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Effect of Pretreatment on Pt/Al_2O_3 and Pt + Re/Al_2O_3 Catalyst Deactivation

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A comparative study of the activity and selectivity maintenance of reforming catalysts is presented. The stability of the catalysts is not significantly affected by varying the drying temperature but it is very definitely affected by sulfur pretreatments. The sulfided bimetallic catalyst is fouled by a mechanism that is easily distinguishable from the monometallic catalyst and mixtures of monometallic catalysts included in this study. © 1985 Academic Press, Inc.

INTRODUCTION

There have been many research investigations concerned with identifying the state of rhenium in $Pt+Re/Al_2O_3$ bimetallic catalysts (*1*–*6*). There are some controversial aspects of this question, but one aspect is clear. That is that the catalyst pretreatment can have a very significant effect on the resulting catalyst, including the state of the rhenium. This has been illustrated, for example, by observing the effect of varying the pretreatment conditions on the resulting temperature-programmed reduction (*7*, *8*).

It has been observed that the drying temperature used in catalyst pretreatment can affect the temperature-programmed reduction results of the bimetallic catalyst enormously (*7*). It is thought that these differences may be due to the amount of H_2O on the catalyst surface possibly present as hydrated rhenium oxide. Whatever, the reason, these results raise the question of what effect, if any, does the drying temperature have on activity and/or selectivity maintenance of the catalyst? Furthermore, are there any advantages or disadvantages to the lower reduction temperature that can apparently be employed if the catalyst is not severely calcined?

In considering the effect of drying and reduction temperature, it is helpful to note that supported platinum reforming catalysts are presulfided in commercial application (*9*–*11*). Therefore, the role of sulfur should be a major concern of any study involved with the stability of reforming catalysts.

A recent observation (*12*, *13*) that physical mixtures of monometallic catalysts can behave similar to the bimetallic $Pt+Re/Al_2O_3$ introduces another challenge that must be taken into account in any study concerned with comparing the stability of these catalysts.

In this study, a series of catalysts and mixtures of catalysts were pretreated under a variety of conditions. The initial activity, selectivity, and the deactivation characteristics of these catalysts are compared. The key variables in question were originally the drying temperature and the reduction temperature. However, as the study progressed it became apparent that the effects, if any, of these two variables are completely overwhelmed by the sensitivity of the bimetallic catalyst to trace levels of H_2S in the system.

EXPERIMENTAL

(1) Reactor system. Two catalytic reactors were used for this study, a gradientless reactor and a single-pellet diffusion reactor.

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The reactors and the associated peripherals have been described elsewhere (*14*). They are both isothermal and have an external recycle stream ($\geq 10/1$) and a very short residence time (3 s for gradientless reactor and 9 s for diffusion reactor). The gradientless reactor employs a nominal particle size of 80 μm. The single-pellet reactor employs a single catalyst pellet composed of 40-μm particles and pressed to 15,000 psi for 20 min. Approximately 0.2 mm of thickness is removed from each side of the finished pellet to avoid any "skin effects." The catalyst pellets used in this study were all approximately 2 mm in finished thickness.

(2) Catalyst pretreatment and fouling conditions. The experimental procedures have been described in detail elsewhere (*15*). In this study, the pretreatment temperatures and durations are adjusted as indicated under Results. All the pretreatment and fouling conditions of each comparative study are given with each individual comparison.

In some experiments, the catalyst pretreatment included a "standard" sulfiding treatment. This involves exposing the catalyst to 5 molecules of H_2S per platinum atom. It is accomplished by introducing the necessary number of 3-cm^3 aliquots of 1000 ppm H_2S into a flowing stream of hydrogen that passes over the catalyst. This treatment, if applicable, immediately follows the reduction period and precedes the activity measurements by about 24 h. During this 24-h interval, the catalyst is held in flowing hydrogen at 360°C.

