Catalyst Sintering in Fixed-Bed Reactors: Deactivation Rate and Thermal History

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An experimental study has been carried out of the in situ thermal degradation of a commercial dehydrogenation catalyst in a fixed-bed reactor. The activity of catalyst particles sampled at different reactor positions after several reaction-regeneration cycles has been related to their time-temperature history, according to the following kinetics:

$$-da_o/dt = 0.147 \exp(-73{,}600/RT)a_o^{2.2}$$

The above equation represents the loss of activity under coke-free conditions, that is, activity loss due to sintering. The results of the study show that important differences in catalytic activity can be obtained for different positions of a fixed-bed catalytic reactor after several operation-regeneration cycles.

Introduction

Most catalysts used in industrial heterogeneous processes undergo a decrease in their activity with time on stream. When the performance of a catalyst, as measured by its activity and/or selectivity, is reduced to a level that makes continued operation uneconomical or very difficult (for example, when high temperatures are needed to maintain the level of activity desired), the catalyst must be regenerated or replaced.

In such cases as irreversible poisoning or in most cases of deactivation by sintering, the initial activity of the catalyst cannot be regained. When coking is the cause of deactivation, however, the catalyst can be regenerated at least partially by gasification of coke deposits with oxygen, carbon dioxide, steam or hydrogen. Oxidative regeneration processes employ gas mixtures containing a low percentage of oxygen to achieve a slow coke burnoff. This is because of the need to avoid high temperature rises caused by the exothermic oxidation of the coke, which can lead to the sintering of the catalyst and/or damage to the reaction equipment.

When fixed-bed catalytic reactors are employed, the regeneration usually gives rise to the formation of a high-temperature front, which travels along the bed as it burns off the coke deposited on the catalyst. Another example of propagation of hot spots in fixed-bed reactors corresponds to the case of rapid poisoning coupled with an exothermic main reactor. Blaum (1974) discussed this interaction in a simulation study, in which the shape and velocity of the thermal waves were predicted for different relative rates of the main and deactivation reactions.

In fixed-bed regeneration, since coke deposition does not usually occur uniformly in the reactor, the amount of heat evolved in the combustion of the coke deposits may vary locally within the bed. For a given reactor and operating conditions, this may lead to different maximum temperatures reached along the bed during the course of the regeneration process. The intrinsic dynamics of propagation of the hot fronts generated also contribute to the heterogeneity of the thermal history of catalyst particles located at different reactor positions. Thus, numerous theoretical investigations have been carried out to predict the temperature profiles attained during regeneration of fixed-bed reactors including the early work of Van Deempter (1953, 1954) and the more recent contributions of Hatcher and Burton (1984) Byrne et al. (1985, 1989), and Santamaria et al. (1990).

The general subject of catalyst sintering has also attracted a strong research effort, as evidenced by recent reviews of the subject (for example, Lee and Ruckenstein, 1983; Hughes, 1984; Wanke et al., 1987; Butt and Petersen, 1988). Most of the work to date has concentrated on elucidating the mechanisms of catalyst sintering and on the study of structural changes

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on the catalyst surface. The long-term goal of these studies was to relate the sintering behavior of a given catalyst to the main process variables on sintering: temperature, pressure and types of gas, and substrate used for a particular case. Some models for sintering of supported metal catalysts were reviewed by Dadyburjor (1987). In a recent work, Ruckenstein (1991) discussed new mechanisms of sintering, involving wetting and spreading in addition to the traditional sintering pathways.

This work discusses the thermal aging of catalysts in fixed-bed reactors subjected to oxidative regeneration. Several authors have investigated the effect of one or more regenerations on the activity or on the surface characteristics of different catalysts. Such is the case of the works by George et al. (1980), Pennline and Pollack (1986), Bogdanor and Rase (1986), Arteaga et al. (1986, 1987a,b), and Cabrera et al. (1988).

