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Experimental Investigation of Temperature Fields and Multiple Steady States in Deactivated Fixed-Bed Reactors

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An experimental study of CO oxidation on a commercial deactivated Pt/Al_2O_3 catalyst is presented. The axial temperature profiles, exit conversion, and parametric sensitivity of a tubular catalytic fixed-bed reactor were investigated for different inlet concentrations of the reacting gas and degree of deactivation. Tetraethyl lead was used as a poison which guarantees an irreversible deactivation. During injection of the poison the temperature of the hot spot increases as a result of a rapid deactivation process. A partially deactivated bed exhibits unexpected trends. For lower values of the inlet temperature an increase of the hot-spot temperature results. For a low degree of deactivation the ignition temperature moves with increasing deactivation to a lower value. The same trend was also observed for the extinction temperature. For higher poisoning rates both the ignition and the extinction temperatures are shifted to higher values of temperature and the domain of multiple steady states becomes narrow. It was shown that for a strong deactivation the reverse flow in the reactor may improve the exit conversion.

INTRODUCTION

Although much fundamental experimental work on deactivation has been done (for a review see (*1*)) very little is known on the behavior of temperature fields and the occurrence of multiple steady states associated with hysteresis loops in a poisoned catalyst bed. The purpose of this work is to obtain information on the behavior of tubular reactors with a strong exothermic reaction over a wide range of irreversible deactivation and to provide some insight into the mechanism of interaction of heat and mass transfer, exothermic chemical reaction, and irreversible deactivation processes. This study was also undertaken to obtain experimental data on the deactivation of the commercial Pt/Al_2O_3 catalyst by $(C_2H_5)_4Pb$ which may assist in the design of afterburner units. This study is apparently the first report on the behavior of multiple steady states in deactivated fixed-bed tubular reactors.

EXPERIMENTAL

Oxidation of CO in a deactivated bed was investigated in a tubular reactor provided with an evacuated jacket covered by a silver coating. The reactor was placed vertically and the feed of reacting gas was sent to the bottom or to the top of the reactor, i.e., an upflow or a downflow resulted. $(C_2H_5)_4Pb$ was used as a catalyst poison. This poison was fed to the reactor by bubbling the mixture of $CO + O_2$ through liquid $(C_2H_5)_4Pb$ at 40°C. The deactivation process was performed at an inlet temperature of 200°C and an inlet concentration of 3% CO. The reactor was placed in a bath which was kept at the temperature of the inlet gas. The reactor temperature was measured by an iron–constantan thermocouple placed in an axial thermowell. Iron–constantan thermocouples placed at different radial positions indicated that the radial temperature profile is not important. The composition of the exit gas was analyzed by a thermal conductivity cell. The characteristics of the reactor and catalyst used are presented in Tables 1 and 2.

The general procedure for experimental

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TABLE 1

Characteristics of Reactor and Catalyst

Reactor length	0.4 m
Catalyst bed length	0.14 m
Reactor internal diameter	0.023 m
Reactor external diameter	0.042 m
Thermowell internal diameter	0.0015 m
Thermowell external diameter	0.0048 m
Catalyst	commercial Pt/Al_2O_3 spherical particles
Catalyst particle diameter	0.0034 m

runs consisted of two steps: partial deactivation and measurements of hysteresis loops (or thermal sensitivity). The first step involved an injection of 1.65 g (1 cm^3 at 20°C) of catalyst poison in the inlet gas. During the deactivation process the axial temperature profiles were recorded (Figs. 1, 2). The deactivation of the bed was performed at 200°C and 3% CO. A high inlet temperature is necessary in order to prevent condensation of $(C_2H_5)_4Pb$ in the reactor. The deactivation was accomplished only for the upflow conditions (also referred to as the normal flow conditions). The second step consisted of measurements of the dependence of the exit conversion on the inlet temperature in a partially deactivated bed. The inlet temperature was systematically increased and then decreased in order to evaluate the whole hysteresis loop. After the disappearance of the hysteresis loop the temperature profiles were measured also for the downflow conditions (also referred to as the reverse flow) and 5% CO. After performing all these observations a new partial deactivation was carried out.

