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Oscillatory Behavior of Long and Short Isothermal Beds Packed with Pt/Al_2O_3 Catalyst

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In an isothermal catalytic system (Pt/Al_2O_3) a complex dynamic behavior was observed. Experiments were performed on CO oxidation for a long and a short catalyst bed. Multiplicity of steady states and periodic activity was observed. For a long bed the oscillations are periodic; the periodic character is lost only at the extinction boundary. For a short bed a complex interaction of individual particles may be expected. The hysteresis curve is qualitatively identical for a short as well as for a long bed. The onset of oscillations occurs at a lower temperature than the extinction of oscillations. The chaotic behavior was observed for a certain concentration of CO in a narrow range of temperatures. The experiments reveal that the chaotic behavior is caused by an interaction of two oscillatory processes.

INTRODUCTION

Recent experimental observations reveal that under certain conditions oxidation of CO by O_2 may result in periodic activity behavior (*1–13*). The occurrence of oscillations in an isothermal system indicates that the periodic activity behavior is caused by the kinetic rate processes.

This work reports on a systematic investigation of oscillatory states observed in an isothermal laboratory recycle reactor packed with a Pt/Al_2O_3 catalyst. A long and a short bed were investigated. This information should be useful in elucidating the laws governing the periodic activity behavior of the catalytic CO oxidation in isothermal beds.

EXPERIMENTAL

The catalytic CO oxidation by pure oxygen was selected as a model reaction. The catalyst used was Pt/Al_2O_3 in the form of 3.4-mm spherical pellets. The CO used in this experiment was obtained by thermal decomposition of formic acid in hot sulphuric acid. The gas was purified by chromium sulphuric acid, NaOH and active char and dried before use. For measurements a laboratory recycle reactor was used. The recirculation ratio was $\approx 1:100$, i.e., the reactor behaves as isothermal equipment. In this reactor the temperature of the bed as well as of the gas in the fore and aft sections were measured. The maximum axial temperature difference in the bed for the highest concentration was $\approx 3°C$. For a continuous analysis of CO concentration a precalibrated fast response thermal conductivity cell has been used. Two different amounts of catalyst, 1.6 and 10 g, were used for measurements. The details of the experimental conditions for the long bed are reported in Tables 1 and 2.

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RESULTS

Long Bed

For this arrangement oxidation of CO was investigated for three different CO concentrations: 0.5, 2, and 5% vol CO.

Observations for 0.5% CO

For the concentration of 0.5% CO the reaction behaves differently in comparison

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TABLE 1

Reactor Parameters, Long Bed

Amount of catalyst	10.01×10^{-3} kg
Diameter of the catalyst bed	1.8×10^{-2} m
Length of the bed	8×10^{-2} m

TABLE 2

Experimental Conditions, Long Bed

Inlet CO concentration	0.5, 2, 5 vol%
Reactor temperature	90–180°C
Inlet gas flow rate ($CO + O_2$)	4×10^{-6} m^3/s
Recycle	1 : 100

with the cases of 2 and 5% CO. The region of multiple steady states does not exist; however, multiplicity of a steady state and an oscillatory state was observed. Starting experiments at the steady state with low conversion by increasing the inlet temperature the oscillations appear at $T = 102$°C and disappear at $T \approx 130$°C (see Fig. 1).[2] At the onset of periodic activity, i.e., in the region 102–110°C, the oscillations are periodic but not symmetrical. For higher temperatures oscillations become more symmetrical. With increasing temperature the period of oscillations decreases. For high inlet temperatures oscillatory behavior disappears (see Fig. 1).

Starting experiments at high inlet temperature and decreasing this temperature we may observe that multiplicity of oscillatory states can be observed (cf. Fig. 1 and Figs. 2 and 3).

A strange behavior of oscillations was observed for temperatures 117–125°C. After adjusting the particular temperature by approaching it from the steady state with high conversion, a quasi-steady state resulted which produced oscillations after several hours (see Fig. 3). With decreasing temperature the length of this quasi-steady-state regime increases, 125°C ~ 70 min, 120°C ~ 150 min, 117°C ~ 200 min. A similar behavior of CO oxidation was observed by Barelko and Zhukov (*8*) by studying the characteristics of the hysteresis loop. They claimed that this fact may be explained by the existence of an induction period. Periods of oscillations are reported in Table 3.

[2] In all figures representing hysteresis behavior the development of the situation resulting after increasing and decreasing the inlet temperature is drawn by empty and solid marks, respectively. Thus here ○ and ● are stable states resulting after increasing and decreasing the inlet temperature, respectively; △ and ▲ are oscillatory states adjusted from low and high temperatures, respectively. The distance between arrows represents the amplitude of oscillations.

Observations for 2% CO

The hysteresis loop "Y vs T" is drawn in Fig. 4. The oscillations resulting after increasing the inlet temperature are not symmetrical but periodic. For a higher T oscillations become symmetrical. For $T = 155$°C a second oscillatory process may be observed which perturbs the state with high activity. This behavior is shown in Fig. 5.

Observations for 5% CO

In Fig. 6 the region of multiple stable states and oscillatory periodic and aperiodic states are drawn. These states were obtained by increasing as well as by decreasing the inlet temperature.