In most of these works, however, the loss of catalytic activity due to catalyst sintering was not quantitatively related to the reaction conditions seen by the catalyst during regeneration. Furthermore, laboratory studies are usually carried out by subjecting the catalyst sample to carefully controlled, constant environmental conditions. In the preceding discussion, however, it was shown that the conditions seen by a catalyst particle during regeneration of a fixed-bed catalytic reactor can vary considerably for different regeneration times and reactor positions. It would therefore be useful to assess the extent of differential sintering that can be induced by the heterogeneity of the local temperature history in a fixed-bed reactor.

In a previous work (Blasco et al., 1991), some experimental evidence showed that significant differences between the catalytic activity of particles located at different positions of the same reactor could develop after a relatively short number of reaction-regeneration cycles. In the present work, enough results have been obtained over a wider range of operating conditions to further confirm the possibility of nonuniform sintering in fixed-bed reactors and to obtain a quantitative relationship between the loss of activity and the time-temperature history of a commercial dehydrogenation catalyst.

Experimental Procedure

The reaction used was the dehydrogenation of 1-butene over a commercial Cr_2O_3/Al_2O_3 catalyst (4 mm × 4 mm cylindrical pellets provided by Harshaw). The reactor employed was a 4-cm-id, 78-cm-long stainless-steel tube provided with three independent heating sections to achieve a more uniform temperature along the bed at the start of the experiments. The catalyst bed itself was 40-cm-long, although a longer bed was employed in some of the experiments performed. At the top and bottom of the catalyst bed, preheating and cooling sections were provided by packing enough 8-mm inert ceramic rings to complete the 78-cm reactor length.

An operation cycle consisted of a reaction period, during which coke was produced as the dehydrogenation reaction was taking place, and a regeneration stage, in which all or part of this coke was eliminated by combustion with oxygen. The first part of the cycle was started by heating the bed in a nitrogen stream until the reaction temperature (either 480 or 620°C) was reached. The feed was then replaced by a 50% butene/nitrogen mixture and the reaction was continued for 4 to 6 hours, until a certain level of coking was achieved. The catalyst bed was then cooled in a N_2 stream to room temperature. The regeneration run was started by purging the reactor in a N_2 stream at the regeneration temperature to eliminate combustible gases and volatile fractions of the coke. Then, the regeneration itself was started by feeding O_2/N_2 mixtures, which caused the combustion of the coke deposits on the catalyst. The flows to the reactor during the coking and regeneration runs were kept constant by means of mass flow controllers.

The temperature inside the catalyst bed was continuously monitored at a minimum of six axial positions. Temperature readings were taken at regular intervals using a computer-controlled data acquisition system. This yielded the thermal history of the catalyst particles at six different locations in the catalyst bed.

After a certain number of coking/regeneration cycles, catalyst particles were sampled from zones very close to the measuring points. This was achieved by gradually emptying the reactor using a vacuum line. Thin layers of catalyst were successively removed from the top to bottom of the reactor until each of the thermocouple locations were reached. The catalyst particles surrounding a temperature probe were then stored separately for later kinetic measurements.

The precision of the sampling procedure was critical for this work, since the temperature gradients in the reactor are likely to be high during regeneration. Test loadings with colored catalyst particles showed the accuracy of sampling to be better than 1 cm.

After sampling, regenerated catalyst particles with a known thermal history were subjected to kinetic measurements in a separate unit. This consisted of a 16-mm-ID fixed-bed reactor provided with automatic controls of temperature and mass flow of reactants. The reactor was submersed in a fluidized sand bed to ensure its isothermality. Usual precautions required in kinetic experiments were taken: dilution of the bed with inert ceramic beads, blank experiments to check that contribution to the catalytic reaction of the solid diluent and of the reactor walls could be neglected under the conditions employed, and selection of conditions (particle size and gas velocity) under which internal and external transport resistances were negligible. Conversion at the reactor exit in any of the kinetic experiments was below 7%.