In some of the experiments performed in the gradientless reactor, a mixture of two different catalysts was used. A "physical mixture" refers to the case in which the two components of the catalyst mixture are physically separated by a fine mesh screen. An "intimate mixture" refers to the case in which the two components of the catalyst mixture are well mixed and are in direct physical contact during the experiment.

(3) Materials. The feedstock for all studies is Kodak spectroquality methylcyclohexane (MCH). The carrier gases are Matheson UHP hydrogen (99.999%) and distilled helium (99.995%). The catalysts were generously donated by Cheron Research Company and their properties have been reported elsewhere (*7*). The active metal loadings are nominally 0.3 wt% and all catalysts contain 0.6 wt% Cl. The surface area of the support is nominally 200 m^2/g.

TABLE 1

Symbol Key for the Selectivity Data in Figs. 1, 3, and 4

Monometallic	Bimetallic	GC peak ratio
△	○	Cracked products/toluene
◭	◒	Benzene/toluene
▲	●	$\mathrm{MCH}^=/\mathrm{MCH}$

RESULTS

Catalyst fouling data from two deactivation experiments in the gradientless reactor are presented in Fig. 1 (see Table 1 for symbols). These catalyst loadings were dried at 100°C, reduced at 360°C, and were not exposed to any sulfiding pretreatment. There are no significant differences in either the rate (activity) versus time data or the selectivity versus time data under these conditions.

Catalyst fouling data from three additional deactivation experiments in the gradientless reactor are presented in Fig. 2. These catalyst loadings were calcined at 500°C, reduced at 360°C, and were not exposed to any sulfiding pretreatment.

There are only very small differences in the rate (activity) versus time data, and only after several hundred minutes on stream. The bimetallic is the most stable under these conditions. However, these differences in stability are quite small relative to the differences observed for sulfided catalysts, as will be shown in subsequent results.

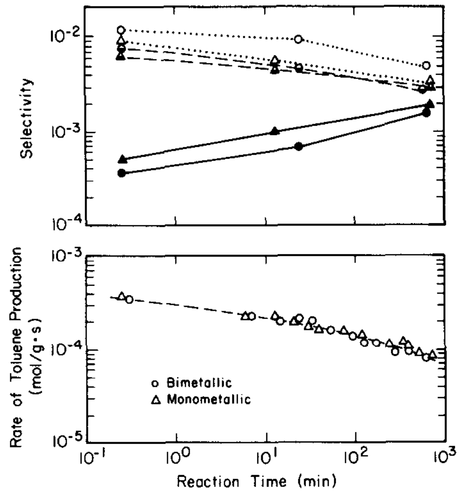

FIG. 1. Unsulfided catalyst fouling data. Pretreatment calcination $T = 100°C$, reduction $T = 360°C$. Reaction conditions: 425°C, 8 Torr MCH, 4 Torr toluene, 800 Torr H_2 (see Table 1 for symbol key).

It is useful to note that, along with the small differences in the activity versus time data, there are very significant differences in the selectivities of these catalysts after several hundred minutes on stream. The bimetallic catalyst becomes much more selective toward the desired product, toluene, than either of the other two catalyst loadings. Furthermore, the physical mixture behaves much more like the monometallic catalyst than the bimetallic. These experiments (Fig. 2) were conducted with such short elution times for the GC samples that the $MCH^{=}$ yield could not be determined.

Catalyst fouling data from two additional deactivation experiments in the gradientless reactor are presented in Fig. 3. These catalyst loadings were calcined at 500°C, reduced at 485°C, and were not exposed to any sulfiding pretreatment.

The initial rate of toluene production is about threefold lower for the bimetallic catalyst than it is for the monometallic catalyst under these conditions. The decay of initial activity is very similar for the two catalysts.

Along with the differences in initial activity, the initial dealkylation selectivity of the bimetallic catalyst is also about threefold lower than it is for the monometallic catalyst. Furthermore, while the dealkylation selectivity for the bimetallic catalyst decreases further by a factor of about 6 during the deactivation experiment, the dealkylation selectivity of the monometallic remains unchanged during the deactivation experiment.

