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Activity and Lifetime of a Composite Automobile Catalyst Pellet

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This work analyzes the performance of a composite catalyst pellet under deactivation conditions characteristic of those found in automobile catalysis. The composite pellet is made of two layers, the inner layer supports the active metal in a high area support, whereas the outer layer is made of a different inert support. Analytical solutions relating activity and lifetime are obtained for a first order reaction and pore mouth poisoning. The results indicate that when the effective diffusivity of the outer layer is higher than in the inner support, the activity relative to initial activity can be maintained at a higher level for a longer period of time than when using a single supported catalyst. The results presented in this work indicate a significant potential to develop such catalyst for application in automobile catalysis.

NOMENCLATURE

A	Pellet cross-sectional area, cm^2.
$C(z)$	reactant concentration inside the pellet, mol/cm^3.
$C_p(z)$	poison concentration inside the pellet, mol/cm^3.
CW	support saturation capacity for poison adsorption.
$\mathfrak{D}$	reactant effective diffusivity, cm^2/sec.
$\mathfrak{D}_p$	poison effective diffusivity, cm^2/sec.
h_0	Thiele modulus of the unpoisoned active layer II.
h	Thiele modulus of the poisoned catalyst.
k	reaction rate constant, 1./sec.
L_0	thickness of the inert layer I.
L	thickness of the active layer II.
R_0	reaction rate in the unpoisoned layer II, mol/sec.
R	reaction rate in the composite catalyst, mol/sec.
t	time, sec.
z	distance inside pellet, cm.
$\bar{z}$	depth of poison penetration, cm.
Δ	fractional depth of poison penetration of the composite catalyst.
η	$\bar{z}/L$.
ξ	effectiveness factor.
τ	dimensionless time.

INTRODUCTION

The activity of automobile catalysts pellets is limited by the poisoning of the active sites by impurities present in the feed mainly lead, sulfur and phosphorous (*1*, *2*). The objective of this work is to analyze the performance of a novel composite catalyst pellet designed to improve both catalyst activity and lifetime.

Automobile catalysts operate at temperatures high enough so that the reaction rate is diffusion controlled and the reaction is confined to the external catalyst area. It follows that the deposition of impurities such as S, Pb and phosphorous contained in the exhaust gases drastically decreases the reaction rate, thus deactivating the catalyst and reducing its durability. Poisons such as the ones indicated, are strongly adsorbed upon the catalyst forming a

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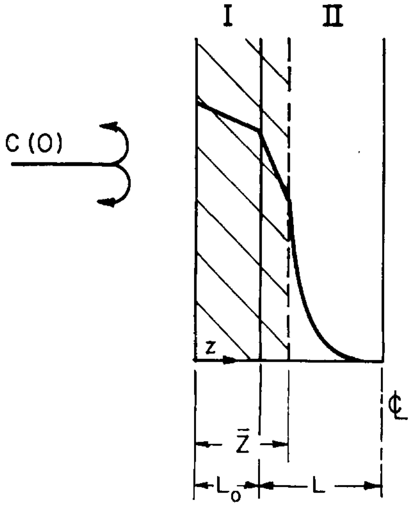

FIG. 1. Schematic diagram of the composite pellet. Region I is the outer inert support, Region II is the support containing the active metal.

well-defined inactive layer growing from external catalyst surface into the catalyst interior (*2*). Under these conditions, the catalyst activity and lifetime are well described by the pore mouth poisoning model proposed by Wheeler (*3*).

In the case of a diffusion influenced reaction where deactivation or selectivity plays a role, a number of workers have shown that catalyst activity and lifetime can be improved by using catalysts possessing a nonuniform activity distribution (*4*–*7*). Such catalysts can be prepared by varying the depth of impregnation of the active metal into the support. Minhas and Carberry (*4*) found optimal conversion during SO_2 oxidation over a Pt catalyst having a finite impregnation depth. Shadman-Yazdi and Petersen (*5*) analyzed the reaction $A \rightarrow B \rightarrow C$ with simultaneous series self-poisoning and found that the selective toward B increases when the activity decreases toward the center. DeLancey (*6*) analyzed the reaction A → products with uniform poisoning and found that impregnation of the catalyst to a finite depth gives optimal catalyst utilization. Corbett and Luss (*7*) analyzed the case of spherical pellet having different activity distributions for the reaction $A \rightarrow B \rightarrow C$ with impurity and self-poisoning deactivation mechanisms. These authors concluded that confining the activity to an external layer most often yields the maximum selectivity but also yields minimal resistance to deactivation. It follows that where it is important to maintain a high level of activity for a long period of operation, it may be desirable to use a catalyst in which the activity is confined to an inner core. In this case, the increase in catalyst lifetime is obtained at the expense of a decrease in initial activity.