TABLE 2

Characteristic Operating Conditions and Ranges for the Variables

Volumetric flow rate (standard conditions: 293°C, 1.013×10^5 N/m^2)	3×10^{-5} m^3/s
Linear flow rate (interstitial, standard conditions)	1.66×10^{-1} m/s
Inlet CO concentration (mol%)	1, 3, 5
Inlet $Pb(C_2H_5)_4$ concentration (mol%) during deactivation period	0.04

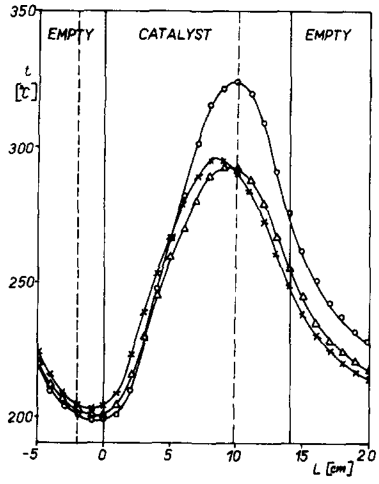

FIG. 1. Axial temperature profiles (3% CO). (x) Bed deactivated by 7 ml of $(C_2H_5)_4Pb$; (△) bed deactivated by 8 ml of $(C_2H_5)_4Pb$; (O) maximum temperature during deactivation.

RESULTS

Axial Temperature Profiles during Deactivation

In our quasi-adiabatic arrangement a hot

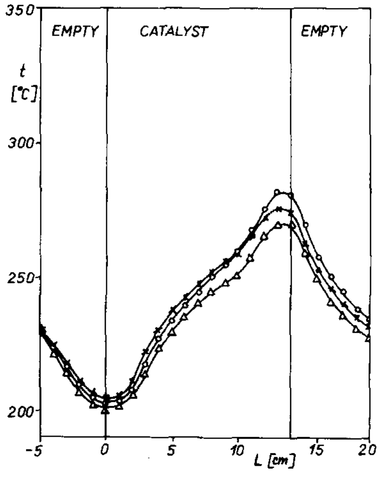

FIG. 2. Axial temperature profiles (3% CO). (x) Bed deactivated by 16 ml of $(C_2H_5)_4Pb$; (△) bed deactivated by 17 ml of $(C_2H_5)_4Pb$; (O) maximum temperature during deactivation.

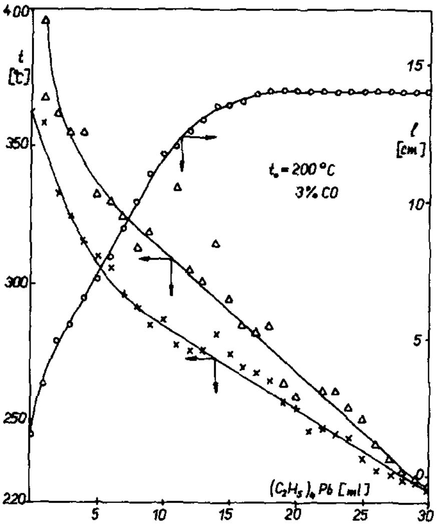

FIG. 3. Steady-state hot-spot temperature as a function of catalyst poison injected (x). Maximum transient hot-spot temperature during deactivation (Δ). Coordinate of the steady-state hot-spot temperature (O).

spot in the temperature profile may be expected. During deactivation of the bed by $(C_2H_5)_4Pb$ the hot-spot temperature increases as a result of the transient behavior of the deactivation process (*2*, *3*) and also oxidation of the catalyst poison. These hot spots will be further referred to as the transient hot spots. Figure 3 shows the steady-state temperature profiles as well as the maximum transient temperature profile in the bed. The steady-state profiles were measured for two successive deactivations of the bed. These figures reveal that the maximum transient hot-spot temperature for a low degree of deactivation is essentially higher than for the case of a strong deactivation. Based on this observation we may conclude that the oxidation of $(C_2H_5)_4Pb$ is also catalyzed and that the rate of this reaction depends on the catalyst activity.