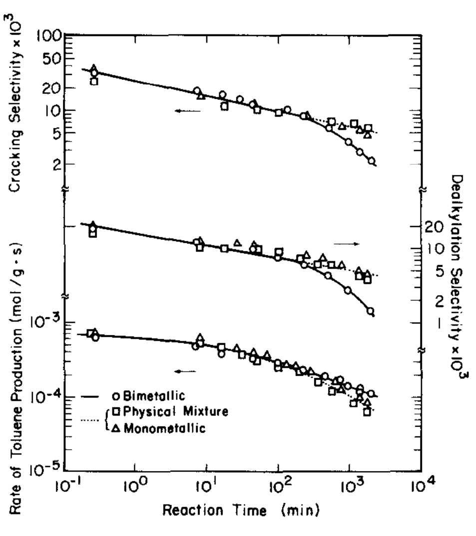

FIG. 2. Unsulfided catalyst fouling data. Pretreatment calcination $T = 500°C$, reduction $T = 360°C$. Reaction conditions: 425°C, 20 Torr MCH, 9 Torr toluene, 800 Torr H_2.

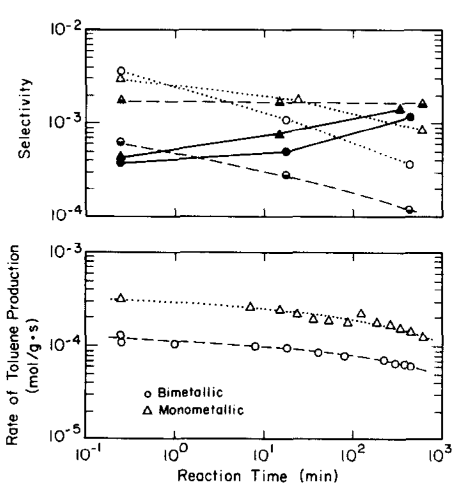

FIG. 3. Unsulfided catalyst fouling data. Pretreatment calcination $T = 500°C$, reduction $T = 485°C$. Reaction conditions: 425°C, 8 Torr MCH, 4 Torr toluene, 800 Torr H_2 (see Table 1 for symbol key).

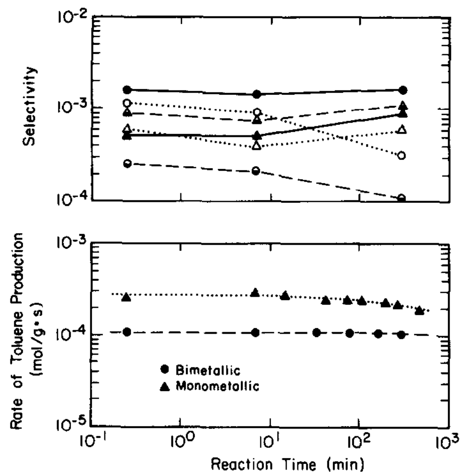

FIG. 4. Unsulfided catalyst fouling data. Pretreatment calcination $T = 100°C$, reduction $T = 360°C$, H_2S treatment $T = 425°C$. Reaction conditions: 425°C, 10 Torr MCH, 4 Torr toluene, 800 Torr H_2 (see Table 1 for symbol key).

In addition to the differences in the dealkylation selectivity, the decay of the cracking selectivity for the two catalysts is also different. The cracking selectivities are nearly equal initially. But, it decays about twice as fast for the bimetallic catalyst as it does for the monometallic.

Catalyst fouling data from two additional deactivation experiments in the gradientless reactor are presented in Fig. 4. These catalyst loadings were dried at 100°C, reduced at 360°C, and were exposed to a "standard" sulfiding pretreatment at 425°C.

The initial rate of toluene production is again about threefold lower for the bimetallic catalyst than it is for the monometallic catalyst. In addition, there is a very slight difference in the decay of this activity. The bimetallic catalyst is a little more stable than the monometallic catalyst for the production of toluene under these conditions.