TABLE 3

Dependence of the Period of Oscillations on the Temperature. $C_0 = 0.5$% CO, 10 g of Catalyst

T (°C)	Period (min) Initial state	
	Lower state	Upper state
102	86–87.5	stab.
110	52	stab.
112	42–53	stab.
115	50–84	stab.
120	31–37	45–85
125	22–33	32–35
130	18–19	17–23

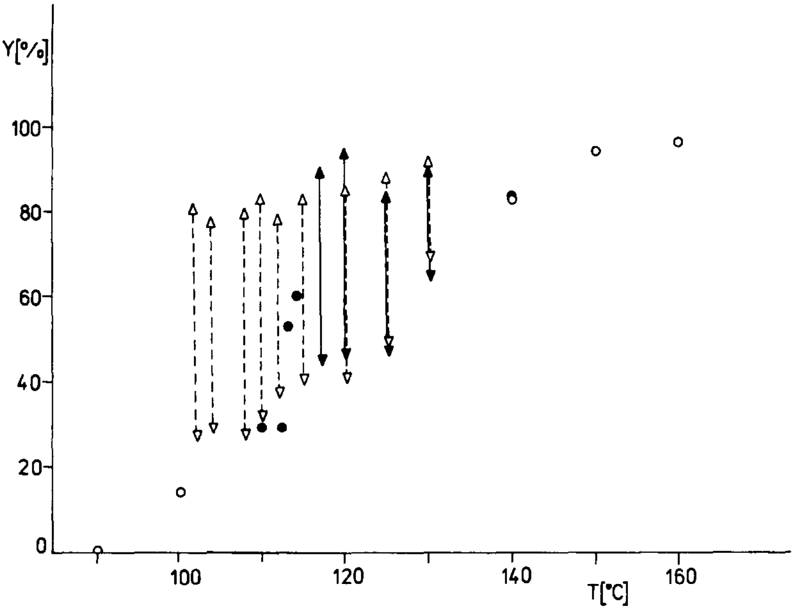


FIG. 1. Dependence of exit conversion on inlet temperature. C_0 = 0.5% CO, 10 g of catalyst.

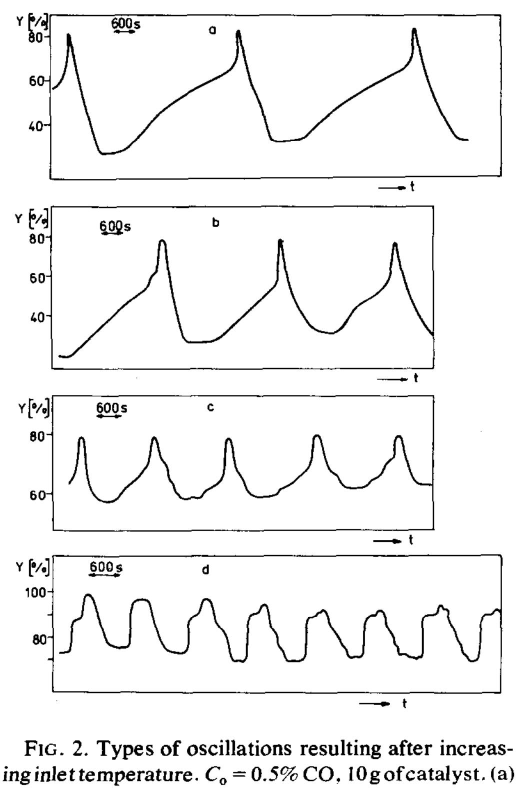


FIG. 2. Types of oscillations resulting after increasing inlet temperature. C_0 = 0.5% CO, 10 g of catalyst. (a) 102°C, (b) 110°C, (c) 112°C, (d) 130°C.

For low temperatures ($T \leq$ 100°C) only one stable steady state with very low conversion ($Y <$ 4%) exists. After crossing T = 100°C multiple steady states may exist. For T = 105–135°C two stable steady states occur. At T = 136°C a complex bifurcation occurs and periodic unsymmetrical oscillations appear (see Fig. 7a). In the region 136–139°C there exists also a stable steady state which can be approached if the initial state is the upper state, i.e., a state with high conversion. The period of periodic asymmetric oscillations observed in the region T = 136–150°C decreases after increasing the temperature. Moreover, oscillations lose their asymmetrical character and for T = 153–167°C the oscillations are periodic and symmetrical. For the inlet temperature T = 162°C a long-range experiment including 70 periods was performed. In this particular experiment no important changes of the period, amplitude, and character of oscillations were observed. For the higher inlet temperature, 168–173°C, the symmetrical oscillations become complicated. Here during the dynamic regime a

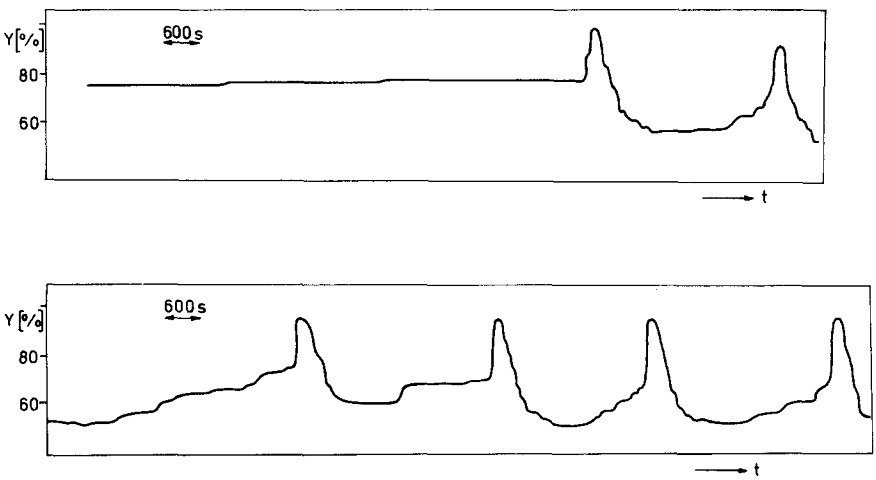


FIG. 3. Types of oscillations resulting after decreasing inlet temperature. C_0 = 0.5% CO (T = 120°C, 125°C), 10 g of catalyst.

