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Deactivation of a Composite Automobile Catalyst Pellet

II. Bimolecular Langmuir Reaction

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In this work, the deactivation of a composite catalyst pellet is analyzed for reaction and deactivation conditions similar to those found in automobile catalytic converters. The composite catalyst is made of two layers; the inner layer supports the active metal in a high-area support, whereas the outer layer consists of an inert support that protects the active metal from poisons that deactivate the catalyst. The reaction kinetics used is a bimolecular Langmuir kinetics characteristic of CO oxidation on Pt/Al_2O_3 catalysts, and it is assumed that the catalyst operates under diffusion-controlled conditions. It is also assumed that the catalyst deactivates following a pore mouth-poisoning mechanism which is characteristic of Pb or P poisoning of automobile catalysts. The results obtained show that using a composite catalyst one obtains an enhancement of the activity when operating in the region of high reactant concentration. However, at low reactant concentration, the kinetics becomes first order and only the catalyst lifetime can be improved. The results presented here further support previous findings for the first-order reaction indicating that both long-term activity and catalyst lifetime can be improved by using a composite catalyst.

NOMENCLATURE

A	Cross-sectional area of catalyst pellet (cm^2)
C	CO concentration ($mole/cm^3$)
C_0	CO concentration at surface ($mole/cm^3$)
C_p	Poison concentration ($mole/cm^3$)
C_{p0}	Poison concentration at pellet external face ($mole/cm^3$)
C_{wi}	Support capacity for poison adsorption in layer i ($mole/cm^3$)
D_i	CO effective diffusivity in layer i (cm^2/sec)
D_{pi}	Poison effective diffusivity in layer i (cm^2/sec)
h_0	Initial Thiele modulus of active catalyst of dimensions $A \times L$
k	Reaction constant (1/sec)
K_A	CO adsorption constant ($cm^3/mole$)
L	Total width of the composite catalyst slab (cm)
L_0	Width of the protective layer of the composite catalyst (cm)
R	Reaction rate of the poisoned composite catalyst
R_{0v}	Initial reaction rate of catalyst of dimensions $A \times L$
t	Time variable (sec)
t_0	Time to completely poison catalyst of dimensions $A \times L$ (sec)
z	Distance inside the pellet (cm)
$\bar{z}$	Depth to which poison has penetrated (cm)
Δ	Dimensionless depth to which poison has penetrated in layer 2 $(\bar{z} - L_0)/L$
Δ_0	Dimensionless width of protective layer 1 (L_0/L)

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η	Dimensionless width variable $(z - \bar{z})/(L - \bar{z})$
τ	Dimensionless time variable (t/t_0)
ξ	Effectiveness factor for poisoned fraction of active layer
ξ_0	Initial effectiveness factor for catalyst of dimensions $A \times L$
ψ	Dimensionless concentration, C/C_0
Subscript 1	Refers to layer I or the inert protective support layer
Subscript 2	Refers to layer II or the active catalyst support layer

INTRODUCTION

A recent important application of heterogeneous catalysis has been in the control of automobile exhaust emissions. A great deal of experimental and theoretical work has been published in the last 5 years to advance the understanding of automobile catalytic converters. One important area of investigation is the effect of mass transfer on the pollutant conversion. These effects have been discussed elsewhere (*1*) and are particularly important in automobile catalysts since minimizing reactor volume is an important concern.

Poisoning of the active catalyst component by impurities contained in the feed is another important factor in the design of catalysts for automobile converters. Both factors, activity and catalyst lifetime, determine the necessary amount of catalyst; a small improvement on either factor could substantially reduce the overall amount of catalyst required by the industry.

Several workers (*2–4*) have reported that impurities contained in the gas, such as Pb, S, and P, are concentrated in narrow bands or shells near the catalyst's surface. Hegedus and Summers (*2*) reported that P is strongly and nonselectively adsorbed on the catalyst and support, forming a well-defined poison layer that deactivates the catalyst. These authors proposed to impregnate the catalyst partially to economize the metal component.