Along with the difference in initial activity the initial dealkylation selectivity of the bimetallic catalyst is again about threefold lower than it is for the monometallic catalyst. And again, the dealkylation selectivity of the bimetallic catalyst decreases (this time by a factor of about 3), while that of the monometallic catalyst remains unchanged.

The cracking selectivity of the bimetallic catalyst is initially twofold higher than that of the monometallic catalyst under these conditions. However, it drops by a factor of about 4 for the bimetallic during the deactivation experiment, while the monometallic remains relatively unchanged. This results in a crossover of the cracking selectivities after about 1 h on stream.

Catalyst fouling data from three additional experiments in the gradientless reactor are presented in Fig. 5. The catalysts in these experiments were calcined at 500°C and reduced at 360°C. These catalysts were all exposed to a standard sulfiding pretreatment at 500°C.

An enormous difference is observed between the deactivation characteristics of the bimetallic and that of monometallic mixtures under these conditions. The bimetallic is much more sensitive to the sulfiding pretreatment, as shown by the lower initial dehydrogenation activity. The bimetallic is also much more stable as a result of the sulfiding, as shown by the crossover in activity after only 10 min on stream.

The cracking and dealkylation selectivities of all three catalyst loading were too

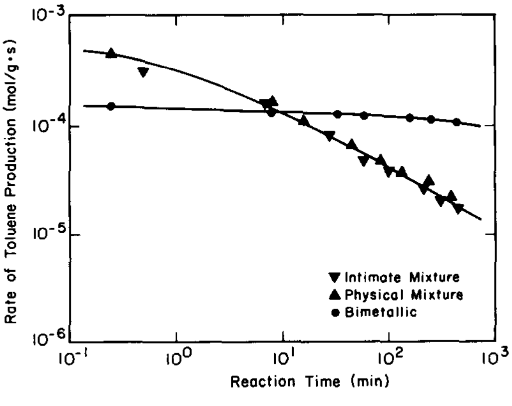

FIG. 5. Sulfided catalyst fouling data. Pretreatment calcination $T = 500°C$, reduction $T = 360°C$. H_2S treatment, $T = 500°C$. Reaction conditions: 440°C, 40 Torr MCH, 4 Torr toluene, 400 Torr H_2.

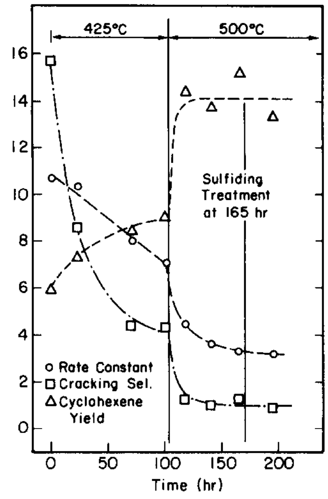

FIG. 6. Bimetallic catalyst stability test in flowing hydrogen. Pretreatment calcination T = 500°C, reduction T = 425°C. Reaction conditions during activity tests: 425°C, 10 Torr MCH, 3 Torr toluene, 800 Torr hydrogen. (Circles) Rate constant (10^2 cm^3/g s), (squares) cracking selectivity × 10^3, (triangles) MCH$^=$ yield × 10^4.

small to measure reliably. They were on the order of 10^{-5}. The methylcyclohexene yield was also too small to measure in the case of the catalyst mixtures. However, the methylcyclohexene yield was about 2×10^{-3} throughout the experiment in the case of the bimetallic.

The results of a catalyst stability test of the bimetallic catalyst conducted in the gradientless reactor are presented in Fig. 6. This catalyst loading was calcined at 500°C, reduced at 425°C for 18 h, and was not exposed to any sulfiding pretreatments prior to the activity tests. Following the 18-h reduction, the catalyst was held at 425°C for an additional 105 h in flowing hydrogen (200 cm^3/m at RTP). During this period, the activity and selectivity of the catalyst was tested with several 15-s steady-state MCH dehydrogenation rate determinations.