Results and Discussion

Nonuniform thermal history of the catalyst particles in the bed

As stated previously, one of the causes for the variation of the temperature history of the catalyst along the bed may be a nonuniform coke laydown. Froment and Bischoff (1961) originally pointed out that the distribution of coke will depend on whether the coke is deposited by a reaction in series or in parallel to the main one, which would give increasing or decreasing coke profiles, respectively. For the system studied in this case, widely different coke profiles were obtained when the operating conditions changed. Figure 1 shows the results obtained after coking for different lengths of time at initial temperatures of 620 and 480°C, respectively. To measure the coke profiles, the catalyst bed was divided into sections, which were individually mixed. Their average concentration of coke was then measured using a thermobalance. It can be observed that the pattern of coke deposition along the bed changed when the temperature was increased. Fluctuations in the coke dep-

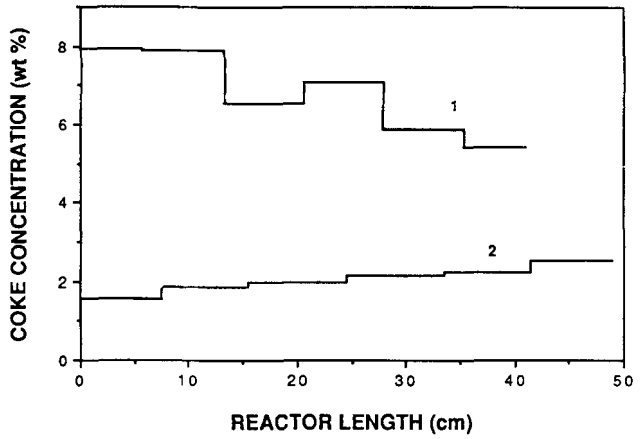

Figure 1. Coke concentration profiles obtained under different operating conditions.

1. coking with a 1:3 butene/nitrogen mixture for 5 hours at 620°C; 2. coking with a 1:3 butene/nitrogen mixture for 5 hours at 480°C. The catalyst bed used in 2 was longer.

osition profile that can be observed in curve 1 are thought to be due to temperature inhomogeneities that appear under reaction conditions, as pointed out by Dumez and Froment (1976) and by Acharya and Hughes (1990). A slow-moving, low-temperature wave during the dehydrogenation of 1-butene was also observed during the course of this work. In any case, variations in the amount of coke deposited at different reactor positions are considerable. Even in curve 2, where the coke profile shows little change in absolute terms, the relative variation is high (about 60%) from reactor inlet to exit.

In addition to the coke distribution in the bed, an important factor influencing the temperature rise attained at a given position during regeneration, is the oxygen input to the reactor. In fact, this is customarily used in industrial practice as a means of controlling the severity of the regeneration process. The general pattern of the evolution of the temperature profiles during regeneration is shown in Figure 2, where the axial temperature profiles in the bed are represented at the times when

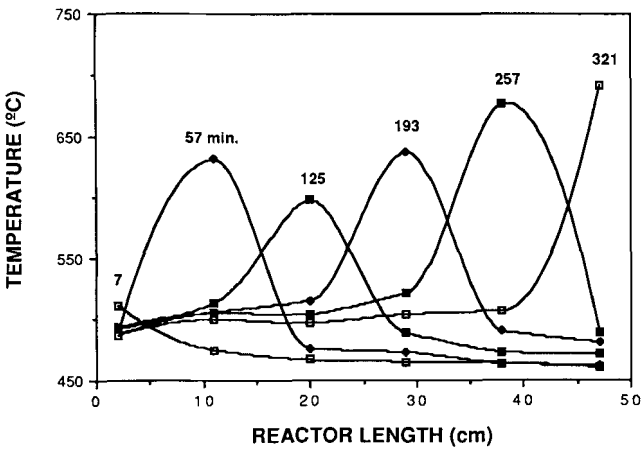

Figure 2. Example of temperature evolution during regeneration.