To improve catalyst lifetime, Wolf (*6*) recently proposed the use of a novel composite catalyst in which the active layer is shielded by an inert support layer. The reactant and poison diffusivities were assumed to be different in each layer. Assuming a pore mouth-poisoning mechanism and a first-order main reaction, Wolf found that, if the diffusivity of the external layer is larger than the diffusivity of the inner layer, a substantial increase in catalyst lifetime can be obtained. The initial activity of the composite catalyst was lower than the initial activity of the unprotected catalyst; however, the unprotected catalyst deactivates faster than the composite catalyst and soon the activity of the latter catalyst surpasses the activity of the unprotected catalyst.

Becker and Wei (*1*) studied the mass transfer effect occurring during CO oxidation over a supported Pt catalyst. This reaction exhibits a bimolecular Langmuir–Hinshelwood-type kinetics which becomes first order at low CO concentrations and negative first order at high CO concentrations (*5*). Becker and Wei (*1*) suggested that for this type of reaction it might be advantageous to have the active catalyst recessed into the support. On the basis of the results obtained with the composite catalyst for a first-order reaction and Becker and Wei's results, it is promising to study the performance of a composite catalyst for the case of a bimolecular Langmuir–Hinshelwood kinetics. Several other oxidation reactions occurring in automobile converters exhibit a bimolecular Langmuir kinetics as well. For diffusion-controlled reactions, such as those occurring in catalytic converters, the bimolecular Langmuir kinetics differs from the first-order reaction in that effectiveness factors larger than 1 can be obtained.

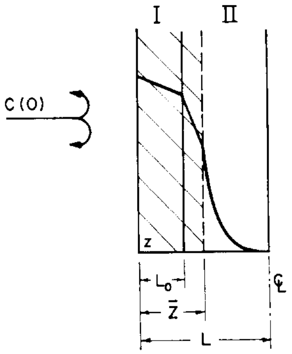

FIG. 1. Schematic diagram of the composite catalyst. Region I is the protective layer; Region II is occupied by the support containing the active metal.

THEORETICAL ANALYSIS

A schematic diagram of a composite pellet is shown in Fig. 1. For simplicity, a pellet with slab geometry has been selected; other geometries can be accounted for by using a modified equivalent radius (*13*). Layer II contains the active metal whereas layer I is only an inert support wherein no reaction takes place. Transport of reactants and poisons inside the pellet is by diffusion only. Acres *et al.* (*8*) reported that the deactivation curve due to phosporous follows a pore mouth-poisoning kinetics. Consequently, in this work, a pore mouth-poisoning mechanism, is postulated. According to this mechanism, the poisons are adsorbed rapidly and irreversibly onto the active metal and support (*7*). Thus the adsorbed poisons form a well-defined front at $z = \bar{z}$, which divides the catalyst into two regions. The region behind the poison front $(0 < z < \bar{z})$ is completely inactive, whereas, in the region ahead of the poison front $(\bar{z} < z < L)$, the activity remains unchanged. Reaction takes place only in the unpoisoned fraction of the active layer. It is assumed that the reaction rate is influenced by transport of reactants into the catalyst pellet. Diffusion governs the transport of reactant and poisons in the inactive layer and in the poisoned fraction of the active layer.

The differential equation describing diffusion and reaction in the active layer, under pseudo-steady-state conditions and with a bimolecular Langmuir reaction, is

$$\bar{z} < z < L \qquad D_2 \frac{\partial^2 C}{\partial z^2} - \frac{kC}{(1 + K_A C)^2} = 0, \tag{1}$$

with the following boundary conditions (BC):

$$\text{BC1:} \qquad C = C(\bar{z}), \quad z = \bar{z}, \tag{2}$$

$$\text{BC2:} \quad \partial C/\partial z = 0, \qquad z = L, \tag{3}$$

where C is the reactant concentration in the catalyst pellet, k is the reaction rate constant, K_A is the adsorption constant, and D_2 is the reactant effective diffusivity in the active layer.

No reaction occurs in the protective layer $(0 < z < L_0)$ and in the poisoned fraction of the active layer $(L_0 < z < \bar{z})$; consequently the concentration profiles are linear. Equating the fluxes at the interfaces, $z = L_0$ and $z = \bar{z}$, one obtains an expression for $C(\bar{z})$ that can be used as BC1.