The foregoing discussion led to the conclusion that catalysts having a nonuniform activity profile are specially attractive in the case of automobile catalyst pellets. Recently, Wei and Becker (*8*) showed that for a negative order reaction, the effectiveness factor can be greater than one and that it is better to spread the active metal over a thicker support layer than to concentrate it over a narrow layer near the pellet surface. Hegedus and Summers (*1*) showed that for a first order reaction with pore mouth poisoning, impregnation to a final depth near the surface leads to optimal utilization of the active metal. The depth of impregnation is determined by the catalyst minimum tolerable activity and lifetime.

Under the conditions of a first order, diffusion controlled reaction with impurity poisoning, confining the active metal to an inner layer decreases the initial catalyst activity, but increases its lifetime. As shown below, when the active metal is confined to an inner layer, the catalyst activity is equivalent to that of a catalyst already poisoned since diffusion of reactants through the outer layer limits the rate. Consequently, if diffusion can be enhanced in the outer layer both activity and lifetime can be improved. Ruckenstein (*9*) analyzed the effect of mixing small particles of active catalysts with an inert support on the effective diffusivity. Delancey (*10*) analyzed the problem of optimal support composition for the case when both supports can be active at the same or different levels for a first order reaction. In these studies (*9, 10*) the possibility of poisoning was not considered and the activity was assumed to be constant.

The foregoing discussion suggests that catalyst lifetime can be increased without a substantial reduction of activity by using a catalyst pellet composited of two supports. The active metal is deposited in a high area support forming the inner pellet core or layer, whereas a different inert support with an open pore structure surrounds the inner layer. A simple model of the composite pellet is shown in Fig. 1. The external layer will perform as a screen to capture the poisons before they reach the active inner layer. The porous structure of the external layer will be such as to decrease diffusion of reactants, to increase the poison diffusion resistance and exhibit a large saturation capacity to adsorb the poisons. The support of the inner layer can be chosen to optimize the reaction rate at the surface.

For simplicity, the pellet will be assumed to have a slab geometry. Other geometries can be accounted by using a modified equivalent radius (*11*). In order to be able to obtain analytical solutions, the reaction is assumed to be first order and the poisoning to occur by a pore mouth poisoning mechanism (*12–14*).

THEORETICAL ANALYSIS

A schematic diagram of the composite pellet showing the coordinate system is shown in Fig. 1. The outer layer is made of support I, which is nonreactive, contains no active metal and has a thickness L_0. The inner layer is made of support II and contains the active metal uniformly distributed to a depth L. Let us assume that the catalyst has already been poisoned to a depth $\bar{z}$ inside layer II. Transport of reactants through the poisoned region is due to diffusion only. However, because the supports are different, the effective diffusivity in layer I is different than in layer II.

The initial rate of the unprotected catalyst is used as a reference to compare activity and lifetime. The reaction rate of the unpoisoned layer II without the protective layer I is given by

$$R_0 = kALC(0)\xi, \tag{1}$$

$C(0)$ is the reactant bulk concentration, k a first order reaction rate constant, A is the cross-sectional area of the pellet, L the pellet thickness and ξ the effectiveness factor. For a first order reaction ξ is given by

$$\xi = \frac{\tanh(h_0)}{h_0}, \tag{2}$$

where $h_0 = L(k/\mathfrak{D}_2)^{\frac{1}{2}}$ is the Thiele modulus of the active layer and $\mathfrak{D}_2$ the reactant effective diffusivity in layer II.

In the case of the composite catalyst and pore mouth poisoning, the analysis must take into account the different effective diffusivities in layers I and II. Consequently, the composite pellet is divided into two zones. From the external surface of the pellet to a depth $\bar{z}$ the catalyst is completely poisoned. In the case in point (Fig. 1) the poisoned region consists of L_0 in layer I and $(\bar{z} - L_0)$ in layer II. In the remainder fraction of the pellet, $(L + L_0 - \bar{z})$ the activity is uniform to its original level. The equation describing the rate in the unpoisoned region is similar to Eq. (1) (*12, 14*), the concentration at $\bar{z}$, $C(\bar{z})$, replaces the bulk concentration, $C(0)$; and the length $(L + L_0 - \bar{z})$ replaces the total length of the pellet