As shown in Fig. 6, the activity and selectivity of the bimetallic catalyst were not stable even after 120 h at 425°C in flowing hydrogen. The rate of toluene production was about a factor of 2 or 3 below that of a fresh Pt/Al$_2$O$_3$ catalyst after the 18-h reduction and continued to drop very significantly over the subsequent 100 h. The cracking selectivity also decreased and the MCH$^=$ yield increased over this same time period.

Following the 105-h period at 425°C, the reactor temperature was raised to 500°C and held for another 60 h under flowing hydrogen. Periodically, the reactor temperature was lowered from 500°C for a 15-s rate determination. The total time required to change from 500 to 425°C, make the activity check, and return the temperature to 500°C was less than 1 h. The rate determinations were all made under the same reaction conditions which simplifies the interpretation. The results of this extended test are also shown in Fig. 6. The trends of activity and selectivity are accelerated at 500°C but they are directionally the same as they were at 425°C.

The catalyst appeared to be relatively stable 165 h after the first activity test. At this point, the catalyst loading was exposed to a "standard" sulfiding treatment. Also shown in Fig. 6, the sulfiding treatment resulted in no significant changes in the activity or selectivity of the catalyst.

The single-pellet diffusion reactor was used to further explore the enormous difference in the deactivation curves shown in Fig. 5. In this case, layered "sandwich-pellets" of the kind illustrated in Fig. 7 were used to study the deactivation characteristics of various catalysts and catalyst mixtures in the diffusion reactor. The single pellets prepared for this study were composed of two layers of catalyst component mixtures. The reaction-half was compressed first, the interfacial surface was shaved by approximately 0.2 mm and then the center-plane-half of the pellet was compressed onto the original pellet. Each half was composed of either a 50/50 mixture of two catalyst components or pure γ-alumina. The nominal composition of the pellets are summarized in Table 2.

The initial rate and center-plane concentration data for the four pellets are summa-

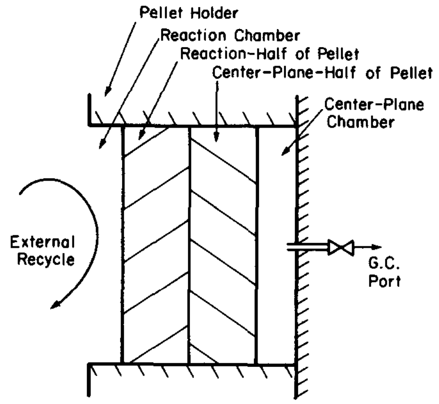

FIG. 7. Cross section of "sandwich-pellets" used to study the deactivation characteristics of catalyst mixtures in the single-pellet diffusion reactor.

TABLE 3

Summary of the Observed Initial Rate of Toluene Production for the "Sandwich-Pellets" in the Diffusion Reactor[a]

Catalyst pellet description	Observed initial rate (10^{-4} mol/g s)	Observed initial CP conc. $[MCH]_{cp}/[MCH]_{prod}$	First-order Thiele modulus
Bimetallic	0.47	0.015	5.0
Monometallic	0.77	0.0044	6.1
Layered mixture	0.75	0.0032	6.4
Intimate mixture	0.58	0.0030	6.5

[a] Basis: mol/s of toluene produced per gram of Pt containing component after 45 s on stream.

rized in Table 3, and the deactivation data are summarized on the diagnostic plot in Fig. 8. These pellets were calcined at 500°C, reduced at 360°C, and exposed to a standard sulfiding pretreatment at 500°C.

The Thiele modulus corresponding to the observed center-plane concentration for a first-order reaction is shown in Table 3 for the four pellets. Also, deactivation curves corresponding to uniform poisoning are shown in Fig. 8 for a Thiele modulus of 5 and 6.