Using the following variables $\eta = (z - \bar{z})/(L - \bar{z})$ and $\psi = C/C_0$, Eq. (1) can be written in the following dimensionless form,

$$\frac{\partial^2 \psi}{\partial \eta^2} - \frac{h_0^2(1 - \Delta - \Delta_0)^2 \psi}{(1 + K_A C_0 \psi)^2} = 0 \tag{4}$$

with

BC1:

$$\psi(0) = 1 + \frac{(D_2/D_1)\Delta_0 + \Delta}{1 - \Delta - \Delta_0} \left.\frac{\partial \psi}{\partial \eta}\right|_{\eta=0} \tag{5}$$

and

$$\text{BC2:} \quad \left.\frac{\partial \psi}{\partial \eta}\right|_{\eta=1} = 0 \tag{6}$$

where

$$\Delta = (\bar{z} - L_0)/L; \quad \Delta_0 = L_0/L;$$

and

$$h_0 = L(k/D_2)^{\frac{1}{2}}.$$

h_0 is the Thiele modulus, Δ is the poisoned fraction of the active layer, Δ_0 is the fraction of inert layer, and C_0 is the reactant concentration at $z = 0$. In obtaining Eq. (5), it has been assumed that the diffusion resistance in the gas film is negligible compared with the diffusion resistance inside the catalyst. Given h_0, K_AC_0, D_1/D_2, Δ_0, and Δ, the performance of the composite catalyst is evaluated by calculating the overall reaction rate R using the concentration gradients obtained from the solution of Eq. (4). The effect of diffusion on the reaction is evaluated by calculating the effectiveness factor ξ in the unpoisoned region of the composite catalyst.

To relate the reaction rate with time, it is necessary to develop an expression between Δ and time. Gorring and Carberry (*9*) obtained a relation between time and Δ for a single supported catalyst under pore mouth poisoning. Wolf (*6*) developed the corresponding expression for the composite catalyst. Since the Δ-time relation is independent of the kinetics of the main reaction, then Wolf's development also applies to this work. Consequently only the final expression will be presented here.

The time required for the poisoning front to penetrate a fraction Δ into the active region is

$$t = \frac{C_{w1}L_0^2}{2D_{p1}C_{p0}} + \frac{C_{w2}}{D_{p1}C_{p0}} LL_0\Delta + \frac{C_{w2}}{2D_{p2}C_{p0}} L^2\Delta^2, \quad (7)$$

where C_{w1}, C_{w2}, and D_{p1}, D_{p2} are the poison adsorption capacities and diffusivities in supports I and II, respectively. C_{p0} is the poison bulk concentration.

Substituting $\Delta = 1$ and $L_0 = 0$ into Eq. (7) one obtains the time required to poison completely an unprotected catalyst of length L,

$$t_0 = \frac{C_{w2}L^2}{2D_{p2}C_{p0}};$$

t_0 can be used to define a dimensionless time $\tau = t/t_0$; τ is then a measure of the catalyst lifetime relative to the lifetime of an unprotected catalyst of the same length. Dividing Eq. (7) by t_0 one obtains,

$$\tau = \Delta^2 + 2\frac{D_{p2}}{D_{p1}}\Delta_0\Delta + \frac{C_{w1}}{C_{w2}}\frac{D_{p2}}{D_{p1}}\Delta_0^2. \quad (8)$$

The value of τ is independent of the reaction parameters and depends only on the ratios D_{p2}/D_{p1}, C_{w1}/C_{w2}, and Δ_0. Given the reaction parameters h_0, K_AC_0; the support characteristics D_1/D_2, D_{p1}/D_{p2}, C_{w1}/C_{w2}, and the fraction of protective layer Δ_0, one can calculate a reaction rate R by solving Eq. (4) and the corresponding dimensionless time from Eq. (8).

RESULTS AND DISCUSSION

Equation (4) was solved numerically using the quasi-linearization technique described by Lee (*10*). The equation is first linearized, then the derivatives are substituted by finite differences. The resulting system of difference equations is solved by matrix inversion using the Thomas method. The procedure is repeated until convergence is attained.