Temperature profiles in the reactor at the times when each of the six thermocouples measured its maximum temperature. Regeneration with a 6% oxygen in nitrogen mixture at 460°C initial temperature.

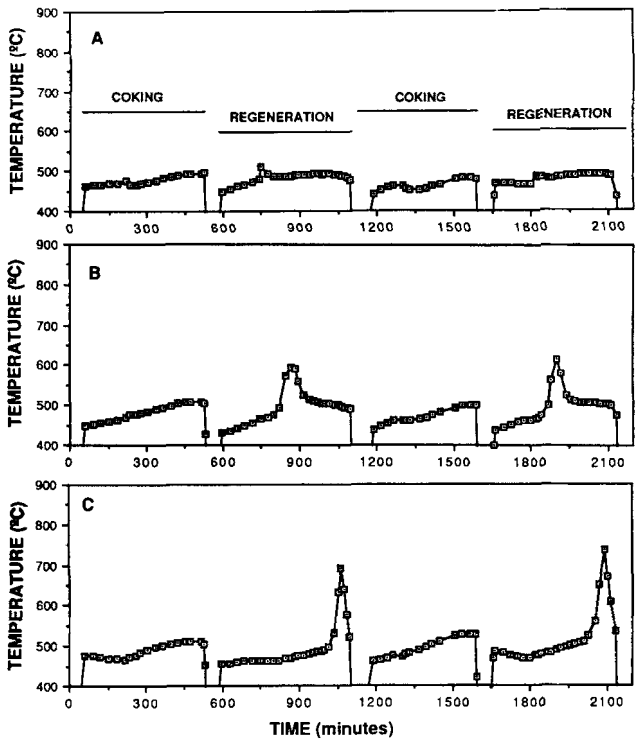

Figure 3. Thermal history of different reactor regions over two operation-regeneration cycles.

Regeneration with 6% oxygen concentration in the feed to the reactor. The initial temperatures for coking and regeneration were 480 and 460°C, respectively.

A. 2 cm; B. 20 cm; and C. 47 cm from the bed inlet.

each of the thermocouples reached its maximum temperature. A high-temperature wave progresses along the bed as time increases, corresponding to the displacement of the reaction zone where most of the oxygen input to the reactor is consumed (Byrne et al., 1986).

Figure 3 shows the thermal history for different reactor regions during two full cycles (operation-coking and regeneration). Changes in temperature during the coking periods were moderate for any reactor zone as shown in the figure. However, during regeneration, which was carried out with 6% oxygen concentration in the feed stream, temperatures reached in various zones of the reactor were considerably different. Figure 3A shows that under these conditions, very small temperature increments occur in the inlet region of the catalysts bed during regeneration, while temperature increments in excess of 200°C are reached at the bed exit (3C). This changes considerably when the conditions of coking (and therefore the amount of coke deposited) and/or of regeneration are changed. Figure 4 shows the results obtained with a higher coke loading (achieved using a higher temperature during coking) and with 10% oxygen concentration in the feed during regeneration. It can be observed that the maximum temperatures reached are now much higher, both at the inlet (754°C) and at the exit (855°C) of the catalyst bed. When the same conditions for coking as those in Figure 4 are used in conjunction with 8% oxygen concentration during regeneration, the results obtained (not shown) gave a maximum temperature in the bed of 788°C, which compares with 736°C and 855°C for 6% and 10% oxygen concentration, respectively.