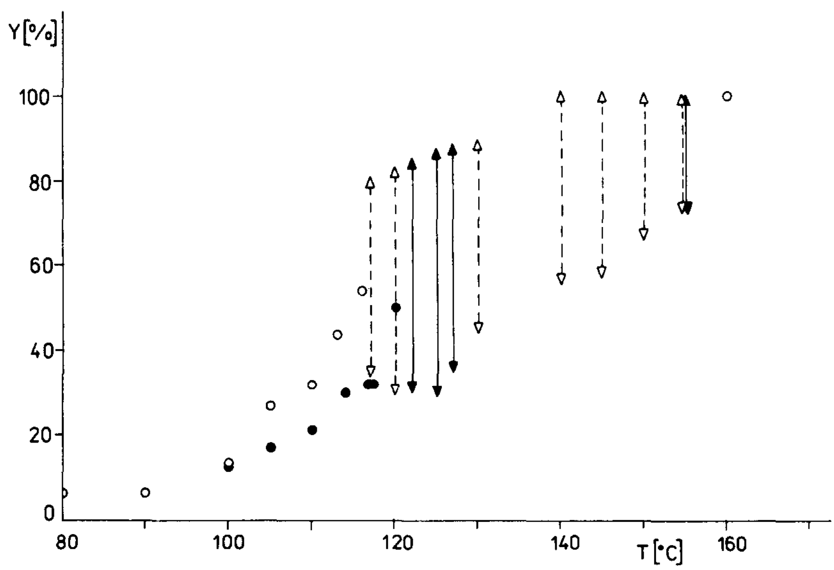


FIG. 4. Dependence of exit conversion on inlet temperature. C_0 = 2% CO, 10 g of catalyst.

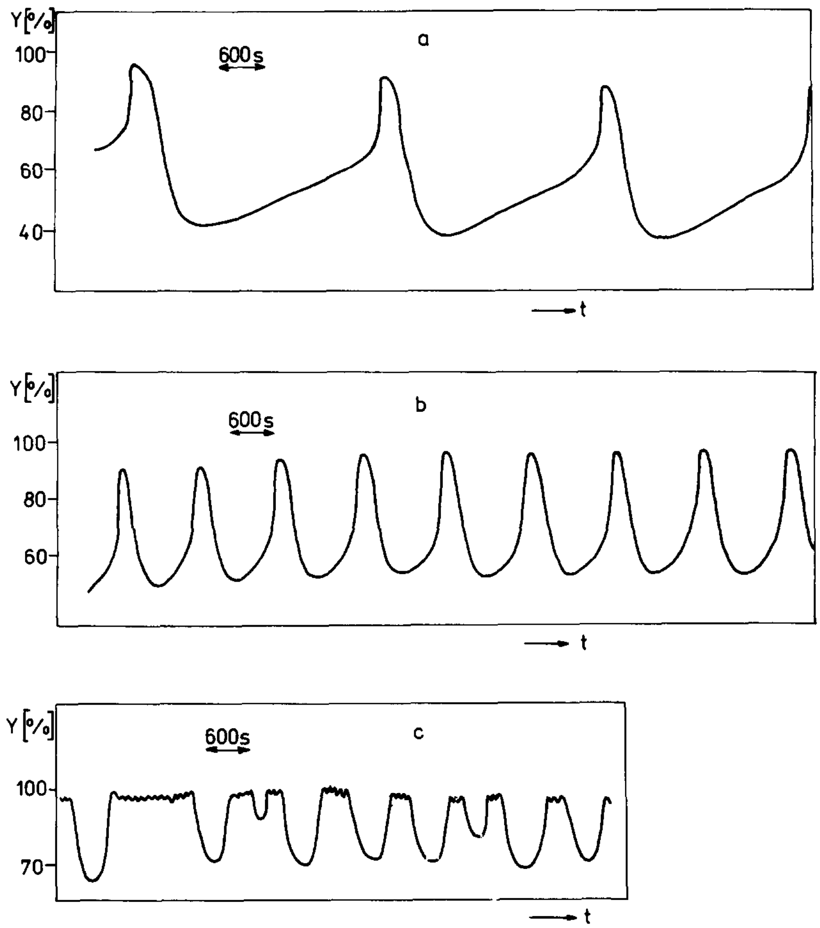


FIG. 5. Types of oscillations resulting after increasing inlet temperature. C_0 = 2% CO, 10 g of catalyst. (a) 127°C, (b) 140°C, (c) 155°C.

