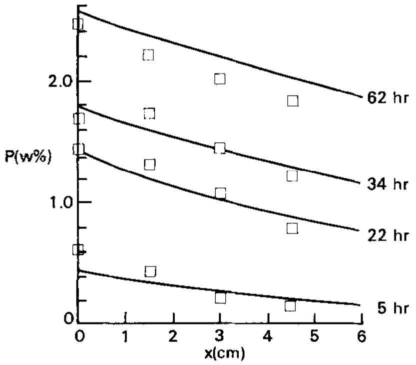

Fig. 5. Comparison of measured and calculated phosphorus profiles in the four-stage reactor.

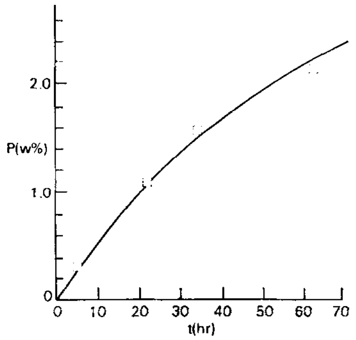

Fig. 6. Comparison of measured and calculated total (integral averaged) phosphorus accumulation in the four-stage reactor.

For the total amount of phosphorus accumulated over the catalyst, Fig. 6 compares Eq. (10) with the experimental data. Again, excellent agreement was obtained.

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