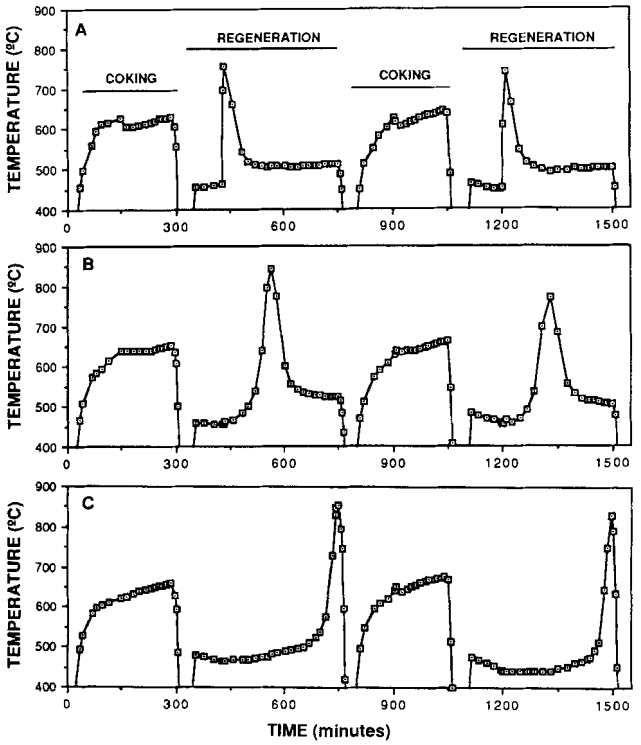

Figure 4. Thermal history of different reactor regions over two operation-regeneration cycles.

Regeneration with 10% oxygen concentration in the feed to the reactor. The initial temperatures for coking and regeneration were 630 and 450°C, respectively.

A. 2 cm; B. 16.8 cm; and C. 39 cm from the bed inlet.

During any regeneration, it can be observed that only small temperature increases occur at a given reactor position until the moving high-temperature reaction zone reaches it. Then, a very fast temperature peak is observed due to the combustion of coke, followed by a somewhat slower decrease as the coke deposits are depleted. The temperature peaks occur at later times as we move further into the bed, which corresponds to the time required for the displacement of the high-temperature zone from one position of the reactor to another.

Catalytic activity after regeneration

Since the thermal history of catalyst particles may vary considerably for different regions of the reactor, it seems also reasonable to expect various degrees of catalyst loss due to sintering. Some such evidence was presented in a previous work (Blasco et al., 1991), both from activity measurements and XPS analysis of the catalyst surface. In this work, the kinetic measurements have been extended to provide further support for the previous findings and to obtain enough data to derive a quantitative relationship between the loss of activity and the thermal history of the catalyst.

All kinetic measurements were performed on samples of known thermal history, at a temperature of 580°C, with a catalyst load of 1 g. The reaction rates obtained by passing a mass-flow-controlled mixture of 50% butene in nitrogen were compared to those found for the fresh catalyst under the same conditions. This allowed the definition of an activity based on

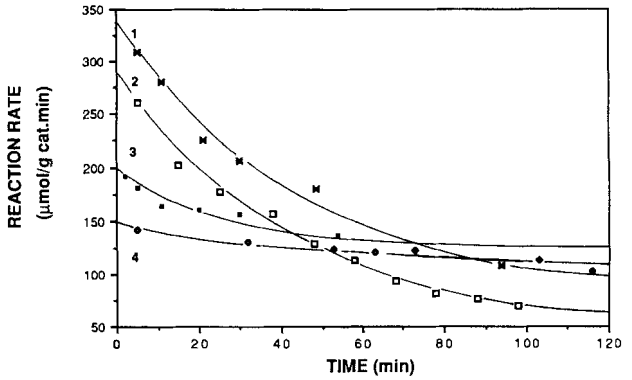

Figure 5. Activity of the same reactor area (exit zone) after different treatments.

1. Fresh catalyst; 2. after one regeneration with 8% oxygen concentration in the feed; 3. after seven regenerations with 6% oxygen concentration in the feed; 4. after seven regenerations with 10% oxygen in the feed.

relative reaction rates according to,

$$a = r_t / r_{fo} \tag{1}$$

During the kinetic measurements, the catalytic activity decreased as a result of coking. Extrapolation to time equal to zero using a nonlinear fitting routine yielded a_o, the activity of the catalyst in the absence of coke. Variations in a_o found for different catalyst samples could then be ascribed to the differences in their thermal history.