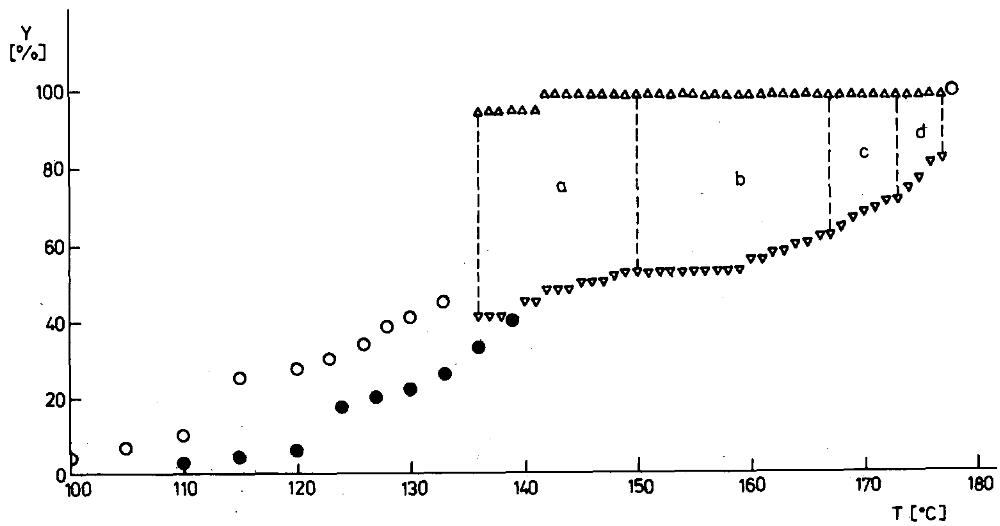


FIG. 6. Dependence of exit conversion on inlet temperature. C_0 = 5% CO, 10 g of catalyst. (a) Periodic but not symmetrical oscillations, (b) periodic symmetric oscillations, (c) periodic oscillations, a new oscillatory process occurs, (d) chaotic and chaotic-like oscillations.

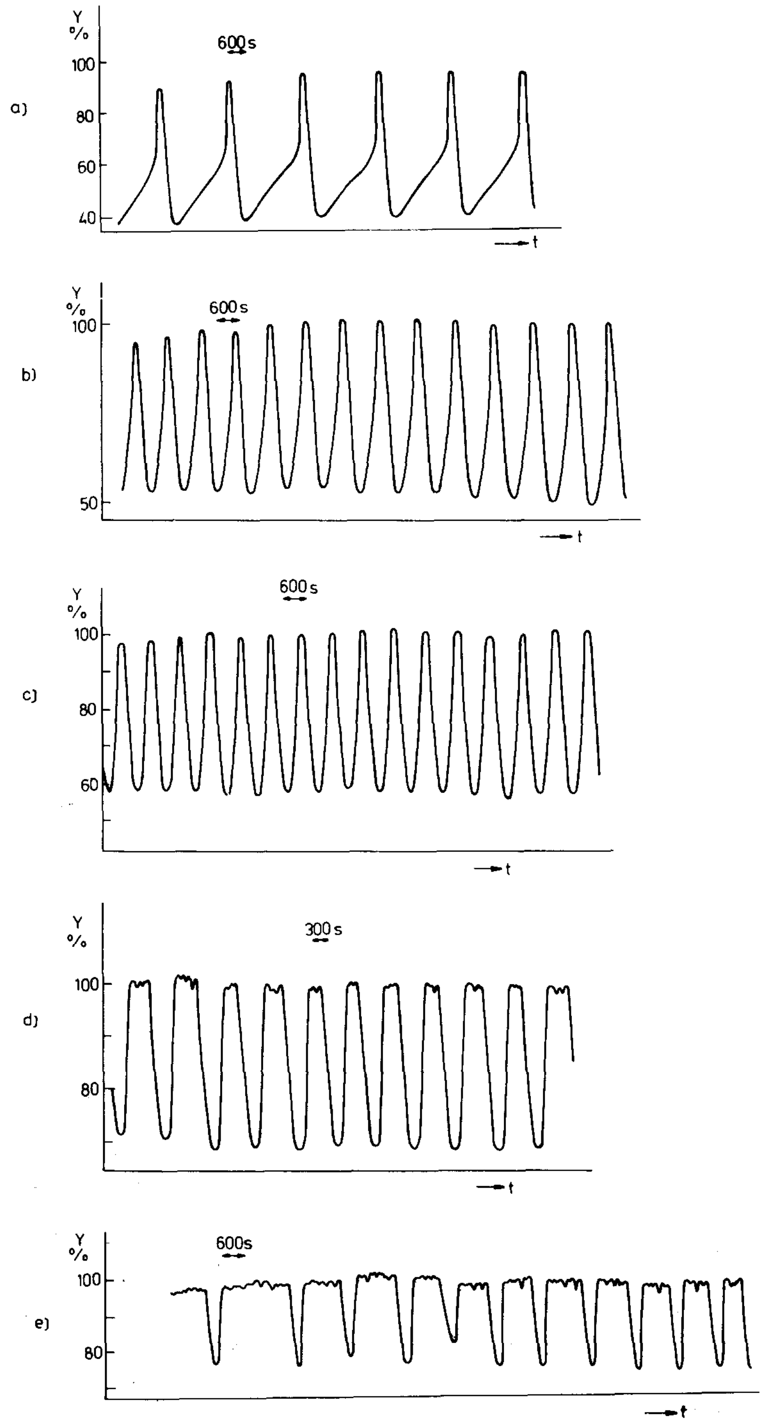


FIG. 7. Types of oscillations resulting after increasing inlet temperature. C_0 = 5% CO, 10 g of catalyst. (a) 139°C, (b) 155°C, (c) 162°C, (d) 171°C, (e) 175°C.

new oscillatory process occurs. This effect results only in a slight perturbation of the conversion near 100%. For T = 171°C the frequency of the basic oscillations is not strongly influenced. However, after increasing the inlet temperature the interaction with the second oscillatory process becomes strong and the periodic behavior of the oscillations disappears, see Figs. 6–8. For oscillations appearing after increasing the inlet temperature 42 experiments were performed. Periods of oscillations are reported in Tables 4 and 5. From these tables information on unicity and multiplicity of oscillations can be inferred.