Prior to solving the equations, the constants k and K_AC_0 were estimated using the data of Voltz's *et al.* (*5*). At 700°F (which is the upper temperature used by Voltz) and a feed containing 1% vol of O_2 and 0.3% vol of CO, one obtains $k = 1.83 \times 10^{12} \exp(-22600/(700+460)) = 6.32 \times 10^3$ (1/sec) and $K_AC_0 = 0.655 \exp(1730/(700+460)) \times 0.3 = 0.873$. These values indicate that, under the above operating conditions, the reaction kinetics is essentially first order. Furthermore, at steady-state conditions, catalytic converters operate at higher temperatures (~1000°F) and therefore the first-order dependence becomes more predominant. Consequently, under such operating conditions, the bimolecular kinetics gives the same results as the first order kinetics which has already

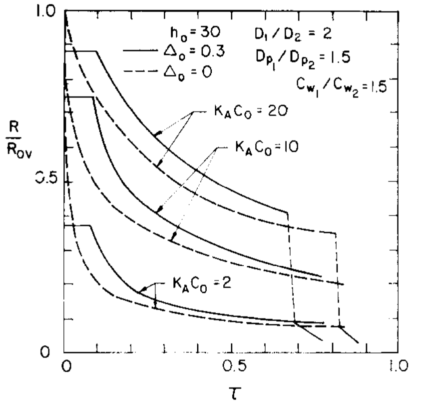

FIG. 2. Relative rate vs dimensionless time. Effect of K_AC_0.

been analyzed by Wolf (6). However, at high CO concentration and lower temperatures, higher values of K_AC_0 and lower values of k are obtained. Under these conditions the bimolecular kinetics exhibits a behavior which is completely different from the first-order kinetics. In this work, k and K_AC_0 values corresponding to low temperature, high CO concentration are used in order to explore the peculiar results characteristic of the bimolecular Langmuir kinetics.

The results obtained are expressed in terms of relative rates versus dimensionless time. The relative rate is the reaction rate of the composite catalyst pellet relative to the initial reaction rate of an unprotected catalyst pellet having the same total volume. This basis allows direct comparison of the deactivation curves of the composite and unprotected catalysts. The dimensionless time is the time on stream of the composite catalyst divided by the time required to poison completely an unprotected catalyst of the same volume. The effect of each parameter is investigated keeping all others constant. A standard case, $\Delta_0 = 0.3$, $h_0 = 30$, $K_AC_0 = 20$, $D_1/D_2 = 2$, $D_{p1}/D_{p2} = 1.5$ and $C_{w1}/C_{w2} = 1.5$ is presented in all figures for comparison with all other combinations of parameters.

The effects of the reaction parameters K_AC_0 and h_0 are analyzed first. Figure 2 shows the effects of K_AC_0 in the deactivation curves of the composite pellet (solid line) and the unprotected pellet (broken line, $\Delta_0 = 0$). The values used for all other parameters are given in Fig. 2. The results indicate that, with the exception of a short initial period, the relative rate of the composite catalyst is higher than the relative rate of the unprotected catalyst, even though the former has a 30% less amount of active component. Initially, the unprotected catalyst has a higher activity than the composite catalyst, but it deactivates rapidly reaching a lower activity than that of the composite catalyst in a short period. The activity of the composite catalyst remains constant until the poisoning front reaches the active layer. At this time the activity begins to decrease. The results show that the rate of deactivation decreases as K_AC_0 increases. For $h_0 = 30$ and low K_AC_0 values, the reaction is strongly influenced by diffusion ($\xi \ll 1$) and thus the reaction rate is drastically reduced as the poisoning front advances. Increasing K_AC_0 increases ξ and this contributes in part to the lower deactivation rates obtained for $K_AC_0 = 20$. Figure 2 also shows that, for $K_AC_0 = 20$, there is an abrupt change in activity for both unprotected and composite catalysts. Such a change was observed for several other combinations of K_AC_0 and h_0. The abrupt change is the result of a complex interaction between the poisoning process, the diffusion, and the reaction kinetics. For large K_AC_0 values, the catalyst starts operating in the region where decreasing the reactant concentration increases the reaction rate. As poisoning proceeds, $C(\bar{z})$ decreases, which produces an increase in the reaction rate depleting further the reactant concentration in the active layer. This process continues until the specific reaction rate reaches a maximum and then decreases drastically with small changes in reactant concentration. At this point, a small advance of the poisoning front results in a large decrease in activity. The transition from the upper to lower deactivation curve is continuous, but since it occurs in a very short time interval, it appears as a discontinuity unless the time scale is expanded. The time at which the transition occurs depends on h_0, K_AC_0, Δ_0, D_{p1}/D_{p2}, and C_{w1}/C_{w2}.