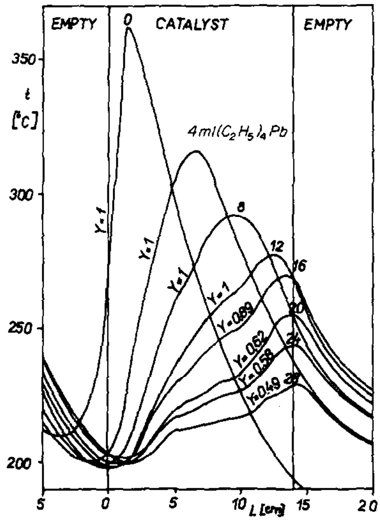

FIG. 4. Axial temperature profiles and exit conversions as a function of $(C_2H_5)_4Pb$ injected (T_0 = 200°C, 3% CO).

Investigation of Temperature Profiles in a Deactivated Bed

A plot of temperature profiles for different degrees of deactivation of the bed is given in Fig. 4. Clearly, for a fresh catalyst the reaction occurs at the reactor inlet. The axial temperature profile exhibits a typical shape with a steep temperature gradient. For successive deactivations of the catalyst the temperature profiles move toward the reactor exit and the value of the hot-spot temperature decreases. The shape of the profiles reveals that for a higher degree of deactivation a number of inflection points exist. This strange behavior of the tempera-

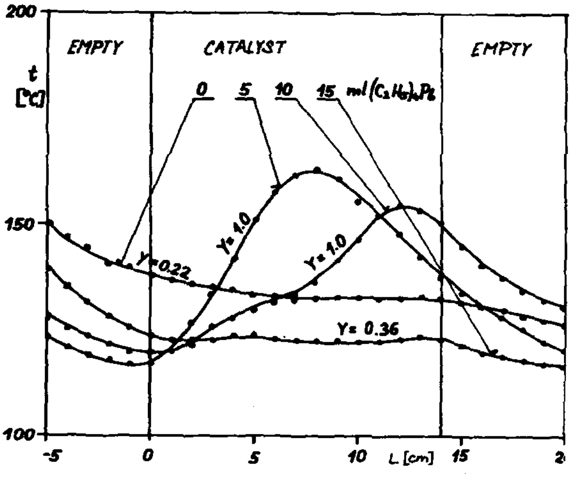

FIG. 5. Axial temperature profiles and exit conversions as a function of $(C_2H_5)_4Pb$ injected (T_0 = 120°C for 5, 10, and 15 ml $(C_2H_5)_4Pb$; T_0 = 138°C for a fresh catalyst, 1% CO).

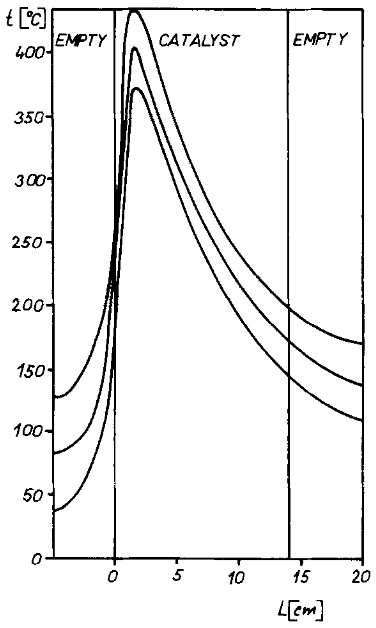

FIG. 6. Axial temperature profiles in a fresh catalyst bed (5% CO).

ture profiles is a result of the profile of the catalyst activity and was theoretically calculated by Blaum (*2*). Similar behavior for tubular reactors with radial heat transfer was predicted by Adler and Hartwig (*4*). As can be expected, the exit conversion decreases for higher values of deactivation of the bed.