TABLE 5

Dependence of the Period of Oscillations on the Temperature. C_o = 5% CO, 10 g of Catalyst

T (°C)	Period (min)
139.5	76–178
141.5	75–135
155	16
170	10–11
174	8–20
175	7–27
176	10–70

Note. The oscillatory states are approached from the state with high conversion.

Short Bed

For this arrangement the oxidation of CO was investigated for four different CO concentrations, viz., 2, 3, 5, and 7% CO. The amount of catalyst was 1.6 g, i.e., the length of the bed was 1.3 cm. For these experiments a catalyst sample with constant activity was taken, which had been used in the former experiments in the long bed. The inlet gas flow rate and recycle ratio were the same as those for the long bed.

TABLE 4

Dependence of the Period of Oscillations on the Temperature. C_o = 5% CO, 10 g of Catalyst

T (°C)	Period (min)
137	72.5–75
138	50 –60
139	39 –41
141	28
142	25.5
144	20 –22
146	18 –19
149	16 –18
152	16 –16.5
155	15 –16
160	13.5–14
165	11.5–12
170	10 –10.5
172	10
173	10 –11
174	14 –22
175	16 –22
176	12 –22
177	10 –29

Note. The oscillatory states are approached from the state with low conversion. For a case of two oscillatory processes the period of the basic oscillation process is presented.

Observations for 2% CO

We have measured two times (with different samples of catalyst) the hysteresis loop "exit conversion versus inlet temperature." We have observed similar behavior; for the second set of experiments the hysteresis loop was shifted ≈5°C towards higher temperatures. Oscillations exist in a region of 10°C. At the onset of periodic activity oscillations are quite symmetrical (see Fig. 10); for a higher temperature oscillations are more complex and the state with highest conversion is for a certain period "frozen," cf. Fig. 11. The oscillations described above were adjusted by increasing the inlet temperature. Periodic activity behavior observed after decreasing the inlet temperature, i.e., from a steady state with high conversion, exhibits different characteristics. For these oscillations the "fro-

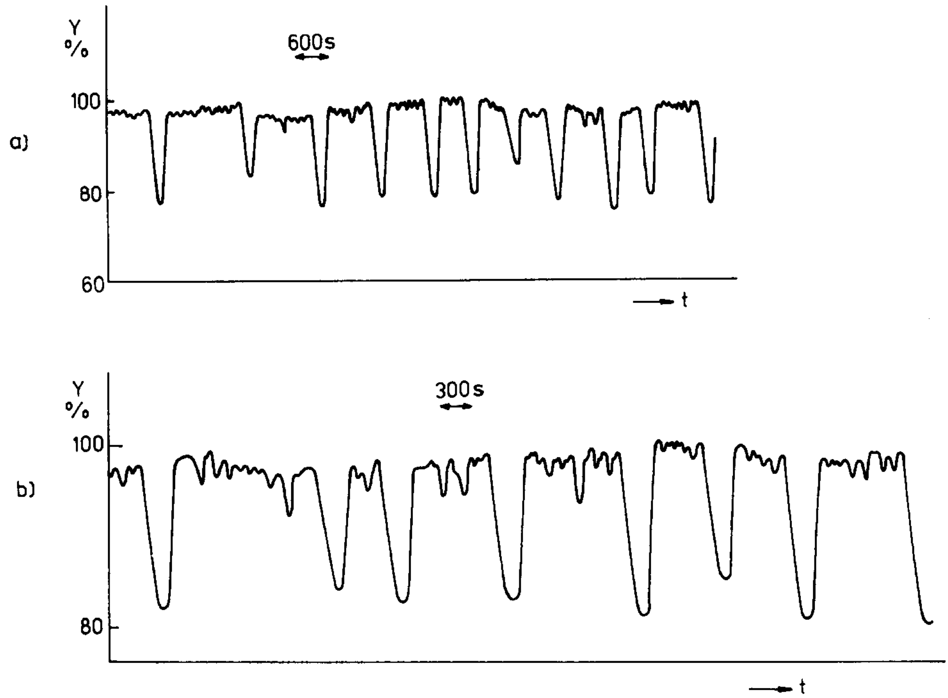
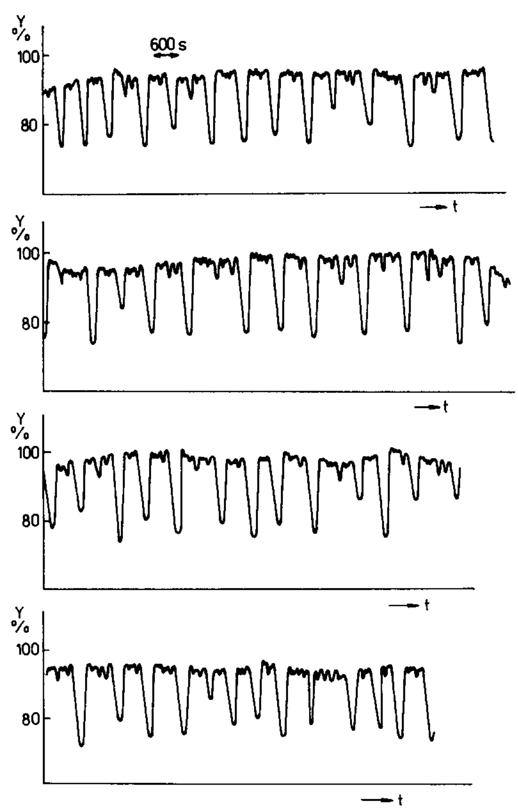


FIG. 8. Aperiodic behavior of the bed resulting after increasing inlet temperature. C_0 = 5% CO, 10 g of catalyst. (a) T = 176°C, (b) T = 177°C.