The product selectivities of the sulfided catalysts were too small to measure reliably in the single-pellet reactor, as in the gradientless reactor; however, the amplifying property of the center-plane measurement permits an additional "fingerprint" of the catalyst deactivation characteristics. In Fig. 9, the ratio of benzene to toluene center-plane concentration is plotted versus time for the four catalyst pellets. There is a very significant difference distinguishing the bimetallic catalyst from the other three loadings. The center-plane ratio of benzene to toluene is consistently a factor of about 3 smaller than that of the monometallic. The layered mixture behaves identical to the monometallic. The intimate mixture starts out more like a bimetallic catalyst but quickly changes its behavior to be more like a monometallic.

TABLE 2

Composition of the Various "Sandwich-Pellets" Used in the Single-Pellet Diffusion Reactor Studies

Catalyst pellet	Reaction-half composition (1 : 1)	Center-plane-half composition (1 : 1)
Bimetallic	Pt + $Re/Al_2O_3 : Al_2O_3$	Al_2O_3
Monometallic	$Pt/Al_2O_3 : Al_2O_3$	Al_2O_3
Layered mixture	$Pt/Al_2O_3 : Al_2O_3$	$Re/Al_2O_3 : Al_2O_3$
Intimate mixture	$Pt/Al_2O_3 : Re/Al_2O_3$	Al_2O_3

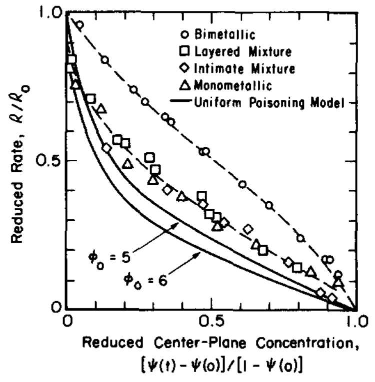

FIG. 8. Single-pellet catalyst deactivation data for the "sandwich-pellets." Solid lines represent the case of uniform poisoning. Dashed lines indicate the trends observed empirically. Pretreatment calcination T = 500°C, reduction T = 360°C, H_2S treatment, T = 500°C. Reaction conditions: 480°C, 30 Torr MCH, 6 Torr toluene, 800 Torr H_2 (see Table 2 for the initial rates and Thiele parameters, ϕ).

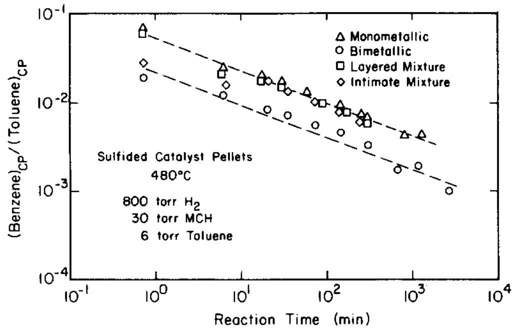

FIG. 9. Ratio of benzene to toluene center-plane concentrations corresponding to the single-pellet deactivation data in Fig. 8.

DISCUSSION

The similarities between the effect of high temperature reduction (Fig. 3) and mild H_2S pretreatment (Fig. 4) led to a study of catalyst stability at elevated temperatures in flowing hydrogen (Fig. 6). The Pt/Al_2O_3 catalyst can be held for several hundred hours in flowing H_2 at 425°C without any measurable effect on the activity and/or selectivity of the catalyst. However, this is not the case for the bimetallic catalyst and this is probably due to two contributing factors. Firsst, the bimetallic catalyst is known to be much more sensitive to sulfur at elevated temperatures. Second, the gradientless reactor used in this study is frequently used to study sulfided as well as unsulfided catalysts. Since the sulfiding is performed *in situ*, it is impossible to avoid low levels ($\leq$ppm) of H_2S in the reaction environment.