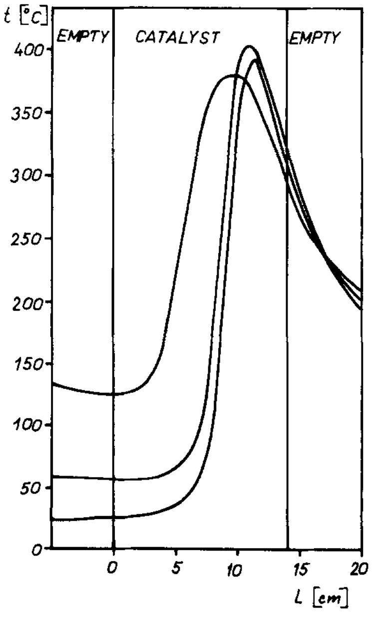

FIG. 7. Axial temperature profiles in a deactivated bed (7 ml $(C_2H_5)_4Pb$, 5% CO).

An opposite effect was observed for an inlet concentration of 1% CO (see Fig. 5). Here the fresh catalyst yields a lower exit conversion (denoted by Y in Fig. 5) than a partially poisoned catalyst. However, after reaching a certain degree of deactivation the process behaves similarly to the 3% CO case. Apparently this strange behavior is caused by strong adsorption effects at low CO concentrations. Similar effects were observed by Cardoso and Luss (*5*) for CO oxidation on wires. A possible explanation of this effect is the fact that in an early stage of deactivation the deposited Pb decreases the adsorption process and exhibits a weak effect on the rate of surface reaction.

Temperature profiles in a fresh catalyst bed are shown in Fig. 6. This figure reveals that a decrease of inlet temperature results in a decrease in the hot-spot temperature. The axial coordinate of the hot spot does not change.

A partially deactivated bed exhibits unexpected trends. For lower values of the inlet temperature an increase of the hot-spot temperature results. For example, a 70°C decrease of the inlet temperature gives rise to a 20°C increase of the hot-spot temperature. However, this strange behavior may

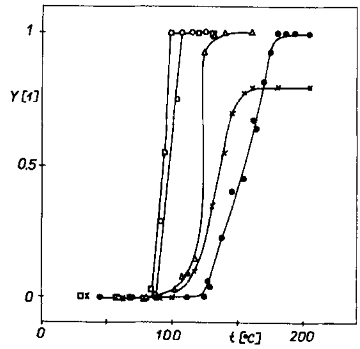

FIG. 8. Dependence of exit conversion on inlet temperature (1% CO). (●) Fresh catalyst; (△) 1 ml $(C_2H_5)_4Pb$; (○) 3 ml $(C_2H_5)_4Pb$; (□) 5 ml $(C_2H_5)_4Pb$; (x) 15 ml $(C_2H_5)_4Pb$.

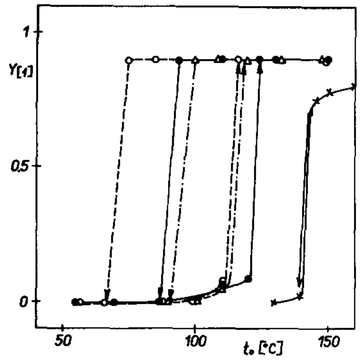

FIG. 9. Dependence of exit conversion on inlet temperature (3% CO). (——) (●) Fresh catalyst; (----) (○) 5 ml $(C_2H_5)_4Pb$; (-·-) (△) 10 ml $(C_2H_5)_4Pb$; (——) (x) 15 ml $(C_2H_5)_4Pb$.

be easily explained by the existence of an activity profile in the bed. For a high inlet temperature the inlet poisoned zone is still capable of oxidizing CO, the reaction zone is long, and the heat liberated is transferred to the surroundings. On the other hand, for a low inlet temperature the deactivated catalyst cannot ignite the reaction and represents an inert layer. The reaction occurs on the fresh catalyst, the reaction zone is thus very narrow, and an almost adiabatic temperature rise results. This situation is depicted in Fig. 7.