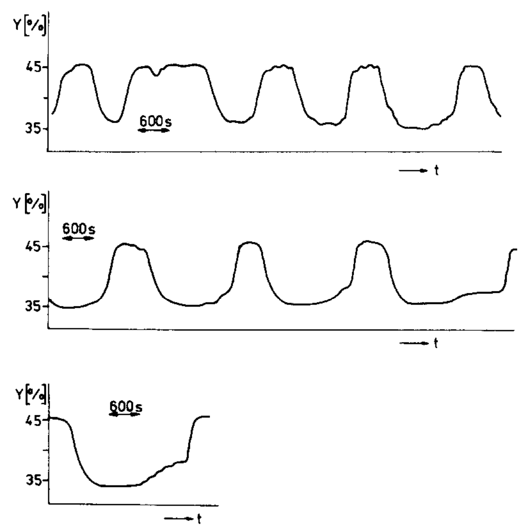


FIG. 10. Types of oscillations resulting after increasing inlet temperature. C_0 = 2% CO, T = 160°C, 1.6 g of catalyst.

FIG. 9. Aperiodic behavior of the bed resulting after decreasing inlet temperature. Long range experiment. C_0 = 5% CO, T = 175°C, 10 g of catalyst.

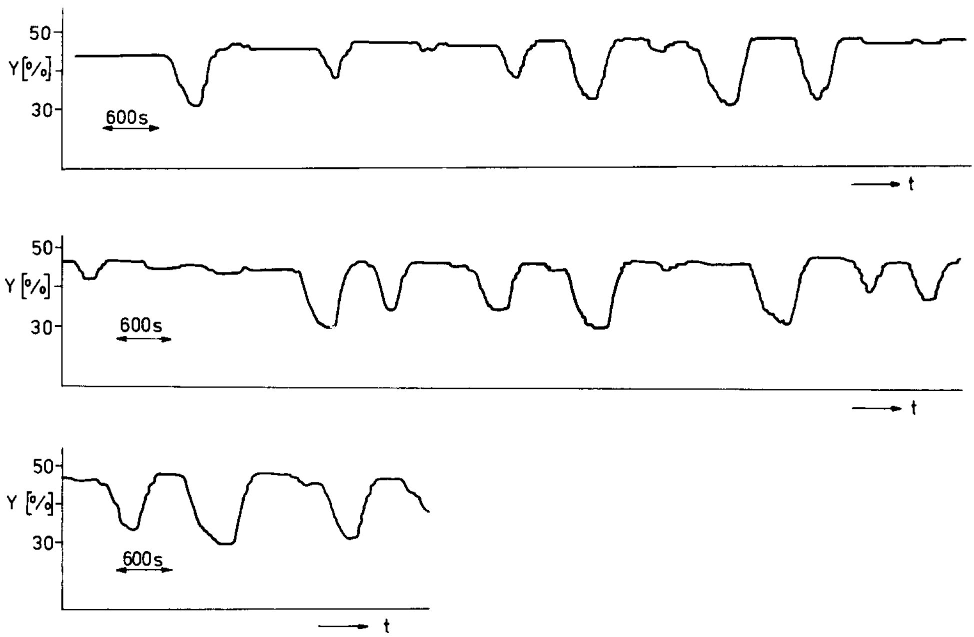


FIG. 11. Types of oscillations resulting after increasing inlet temperature. C_0 = 2% CO, T = 164°C, 1.6 g of catalyst.

zen" state was not observed; see, e.g., Fig. 12.

Observations for 3% CO

The hysteresis loop observed for 3% CO is drawn in Fig. 13. The oscillations in this interval are symmetrical and almost periodic.

Observations for 5% CO

The hysteresis loop observed for 5% CO is shown in Fig. 14. The oscillations for this concentration appearing after increasing and decreasing the inlet temperature are drawn in Figs. 15a and b, respectively. These figures reveal a different type of os-

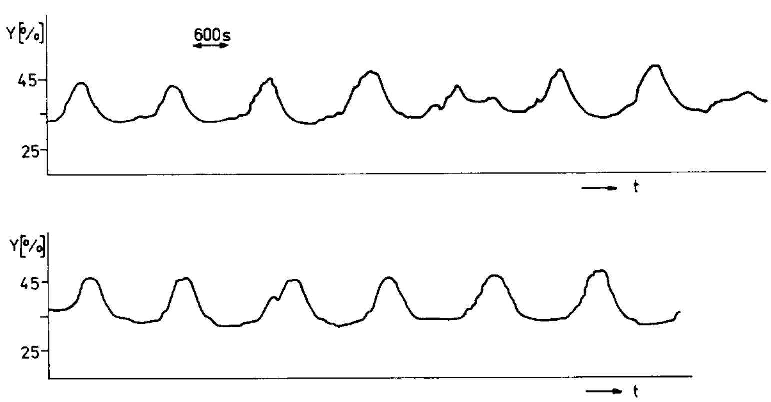


FIG. 12. Types of oscillations resulting after decreasing inlet temperature. C_0 = 2% CO, T = 163.7°C, 1.6 g of catalyst.