$$R = kA(L + L_0 - \bar{z})C(\bar{z})\frac{\tanh(h)}{h}, \tag{3}$$

where

$$h = (L + L_0 - \bar{z})\left(\frac{k}{\mathfrak{D}_2}\right)^{\frac{1}{2}} = (1 - \Delta)h_0,$$

$$\Delta = \frac{\bar{z} - L_0}{L}.$$

$C(\bar{z})$ is determined by the rate of diffusion of reactants through the poisoned region and by the reaction rate. The rate of diffusion of reactants through layer I is equal to the rate of diffusion in the poisoned fraction of layer II, hence

$$A\mathfrak{D}_1 \frac{C(0) - C(L_0)}{L_0} = A\mathfrak{D}_2 \frac{C(L_0) - C(\bar{z})}{\bar{z} - L_0}, \quad (4)$$

where $\mathfrak{D}_1$ is the reactant effective diffusivity in layer I and $C(L_0)$ the reactant concentration at $z = L_0$. At $z = \bar{z}$ the rate of diffusion in the poisoned fraction of layer II is equal to the rate of reaction, hence

$$A\mathfrak{D}_2 \frac{C(L_0) - C(\bar{z})}{\bar{z} - L_0} = kA(L + L_0 - \bar{z}) \frac{\tanh (h)}{h}. \quad (5)$$

Equations (4) and (5) can be combined to obtain an expression for $C(\bar{z})$. Replacing $C(\bar{z})$ into Eq. (3) and combining with Eq. (1) one obtains the expression of the rate relative to the initial rate of the single layer catalyst.

$$\frac{R}{R_0} = \frac{\mathfrak{D}_1/\mathfrak{D}_2 \tanh [(1 - \Delta)h_0]}{\{\mathfrak{D}_1/\mathfrak{D}_2 + (\mathfrak{D}_1/\mathfrak{D}_2\Delta + \Delta_0)h_0 \tanh [(1 - \Delta)h_0]\} \tanh (h_0)}, \quad (6)$$

where $\Delta_0 = L_0/L$. The above equation reduces to the case of the single layer catalysts (*12*) when $\Delta_0 = 0$ and $\mathfrak{D}_1/\mathfrak{D}_2 = 1$. The case of a double layer catalyst made of the same support corresponds to $\mathfrak{D}_1/\mathfrak{D}_2 = 1$.

To obtain the relation between activity and time Δ must be eliminated from Eq. (6). Minhas and Carberry (*4*) have obtained the relation between time and the depth of poisoning for pore mouth poisoning. The model is the analog of the shell progressive mechanism of gas–solid reactions (*13*). For the case of the unprotected layer catalysts, the time required for the poison to penetrate to a depth $\bar{z}$ is given by

$$t' = \frac{CW_2}{2\mathfrak{D}_{p2}C_p(0)} \bar{z}^2, \quad (7)$$

or

$$\tau = \bar{\eta}^2,$$

where

$$\bar{\eta} = \frac{\bar{z}}{L} \qquad \tau = \frac{2\mathfrak{D}_{p2}C_p(0)t'}{L^2CW_2}.$$

t' is the time required for the poison to reach a depth $\bar{z}$, $\mathfrak{D}_{p2}$ is the poison effective diffusivity in support II, $C_p(0)$ is the bulk poison concentration, and CW_2 is the support saturation capacity to adsorb the poison. τ is a dimensionless time relative to the time required to completely poison layer II. In the case of the composite catalyst the poisons effective diffusivities in the two supports are different. The rate of poison accumulation in layer II is equal to the rate of poisons diffusion through the inactive fraction of layer II, i.e.,

$$ACW_2 \frac{d(\bar{z} - L_0)}{dt} = A\mathfrak{D}_{p2} \frac{C_p(L_0) - 0}{\bar{z} - L_0}, \quad (8)$$

where $C_p(L_0)$ is the poison concentration at $z = L_0$ and $C_p(\bar{z}) = 0$. The rate of poison diffusion in the layer I is equal to the rate of diffusion in the inactive fraction of layer II, hence

$$A\mathfrak{D}_{p1} \frac{C_p(0) - C_p(L_0)}{L_0} = A\mathfrak{D}_{p2} \frac{C_p(L_0)}{\bar{z} - L_0}, \quad (9)$$

where $\mathfrak{D}_{p1}$ is the poison effective diffusivity in layer I. Substituting $C_p(L_0)$ from Eq. (9) into Eq. (8) and integrating one obtains

$$t - t' = \frac{L^2CW_2}{\mathfrak{D}_{p1}C_p(0)} \left(\Delta\Delta_0 + \frac{\mathfrak{D}_{p1}}{\mathfrak{D}_{p2}} \frac{\Delta^2}{2} \right). \quad (10)$$