Effect of Poisoning on the Thermal Sensitivity and Multiplicity

Figure 8 shows the effect of poisoning the bed on the exit conversion (1% CO). For this concentration of CO multiple steady states do not exist. For a fresh catalyst the exit conversion is very low up to $T_0 \approx$ 125°C. With higher conversion the exit temperature increases smoothly. After the first deactivation (1 cm^3 $(C_2H_5)_4Pb$) the shape of this dependence is steeper and the ignition temperature moves to lower values (~100°C). The second deactivation gives rise to a further decrease of the ignition temperature. If the bed is deactivated by 3 ml of $(C_2H_5)_4Pb$, the third deactivation, the ignition temperature is about 85°C. For higher degrees of poisoning the ignition temperature moves to higher values. A similar trend was observed also for 5% CO. (This observation is in agreement with a recent experimental study for a single catalyst pellet (*7*).

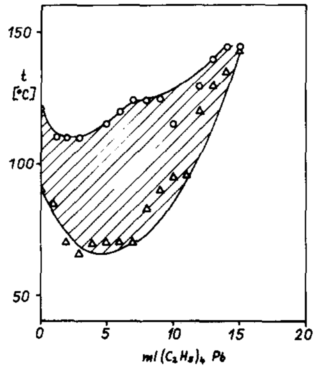

FIG. 10. Region of multiple steady states as a function of poison injected (3% CO). (○) Ignition temperature; (△) extinction temperature.

The effect of deactivation on the domain of multiple steady states is shown in Figs. 9 and 10. For a low degree of deactivation the ignition temperature moves with increasing deactivation to lower values (see Fig. 9). The same trend was also observed for the extinction temperature. For higher poisoning rates both the ignition and the extinction temperatures are shifted to higher values of temperature and the domain of multiple steady states becomes narrow.

Effect of the Flow Direction in the Deactivated Bed on the Occurrence of Multiple Steady States

One can expect that for a deactivation process the direction of flow may exhibit an effect on the behavior of the reactor. For a strong deactivation of the bed the poisoned catalyst is not capable of carrying out the reaction and a small portion of the fresh catalyst at the reactor outlet can no longer accomplish the reactor task. However, after reversing the flow the fresh gas comes into contact with the fresh (or weakly deactivated) bed and the reaction is ignited. The hot partially reacted gas approaches the strongly deactivated part of the bed; however, the high temperature of the gas gives

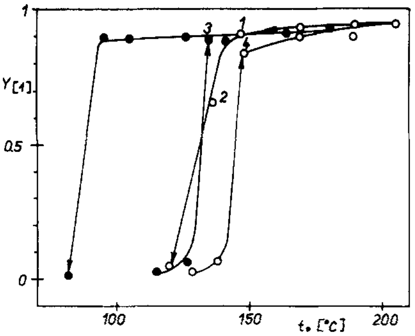

FIG. 11. Effect of the reversed flow on the hysteresis loop (16 ml $(C_2H_5)_4Pb$, 5% CO). (○) Upflow (normal configuration); (●) downflow (reversed configuration).

rise to a reaction also in this section. The effect of the flow direction upon the hysteresis loop in the absence of deactivation was experimentally investigated in Ref. (*6*). It was shown that the flow direction may have a profound effect on the temperature profiles.

Figures 11 and 12 display the effect of reverse flow for a strongly deactivated bed. For 16 ml of $(C_2H_5)_4Pb$ the normal flow configuration results in a narrow hysteresis loop while for a reversed flow a wide hysteresis loop occurs. For 18 ml of poison the hysteresis loop disappears for normal flow conditions; however, multiple steady states still exist for a reverse flow. We may note the strange shape of the hysteresis loop for the upflow conditions. For a high inlet temperature two steady states exist; however, both exhibit a high exit conversion (two upper steady states). The temperature profiles corresponding to the points 1 and 4 in Fig. 11 are drawn in Fig. 13. For profile 4, which was adjusted after successively increasing the inlet temperature, the reaction occurs mainly at the reactor outlet, while for profile 1 the reaction is more or less distributed within the whole bed.