An example of the results obtained in the kinetic tests is shown in Figure 5, where the evolution of the reaction rate for particles with different thermal history sampled from the exit zone of the reactor is represented together with that of the fresh catalyst. The activity of the same reactor area (exit zone) changes considerably for different reaction conditions, the deactivation being higher for more severe treatments in terms of overall thermal history (that is, considering both, the temperature reached and the number of coking-regeneration cycles). Figure 6 shows the reaction rates obtained for two different positions of the same reactor after seven coking-regeneration cycles. Differences in the initial activity are comparable to those shown in Figure 5 (curves 3 and 4) for treatments of considerably different severity (corresponding respectively to 6 and 10% oxygen concentration in the feed), which led to differences in the maximum temperatures of about 100°C, as shown in Figures 3C and 4C. This means that not only the operator-controlled conditions (initial temperature and oxygen concentration) and the number of cycles are relevant to determining the extent of sintering, but also the particular location within the catalyst bed. It is also worth noting that the rate of activity loss by coking also seems to decrease as the catalyst is sintered. This means that after a certain time of operation a sintered catalyst may perform better than a fresh one, as demonstrated in Figures 5 and 6. However, the time at which the curves of the reaction rates of the fresh and sintered catalyst find each other is considerably higher than the usual operation time between regenerations for this system, which is about 15 minutes (Dumez and Froment, 1976).

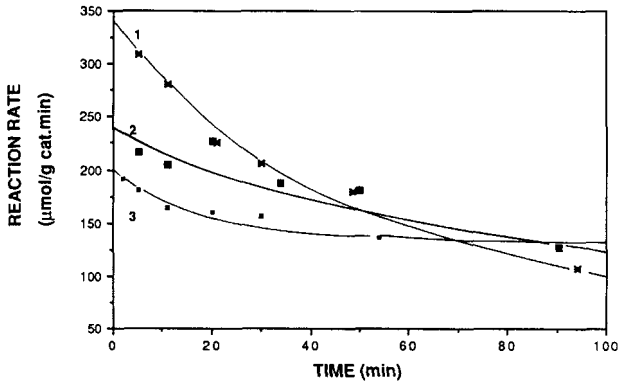

Figure 6. Activity of different zones of the same reactor after seven coking-regeneration cycles with 6% oxygen concentration in the feed.

1. Fresh catalyst; 2. catalyst from the inlet zone of the reactor; 3. catalyst from the exit zone of the reactor.

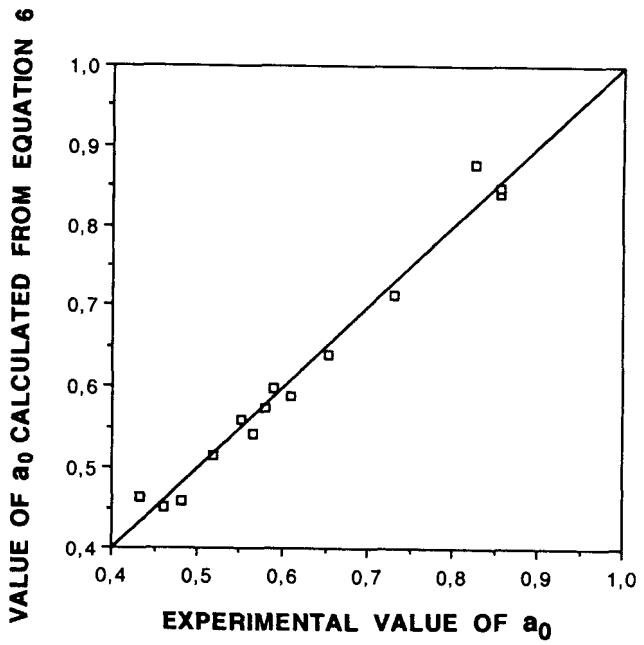

Figure 7. Adequacy of fit of the experimental activity data to Eq. 6.