Replacing t' from Eq. (7) and defining a dimensionless time in the basis of the time required to completely poison layer II one obtains

$$\tau = \Delta_0^2\left(\frac{CW_1}{CW_2} \times \frac{\mathfrak{D}_{p2}}{\mathfrak{D}_{p1}}\right) + 2\Delta\Delta_0\frac{\mathfrak{D}_{p2}}{\mathfrak{D}_{p1}} + \Delta^2. \quad (11)$$

Equation (11) gives the time required to poison the catalyst to a depth Δ as a function of Δ_0 and the support characteristics. Equation (11) reduces to Eq. (7) when $\Delta_0 = 0$ or $CW_1\ \mathfrak{D}_{p2}/CW_2\ \mathfrak{D}_{p1} = 1$.

Eliminating Δ between Eqs. (6) and (11) one obtains a direct relation between activity and time. Since the resulting expression is cumbersome, it is better to use Δ as a parameter. In the calculations, the rate was considered constant and equal to the rate at $\Delta = 0$ when $\bar{z} < L_0$.

DISCUSSION

The results of the foregoing analysis are summarized by Eqs. (6) and (11). Equation (6) indicates that the major parameters influencing the relative rate of the composite pellet are the ratio $\mathfrak{D}_1/\mathfrak{D}_2$ and Δ_0. Adding an inert layer decreases the rate relative to the initial rate of the unprotected catalyst. If $\mathfrak{D}_1 = \mathfrak{D}_2$ the relative rate of the composite catalyst follows the same deactivation curve as the unprotected layer. Consequently, a composite pellet is advantageous only if the supports are chosen so that $\mathfrak{D}_1/\mathfrak{D}_2 > 1$.

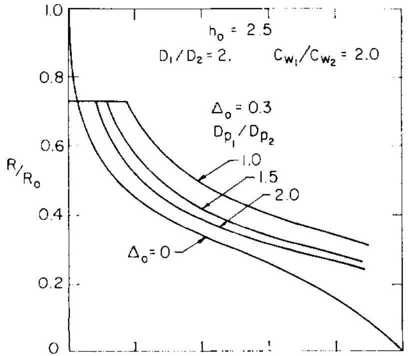

FIG. 2. Relative rate vs dimensionless time. Effect of poison diffusivities $h_0 = 2.5$.

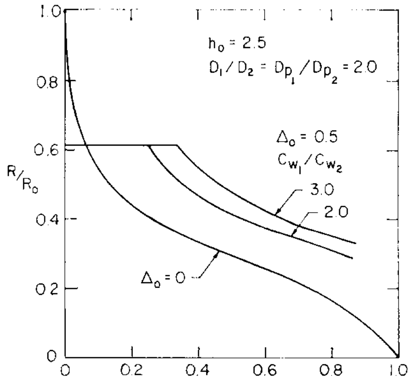

FIG. 3. Relative rate vs dimensionless time. Effect of poison getter capacity and Δ_0. $h_0 = 2.5$.

The advantage of the composite catalyst appears when catalyst lifetime enters in the analysis. The dimensionless time τ or catalyst lifetime is given by Eq. (11) in terms of Δ_0, the ratio $\mathfrak{D}_{p1}/\mathfrak{D}_{p2}$ and CW_1/CW_2. Equation (11) indicates that the catalyst lifetime increases by increasing Δ_0 and having $CW_1/CW_2 > 1$ and $\mathfrak{D}_{p1}/\mathfrak{D}_{p2} < 1$. The later requirement for $\mathfrak{D}_{p1}/\mathfrak{D}_{p2}$ is not consistent with the requirement of $\mathfrak{D}_1/\mathfrak{D}_2 > 1$. Increasing the diffusivity of reactants in one support also increases the poison diffusivity. Thus for computation of realistic cases both ratios $\mathfrak{D}_1/\mathfrak{D}_2$ and $\mathfrak{D}_{p1}/\mathfrak{D}_{p2}$ are taken as larger than one. Data from Hegedus and Summers show that for supports having a bimodal pore distribution $CW_1/CW_2 = 1.75$ and $\mathfrak{D}_{p1}/\mathfrak{D}_{p2} = 1.85$. Thus it is realistic to assume values of $\mathfrak{D}_1/\mathfrak{D}_2 > 1$ and at the same time $CW_1/CW_2 > 1$, i.e., a combination of supports with both higher diffusivities and poison getter capacities. A case where the above combination of parameters cannot be realized is for a reaction operating under Knudsen diffusion. If Knudsen diffu-