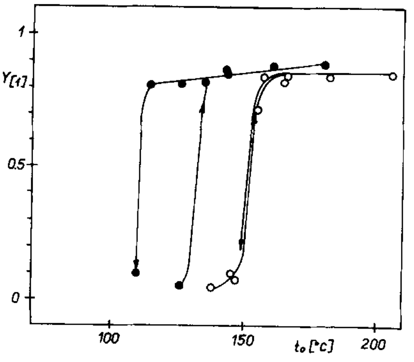

FIG. 12. Effect of the reversed flow on the hysteresis loop (18 ml $(C_2H_5)_4Pb$, 5% CO). (○) Upflow (normal configuration); (●) downflow (reversed configuration).

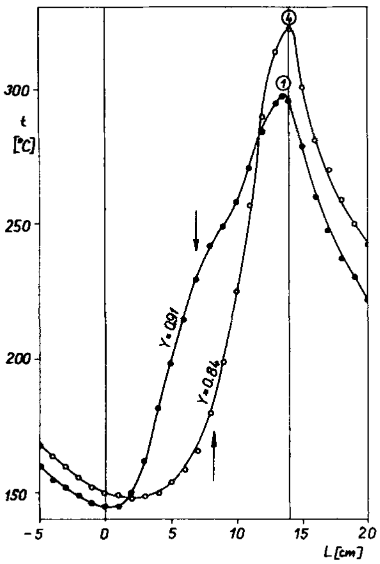

FIG. 13. Two upper steady states (see Fig. 11); temperature profiles.

The temperature profiles corresponding to both flow directions are drawn in Fig. 14. Here profiles 1, 2, and 3 are associated with points 1, 2, and 3, respectively, from Fig. 11. On comparing the profiles for points 1 and 2 we can see that an increase of 10°C in the inlet temperature may completely change the shape of the profiles. While for the lower temperature the reaction is restricted to the reactor outlet, the higher inlet temperature gives rise to a reaction also in the inlet zone. The effect of the reversed flow is obvious after comparing profiles 2 and 3. Evidently, for the reversed feed a fresh portion of the catalyst results in a high hot-spot temperature, the reaction is completed at the reactor inlet, and the

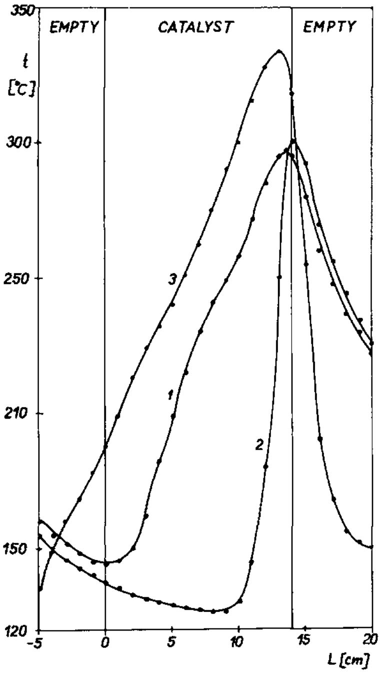

FIG. 14. Axial temperature profiles corresponding to points in Fig. 11 (5% CO). (○) Upflow (normal configuration); (●) downflow (reversed configuration).

majority of the bed serves only for heat exchange.

CONCLUSIONS

It has been the aim of this work to show experimentally the problems connected with simultaneous irreversible deactivation, transport phenomena, and exothermic chemical reaction. A number of unexpected trends (increasing regions of multiple steady states with increasing deactivation, two upper steady states, dependence of the hot-spot temperature on inlet temperature, and occurrence of multiple inflection points at the temperature profile) have been observed. Based on the material presented here it is clear that irreversible deactivation results in a completely different picture from reversible deactivation (*3*). It is hoped that the experimental observations may be of assistance in the design of afterburner units.

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