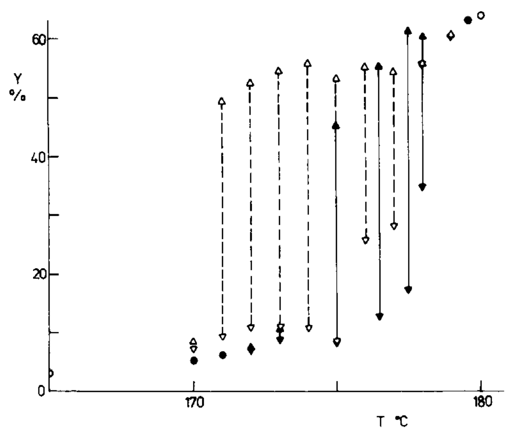


FIG. 13. Dependence of exit conversion on inlet temperature. C_0 = 3% CO, 1.6 g of catalyst.

cillatory behavior. In the former case the low-activity state exists for a long time, while after decreasing the inlet temperature the high-activity state is only temporarily perturbed.

Observations for 7% CO

The hysteresis loop measured for 7% CO is drawn in Fig. 16. Oscillations observed for this concentration are similar to those shown in Fig. 17. We may note that for this particular case two regimes of different activity, low- and high-activity regimes, exist.

DISCUSSION AND CONCLUSIONS

Based on our experiments, the following conclusions can be drawn:

(a) In an isothermal catalytic system complex multiplicity may occur. The following type of multiplicity was observed: (i) two stable steady states, (ii) one stable steady state and one oscillatory state, (iii) two oscillatory states.

(b) For a long bed oscillations of a periodic type result. After the onset of periodic activity the oscillations are not symmetrical; for higher temperature the oscillations

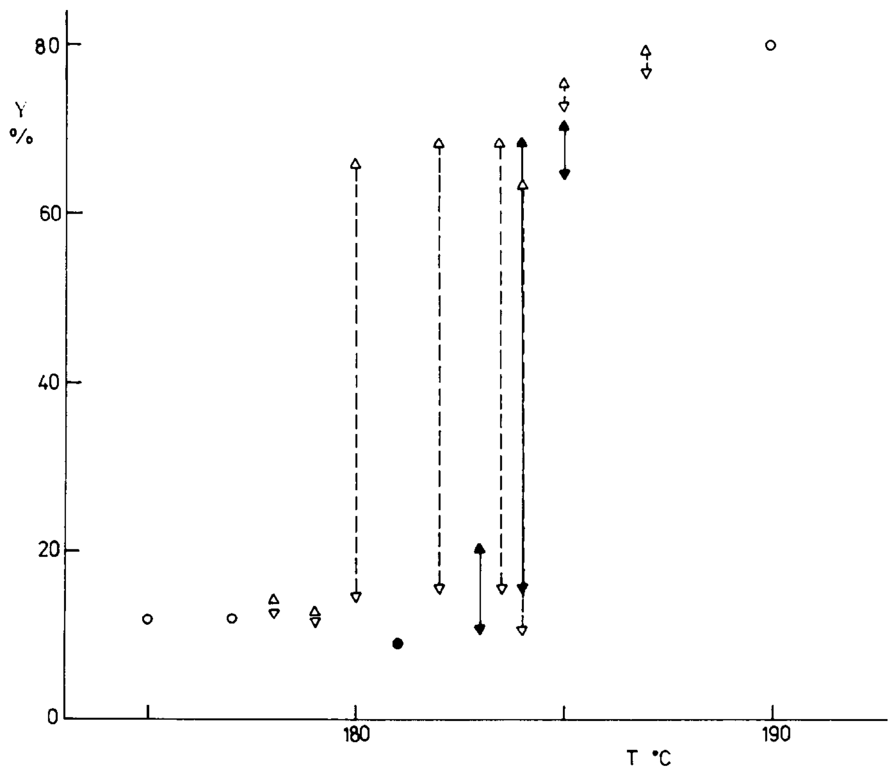


FIG. 14. Dependence of exit conversion on inlet temperature. C_0 = 5% CO, 1.6 g of catalyst.

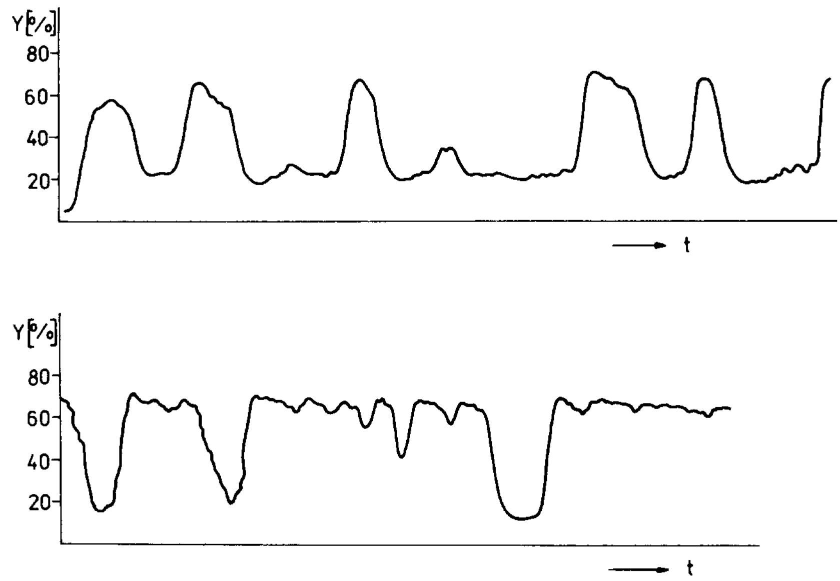


FIG. 15. Types of oscillations. C_0 = 5% CO, 1.6 g of catalyst, T = 184°C. (a) Oscillations resulting after increasing inlet temperature, (b) oscillations resulting after decreasing inlet temperature.

become symmetrical. Chaotic-like and chaotic behavior may be apparently explained by an interaction of two oscillatory processes.