Sintering kinetics

If the sintering process is assumed to follow a simple power law expression, the loss of activity is given by:

$$-da_o/dt = ka_o^{\,d} \tag{2}$$

where k is given by an Arrhenius-type relationship:

$$k = k_o \exp(-E/RT) \tag{3}$$

Since the temperatures at a given position during operation and especially during regeneration can change considerably, the value of k will undergo important changes with time. The integration of Eq. 2 yields:

$$a_{o1}{}^{1-d} - a_{o2}{}^{1-d} = (1-d)k_o l \tag{4}$$

where

$$l = \int_{t1}^{t2} \exp(-E/RT)\,dt \tag{5}$$

Equation 4 is thus an empirical expression containing three parameters (k_o, E, d), that can be used together with Eq. 5 to fit the data obtained. Analytical integration of Eq. 5 is not possible, since the variation of temperature with time is complex. Therefore, numerical integration was performed using the temperature-time data gathered during operation at every position for which activity measurements were undertaken. To this end, the value of E was varied over the activation energy range to be explored. For each assumed value of E, the value of l was calculated according to Eq. 5, using the time-temperature data corresponding to a particular sample, that is, the thermal history over one or more coking-regeneration cycles at a given reactor position. From the set of values of a_o obtained in the kinetic tests and the corresponding values of l, calculated from Eq. 5 as a function of E, a regression analysis was performed using Eq. 4. This yielded the least squares optimum values for E, k_o and d as 73,600 ± 300 kJ/mol, 0.147 ± 0.09 s^{-1}, and 2.2 ± 0.6, respectively. The variation intervals indicated correspond to the standard errors determined for the different parameters. Thus, Eq. 1 can be written as:

$$-da_o/dt = 0.147\exp(-73{,}600/RT)a_o^{\,2.2} \tag{6}$$

The value of d found in this work is close to 2, which is a often quoted value for sintering in air (for example, Maat and Moscou, 1965; Zahradnik et al., 1975; McCarthy et al., 1975; Carberry, 1985). However, considerably higher values of d can also be found in other empirical power-law kinetics reported in the literature of sintering in air. As for the value of E given in Eq. 6, it can easily be accommodated within the wide range of activation energies reported in sintering studies (Hughes, 1984; Butt and Petersen, 1988).

The data used for the derivation of Eq. 6 were obtained in a fixed-bed reactor under cyclic operation. This means that the catalyst bed was subjected to reducing (during the dehydrogenation of 1-butene) and oxydizing (regeneration) atmospheres. There is wide experimental evidence of the complex sintering behavior of many catalysts under these conditions (for example, Sushumna and Ruckenstein, 1987; Wong and McCabe, 1989; Fenoglio et al., 1990). Also, the gas composition in the reactor may also change differently with time for different reactor positions during a given coking or regeneration run. In spite of these facts, the fit of the experimental data by Eq. 6 can be considered satisfactory, as shown in Figure 7. This indicates that the thermal history of the catalyst accounts in this case for most of the loss of activity by sintering observed.

It is interesting to assess the extent of nonuniform sintering that can be expected after a given number of reaction-regeneration cycles. To this end, the sintering kinetics given by Eq. 6 were used to predict the variation of catalytic activity at different positions in a fixed-bed reactor, as a function of the number of reaction-regeneration cycles. It also was necessary to assume a time-temperature history on which the sintering