The special dependence between reaction rate and reactant concentration of the bimolecular kinetics causes the existence of multiple solutions as reported by Hegedus *et al.* (*14*) and by Cutlip *et al.* (*15*). The peculiar behavior of this reaction kinetics is amplified by diffusion, and, as shown here, it also occurs during catalyst poisoning.

Figure 3 shows the results obtained for two values of h_0, when $K_AC_0 = 20$ and all other parameters are the same as in Fig. 2. For $h_0 = 10$, the composite catalyst exhibits a somewhat lower activity than the unprotected catalyst without the abrupt change in activity during the deactivation period.

Figure 4 shows the results of varying Δ_0 with the same set of material parameters as used previously and $h_0 = 30$, $K_AC_0 = 20$. The results indicate that increasing the thickness of the protective layer decreases the value of R/R_{0v} during the period of constant rate and increases the time at constant rate operation. A thicker protective layer also shortens the time of operation in the upper deactivation curve since a less active component is used. For all the values of Δ_0 shown in Fig. 4, the composite catalyst exhibits higher rates than the unprotected catalyst when it operates in the upper deactivation curve. The optimum value of Δ_0 is obtained by comparing the areas under each curve until a minimum acceptable R/R_{0v} is attained.

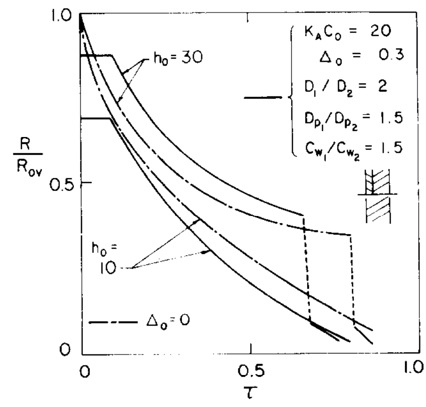

FIG. 3. Relative rate vs dimensionless time. Effect of h_0.

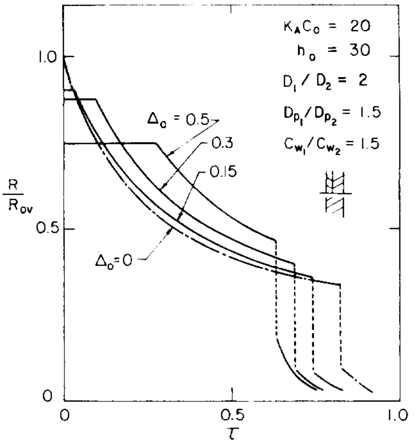

FIG. 4. Relative rate vs dimensionless time. Effect of thickness of the protective layer Δ_0.

The effect of the material parameters is examined for $h_0 = 30$, $K_AC_0 = 20$, and $\Delta_0 = 0.3$. For realistic cases, the ratios D_1/D_2, D_{p1}/D_{p2}, and C_{w1}/C_{w2}. are not entirely independent. We assumed that, if $D_1/D_2 > 1$, then $D_{p1}/D_{p2} > 1$, or inversely, if $D_1/D_2 < 1$, then $D_{p1}/D_{p2} < 1$ and that these ratios are fairly similar. Data from Hegedus and Summers show that, for supports with bimodal pore distribution, one can obtain $D_{p1}/D_{p2} = 1.85$ and $C_{w1}/C_{w2} = 1.75$. This is not true for the case where Knudsen diffusion predominates; hence the use of such supports should be excluded. The results of varying the diffusivity ratio are shown in Fig. 5 for three cases; (i) $D_1/D_2 = 2$, $D_{p1}/D_{p2} = 1.5$; (ii) $D_1/D_2 = 1$,

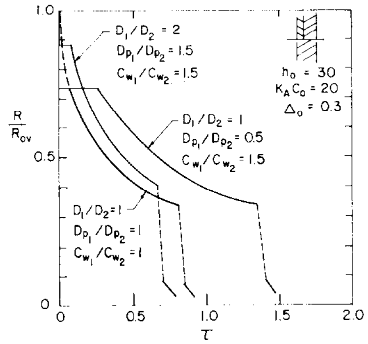

FIG. 5. Relative rate vs dimensionless time. Effect of diffusivities.