(c) For a short bed, on the average, the oscillations are not regular as for a long bed. For a long bed we may expect that the oscillations of individual particles are averaged, while for a short bed a complex interaction of individual oscillators can be observed.

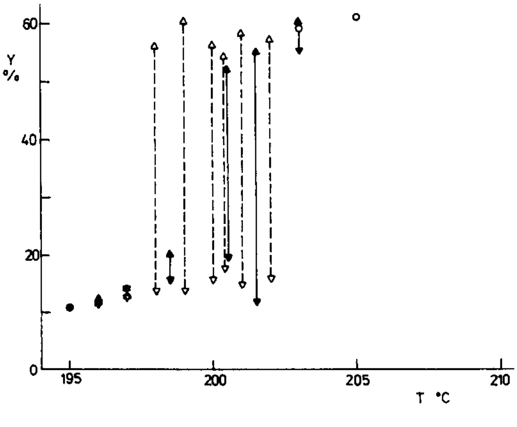


FIG. 16. Dependence of exit conversion on inlet temperature. C_0 = 7% CO, 1.6 g of catalyst.

(d) For both long and short beds the hysteresis curve has an identical character. After increasing the inlet temperature the following sequence of phenomena was observed: steady state, oscillatory behavior, steady state. The same sequence was observed after decreasing the inlet temperature. The onset of oscillations occurs always at lower temperature than an extinction of oscillations. The temperature of the onset of oscillations increases with increasing the CO concentration.

(e) Chaotic behavior is characteristic only for a certain concentration of CO. This effect occurs in a narrow range of temperatures. This effect can be well reproduced and the possibility that this phenomenon is caused by changing catalyst activity seems not to be realistic. Our experiments reveal that the chaotic behavior is apparently caused by the interaction of two oscillatory processes.

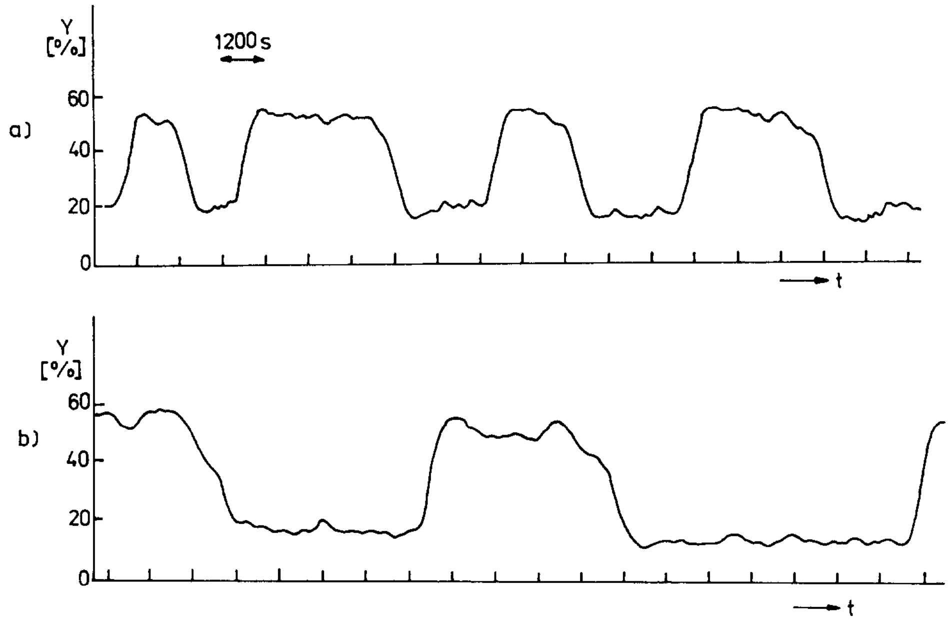


FIG. 17. Types of oscillations resulting after increasing the inlet temperature. C_0 = 7% CO, 1.6 g of catalyst.

REFERENCES

1. Wicke, E., Beusch, H., and Fieguth, P., *Advan. Chem. Ser.* **109**, 615 (1972).
2. McCarthy, E., Zahradník, J., Kuczynski, G. C., and Carberry, J. J., *J. Catal.* **39**, 29 (1975).
3. Cutlip, M. B., and Kenney, C. N., *ACS Symp. Ser.* **65**, 475 (1978).
4. Eckert, E., Hlaváček, V., and Marek, M., *Chem. Eng. Commun.* **1**, 95 (1973).
5. Hugo, P., and Jakubith, M., *Chem. Ing. Techn.* **44**, 383 (1972).
6. Plichta, R. T., and Schmitz, R. A., *Chem. Eng. Commun.* **3**, 387 (1979).
7. Dauchot, J. P., and von Cakenberghe, J., *Nature (London) Phys. Sci.* **246**, 61 (1973).
8. Barelko, V. V., and Zhukov, S. S., *Int. Chem. Eng.*, in press.
9. Varghese, P., Carberry, J. J., and Wolf, E. E., *J. Catal.* **55**, 76 (1978).
10. Keil, W., and Wicke, E., *Ber. Bunsenges. Phys. Chem.* **84**, 377 (1980).
11. Rathouský J., Jíra, E., and Hlaváček, V., *Chem. Eng. Sci.* **36**, 776 (1981).
12. Rathouský, J., Puszynski, J., and Hlaváček, V., *Z. Naturforsch. A* **35**, 1238 (1980).
13. Puszynski, J., Šnita, D., and Hlaváček, V., *Chem. Eng. Sci.* **35**, 1769 (1980).