The results of the long-term stability test shown in Fig. 6 are a very strong indication that all of the catalysts are inadvertently being exposed to a very low level of H_2S in this reactor system. While this low level of H_2 has no observable effect on the monometallic catalyst, it is believed that this inadvertent sulfur poisoning can account for all the differences observed in Figs. 2 and 3 for the bimetallic catalyst. That is to say, it appears as though some sulfur may be necessary in order to observe any differences in the deactivation characteristics of these catalysts.

Comparing Figs. 1 and 2, it is believed that the slight improvements in stability and selectivity of the bimetallic is due to prolonged exposure to low levels of H_2S and not to the difference in the pretreatment, noting that the runs in Fig. 2 are almost four times longer than those in Fig. 1.

Comparing Figs. 3 and 4, there are remarkable similarities between the effect of a high-temperature (485°C) reduction and a moderate (425°C) H_2S pretreatment. Based on these similarities, it is thought that a significant sulfiding of the bimetallic occurs during the high-temperature reduction period.

The 500°C sulfiding (Fig. 5) lowers the activity of the bimetallic roughly six times lower than it does the monometallic. The activity of the sulfided Pt/Al_2O_3 catalyst is about 60% that of the fresh catalyst and the sulfided $Pt+Re/Al_2O_3$ catalyst is about 10%. These observations are consistent with the 65% adsorption capacity of a sulfided Pt/Al_2O_3 catalyst reported by others (*16*). It is also interesting to note the 10% hydrogen uptake for a $Pt+Re/Al_2O_3$ catalyst observed by others (*17*). However, in this last case, the catalyst was not intentionally sulfided.

The initial rate data (Table 3) show that mass transfer moderates the poisoning effect of sulfur on the bimetallic relative to the monometallic. Furthermore, the diagnostic deactivation plot (Fig. 8) indicates a very significant difference in the deactivation characteristics of the bimetallic catalyst from that of the monometallic and mixtures of monometallics. This difference, which is too large to be explained by the small differences in the Thiele modulus, indicates that the bimetallic catalyst is fouled more toward the core of the catalyst pellet than the monometallic.

Figures 5 and 8 clearly demonstrate that the deactivation kinetics of a sulfided bimetallic catalyst are enormously different from that of a monometallic catalyst and mixtures thereof. For this reaction system, there appears to be no significant effect of the second metal (rhenium) unless it is on the same support as the active metal (platinum).

The differences in the fundamental deactivation kinetics of the sulfided catalysts have been explored in detail (*15*) and explained on the basis of a simple multiplet model (*18*). In this model, the role of rhenium is viewed as a sort of footing for strongly adsorbed sulfur to effectiviely partition the platinum particles into very small 2- or 3-atom ensembles (*19*).

The data in Fig. 8 can be interpreted simply on the basis of the fundamental fouling kinetics. In the case of the sulfided bimetallic, toluene has a first-order effect on the rate of fouling. But, in the case of the monometallic catalyst, toluene inhibits the fouling reaction. It is thought that the reason of the bimetallic catalyst fouls more toward the core of the pellet than the monometallic catalyst is due, in part, to this fundamental difference in the toluene kinetics of the deactivation reaction for these catalysts.

The "fingerprint" shown in Fig. 9 is difficult to explain quantitatively. However, it is very useful since it is the only available measure of selectivity differences of the catalysts that have been sulfided at 500°C. It is interesting to note the very subtle similarity between the intimate mixture and the bimetallic for very short times. In addition, the initial rate of the intimate mixture pellet (Table 3) was somewhat intermediate of the bimetallic and the monometallic. However, these similarities seem insignificant in view of the enormous differences observed in Figs. 5 and 8.

CONCLUSION

The calcination and reduction pretreatment temperatures seem to play a relatively insignificant role in the deactivation characteristics of these catalysts. The presence of trace levels of H_2S overwhelm these observations. It is concluded that for this model reaction system the two metals must be cosupported and presulfided in order to achieve any significant differences in the deactivation characteristics. Upon sulfiding these catalysts, the bimetallic becomes much more selective, more stable, and fouls more towards the pellet core than the monometallic or mixtures of monometallics.

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