$D_{p1}/D_{p2} = 0.5$; and (iii) $D_1/D_2 = 1$, $D_{p1}/D_{p2} = 1$, and $C_{w1}/C_{w2} = 1$. Case iii corresponds to a composite catalyst with a protective layer made of the same support as the active layer. Case i is the base case shown in Figs. 1–4 and corresponds to a composite catalyst with a protective layer with a more open pore structure and hence higher diffusivities than in the active support. Case ii corresponds to a composite catalyst with a lower poison diffusivity in the protective layer than in the active layer, whereas the reactant diffusivities are the same. The results show a decrease of R/R_{0v} and an increase of the constant activity period. The catalyst lifetime also increases beyond that of an unprotected catalyst of the same volume ($\tau > 1$). The deactivation curve for case iii is superimposed on that of an unprotected catalyst, except for the initial short period of constant activity. Thus receding the active metal into the catalyst interior only produces a saving of active component.

The effect of C_{w1}/C_{w2} or the poison-getter capacity ratio is shown in Fig. 6 for the material and reaction parameters of the standard case. The results indicate that increasing C_{w1}/C_{w2} increases the constant rate period as well as the transition time from upper to lower deactivation curves. Thus it is advantageous to use a protective layer with larger poison capacities than in the active layer.

During the writing of this paper, Becker and Wei (*11, 12*) published two papers analyzing the effect of nonuniform distribution of catalysts on supports. These authors analyzed the same bimolecular Langmuir kinetics used in this work and concluded that "an egg-yolk catalyst where the active ingredients are deposited toward the interior of a support can have a greater activity than the more traditional uniform distribution, or the egg-shell distribution toward the exterior of the support." Becker and Wei's results are a particular case of the composite catalyst, corresponding to the case where the same support is used as a protective layer. The composite catalyst is a more general concept than nonuniform deposition of the active metal toward the interior of the support. The use of two supports adds an additional degree of freedom to control the activity and lifetime of the catalyst which does not exist in single supported catalyst. On the other hand, the manufacture of a composite catalyst is more costly than a single supported catalyst.

The values of the reaction parameters K_AC_0 and h_0 where enhancement of activity occurs apply only during the warm-up of catalytic converters. During steady-state operation where first-order behavior prevails, the composite catalyst concept leads to longer catalyst lifetime (*6*).

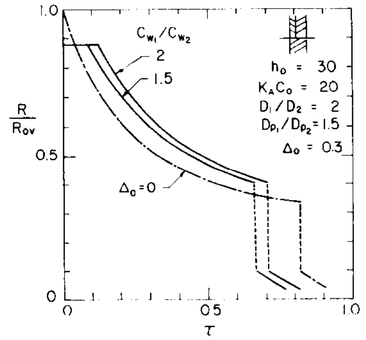

FIG. 6. Relative rate vs dimensionless time. Effect of poison-getter capacity.

CONCLUSIONS

The deactivation of a composite catalyst pellet has been analyzed for a bimolecular Langmuir–Hinshelwood kinetics under diffusion-influenced conditions and pore mouth poisoning. At low K_AC_0 values, the bimolecular kinetics exhibits similar results to that of first-order kinetics. However, at high K_AC_0 values, a different behavior was found. Under the latter conditions, the composite catalyst exhibits higher activity than an unprotected catalyst of the same volume even though it has a less active component.

The enhancement in activity occurs because the presence of the protective layer decreases the reactant concentration and thus increases the reaction rate.

As the catalyst deactivates, the enhancement in activity partially offsets the loss in activity until the kinetics becomes first order and an abrupt decrease in activity occurs.

By proper selection of the protective layer thickness and properties, it is possible to minimize the reduction in reaction rate due to the protective layer and at the same time, extend the catalyst lifetime. It is favorable to select a protective layer with higher reactant diffusivity and lower poison diffusivity than in the active layer. Another desirable property for the protective layer is a high poison-getter capacity. Although all the above properties cannot be independently selected, a compromise between these requirements can be obtained and still obtain favorable results.

The results obtained with the bimolecular kinetics reinforce the previous findings obtained with the first-order kinetics, that the composite catalyst is advantageous to improve the catalyst activity and lifetime under pore mouth-poisoning conditions. As a disadvantage, the composite catalyst can be more difficult to manufacture.

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