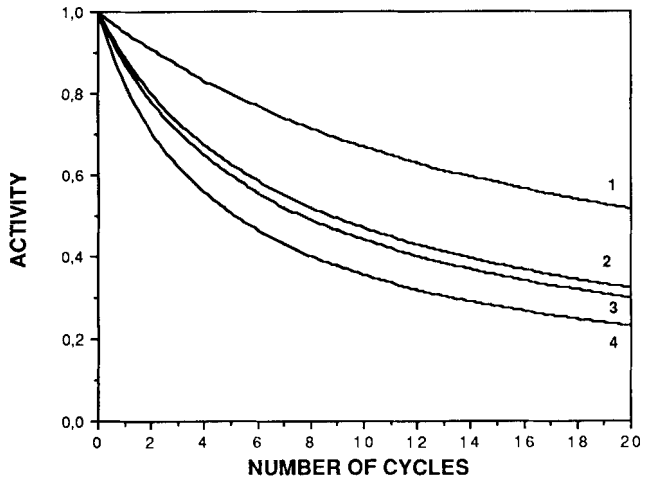

Figure 8. Activity loss as a function of the number of coking-regeneration cycles under a fixed temperature history.

It corresponds to the second coking-regeneration cycle of figures 3A (curve 1), 3C (curve 2), 4A (curve 3) and 4C (curve 4).

kinetics could be applied. The second operation-regeneration cycles in Figures 3A and 3C and in Figures 4A and 4C have been chosen as representative of many experiments carried out. This corresponds to approximately the last 1,000 minutes and 700 minutes represented in each of these figures, respectively. If we assume that each of the thermal histories corresponding to the reaction-regeneration cycles selected in Figures 3A, 3C, 4A and 4C repeats itself exactly every time that a cycle takes place, then the catalyst decay due to sintering after a given number of cycles can be calculated according to Eq. 6. The results of the calculation up to 20 reaction-regeneration cycles are shown in Figure 8. It seems clear that the differences in catalytic activity for different zones of the same catalytic reactor can be substantial. Thus, curves 1 and 2 in Figure 8 show that the remaining activity at the reactor inlet calculated after 20 reaction-regeneration cycles under the conditions of Figure 3 is about 60% higher than at the reactor exit. The difference is reduced to about 30% for the conditions of Figure 4 (curves 3 and 4), which is still considerable.

Conclusions

The experimental study of the loss of catalytic activity by thermal degradation of a commercial dehydrogenation catalyst shows that the evolution of catalytic activity can be very different for catalyst particles located in different zones of a fixed-bed reactor operating in reaction-regeneration cycles. This is due to the differences in the time-temperature history of each of the zones concerned. There are many likely causes for the diverse temperature evolution of the different reactor zones, including a nonuniform coke laydown (which may alter considerably the temperature pattern during regeneration) and the propagation of the hot reaction fronts generated during regeneration, as well as other generally less important causes, such as local inhomogeneities in the bed heat-transfer characteristics and catalyst packing.

The good fit of the data to Eq. 6 seems to indicate that under the conditions employed, the time-temperature history of the catalyst is the only relevant sintering parameter. Other factors, such as the local reaction atmosphere at a given position in the reactor (which were not taken into account in the correlation), either do not have a strong influence on the sintering process in the system studied or experienced similar evolutions for different reactor positions during the course of the experiments.

The sintering kinetics obtained have been used for the prediction of the loss of catalytic activity with successive reaction-regeneration cycles under a fixed set of conditions. The results of the calculation show that considerable differences may arise in the remaining catalytic activity of different zones of the same reactor after a relatively short number of cycles. This implies that when the conversion at the exit of a fixed-bed reactor has fallen below the acceptable limit as a result of irreversible deactivation by sintering, some portions of the reactor may still have considerable activity and can therefore be retained for further use.

Acknowledgment

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Notation

a = catalytic activity, defined by Eq. 1
a_o = activity of fresh or of regenerated catalyst in the absence of coke
d = order of deactivation by sintering, Eq. 1
E = apparent activation energy for catalyst sintering, kJ/kmol
k = kinetic constant for the loss of activity by sintering, Eq. 1, s^{-1}
k_o = frequency factor, Eq. 2, s^{-1}
r_{fo} = initial reaction rate of fresh catalyst, kmol/kg of catalyst·s
r_t = reaction rate at time equal to t, during a kinetic test, kmol/kg of catalyst·s
t = time (s)
T = absolute temperature, K

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