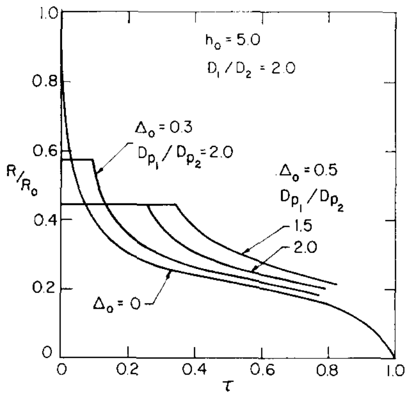

FIG. 4. Relative rate vs dimensionless time for $h_0 = 5$.

sion occurs then $CW_1\mathfrak{D}_{p1}/CW_2\mathfrak{D}_{p2} \simeq 1$, and $\mathfrak{D}_1/\mathfrak{D}_2 = \mathfrak{D}_{p1}/\mathfrak{D}_{p2}$. Therefore it follows that under Knudsen diffusion, increasing getter capacity leads to $\mathfrak{D}_1/\mathfrak{D}_2 < 1$ and a further reduction of reaction rate due to the protective layer. However, Knudsen diffusion should be avoided not only in a composite catalyst but in a single catalyst as well.

The combined effect of the different parameters on the relative rate and catalyst lifetime are shown in Figs. 2, 3, and 4.

The results presented in Fig. 2 show the relative rate versus dimensionless time for $h_0 = 2.5$, $\Delta_0 = 0.3$, $\mathfrak{D}_1/\mathfrak{D}_2 = 2$, $CW_1/CW_2 = 2$ and three different values of $\mathfrak{D}_{p1}/\mathfrak{D}_{p2}$. Also included in Fig. 2 are the results obtained with the unprotected catalyst ($\Delta_0 = 0$). The unprotected catalyst start with a high activity but rapidly deactivates losing about 45% of its initial activity in about 10% of the time required to poison the catalyst completely. The composite catalyst on the other hand, starts at a lower relative rate, but the activity remains constant until the protective layer has been completely poisoned and the poison starts penetrating into the active layer. The lower the poison diffusivity in the outer layer, the longer the period of constant activity. However, even in the case that $\mathfrak{D}_1/\mathfrak{D}_2 = \mathfrak{D}_{p1}/\mathfrak{D}_{p2}$ there is an improvement in lifetime. Figure 3 shows the effect of Δ_0 and CW_1/CW_2 on the relative rate keeping the other parameters constant. A composite catalyst having $\Delta_0 = 0.5$ starts with a lower relative rate than $\Delta_0 = 0.3$, however, the activity remains constant for a longer period of time. The constant activity period increases with the value of CW_1/CW_2. The results of Fig. 3 indicates that for the same relative activity, the composite catalyst can be operated for about twice the time or more than the unprotected catalyst.

Figure 4 shows the results for $h_0 = 5$. In this case the unprotected catalyst loses about 50% of its initial activity in about 4% of the time required to poison completely the pellet. Thus, the composite catalyst is more advantageous for reactions exhibiting high rates. The same observations made for $h_0 = 2.5$ are valid for $h_0 = 5$ in relation to the effects of Δ_0, $\mathfrak{D}_{p1}/\mathfrak{D}_{p2}$ and CW_1/CW_2.

As a disadvantage, the composite catalyst involves a more elaborate manufacture and an increase in reactor volume proportional to Δ_0. However, both factors can be offset by the lowest cost resulting from increasing catalyst lifetime.

The above discussion demonstrated that there is a significant potential for development of a composite automobile catalyst as the one described in this work. The results are subject to the assumptions made in the theoretical analysis and on the values of the parameters used. Other combinations of parameters can be calculated by use of Eqs. (6) and (11). The values used in the calculations presented in Figs. 2–4 are conservative values, some of them reported in the literature (*1*). Further work is underway for the experimental realization of the composite pellet as well as to use more elaborate diffusion and kinetic models.

CONCLUSIONS

A theoretical analysis is presented of the deactivation of a composite automobile catalyst pellet with the active metal confined to the inner layer under pore mouth poisoning conditions and a first order reaction. The results show that the composite pellet exhibits higher relative activity for the same time on stream or longer lifetime for the same relative activity. The results presented here indicate a significant potential to develop such a catalyst.

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