

## NOTES

Oscillations on Individual Catalytic Pellets in a Packed Bed: CO Oxidation on Pt/Al<sub>2</sub>O<sub>3</sub>

Oxidation of carbon monoxide on Pt catalysts is one of the most often used model systems for the study of nonlinear effects in heterogeneous catalysis. Multiple steady states and various types of nonlinear dynamic regimes including periodic, quasiperiodic, and aperiodic (chaotic) oscillations were reported (1) and also used in continuing efforts for an identification of reaction rate models and corresponding parameters (2). It was recently stressed that a behavior of different parts of the same Pt wire (3) and of different pellets of the same batch of the supported catalyst (4, 5) can differ even qualitatively under the same reaction conditions, reflecting minor variations in the catalyst preparation or treatment. It was also stressed that it is dangerous to draw conclusions about dynamic behavior and kinetics from data obtained on a single wire or on one or just a few catalyst pellets.

In recent years there have also been several publications on experimental studies dealing with observations of spatio-temporal oscillations. Such behavior was reported both in situations where significant gradients between the gaseous and solid phase exist (5–8) and also under well-defined UHV conditions (9, 10). Thus Brown *et al.* (5) reported macroscopic spatial variations of temperature on the surface of platinum foils, gauzes, supported wafers, and porous spherical pellets (containing platinum) used for H<sub>2</sub> oxidation. Kaul and Wolf (6–8) followed CO coverage and surface temperature patterns during oscillations in CO oxidation on Pt/SiO<sub>2</sub> and Pd/SiO<sub>2</sub> under atmospheric pressure. The experiments demonstrated that oscillations involve spatially propagating regions of nonuniform species coverage and of surface tempera-

ture. Lindström and Tsotsis (11), on the other hand, reported experimental observations similar to those of Kaul and Wolf (8) showing that the isothermal oscillations observed for CO oxidation over Pt/Al<sub>2</sub>O<sub>3</sub> wafer catalysts at 1–10 Torr are of a temporal and not of a spatio-temporal nature. Cox *et al.* (9, 10) in studies on Pt(100) crystals observed spatio-temporal catalyst surface oscillations in the form of the hex ↔ (1 × 1) phase transition occurring as a wave propagating from one edge of the crystal to the other.

The mechanism of communication between individual parts of the catalyst in the case of a nonstationary course of the reaction was also studied. Brown *et al.* (5) investigated thermal communication between particles of supported catalyst in contact for H<sub>2</sub> oxidation and Jaeger *et al.* (12) studied the effect of thermal coupling among three layers of an amorphous alumina-supported Pd catalyst on the oscillatory course of the oxidation of ethanol. Capsaskis and Kenney (13) suggest that a synchronization among catalyst sites occurs via the gas phase in the oxidation of CO/propene mixture on Pt/Al<sub>2</sub>O<sub>3</sub> catalyst and Sant and Wolf (14) studied the effects of crystallite size and distribution on the propagation of oscillatory states on a Pt/SiO<sub>2</sub> catalyst wafer in the course of CO oxidation.

We report here on observations of synchronization, desynchronization and spatio-temporal patterns in the oscillating oxidation of CO under atmospheric pressure in a bed of catalyst pellets. The catalyst used was an industrial Pt/Al<sub>2</sub>O<sub>3</sub> (CHEROX 39-02) in the form of spherical Al<sub>2</sub>O<sub>3</sub> pellets (diameter 3.5 mm) with Pt (0.6% by weight) deposited in the surface layer (0.3 mm in

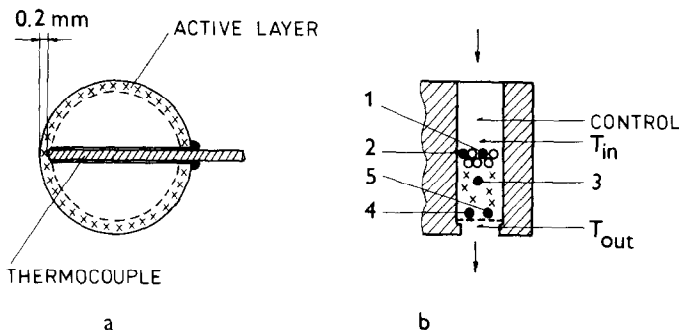


Fig. 1. (a) Position of the thermocouple in the pellet. (b) Position of pellets with embedded thermocouples in the bed.

depth), with BET area  $205 \text{ m}^2/\text{g}$ , and with catalyst metal area  $0.11 \text{ m}^2/\text{g}$ . The reactor, consisting of a stainless-steel block with the catalyst placed in six parallel channels and equipped for external recycling, could be operated either in a CSTR-like regime (ratio of inlet/recycle equal to  $1/90$ ) or in regimes with different gas–solid gradients obtained by decreasing the recycle ratio. The entire volume of the recycle reactor was  $200 \text{ cm}^3$  and it contained  $14.5 \text{ g}$  of catalyst. Outlet concentrations of CO and  $\text{CO}_2$  were monitored (IR absorption) together with gas-phase inlet and outlet temperatures. The temperatures of the active surface layers of five catalyst pellets (placed in one channel of the reactor) were followed by  $0.2\text{-mm}$  Ni–NiCr jacket thermocouples carefully embedded below the surface (Fig. 1a). Temperature differences of  $0.05 \text{ K}$  could be measured after amplification of the signal. The location of the instrumented pellets in the bed is shown in Fig. 1b. The temperature gradient in the gas phase across the catalyst bed was on the order of  $0.5\text{--}1.0 \text{ K}$  in experiments with full recycle, and variations of the surface temperature of pellets less than  $3 \text{ K}$  existed in this case.

We can assume that a variation of the monitored surface temperature of the pellets corresponds to the variation of the local reaction rate and the variation of the outlet gas-phase concentration reflects the changes of the averaged reaction rate.

Periodic oscillations occurring on individual pellets are shown in Fig. 2a. The gas-phase temperature gradient across the bed was negligible, as could be inferred from the course of measured gas-phase temperatures. The temperatures on individual pellets oscillated in phase with the same frequency and with a maximum amplitude of  $2 \text{ K}$  as illustrated in more detail in the recording of part of the period depicted in Fig. 2b. Even though the course of the temperature signals on individual pellets differ in details (fast low-amplitude oscillations on pellets 1, 4, and 5 before the maximum), they coincide within  $1 \text{ s}$ . The oscillations are in phase also with the oscillations of the CO outlet concentration.

It has often been suggested that aperiodic oscillations may result from a loss of synchronization of individual oscillators (Pt crystallites, parts of surface, individual pellets, etc.). Here we present in Fig. 3 an example of aperiodic oscillations, synchronized and in phase both in the bulk gas phase and on the individual pellets. Transitions from periodic to aperiodic behavior could be reached reproducibly by increasing the reaction temperature or decreasing the inlet CO flux.

Desynchronization of oscillations on individual pellets was observed only in situations where larger temperature gradients between the gas phase and the surface of the pellets exist. Such a case is depicted in

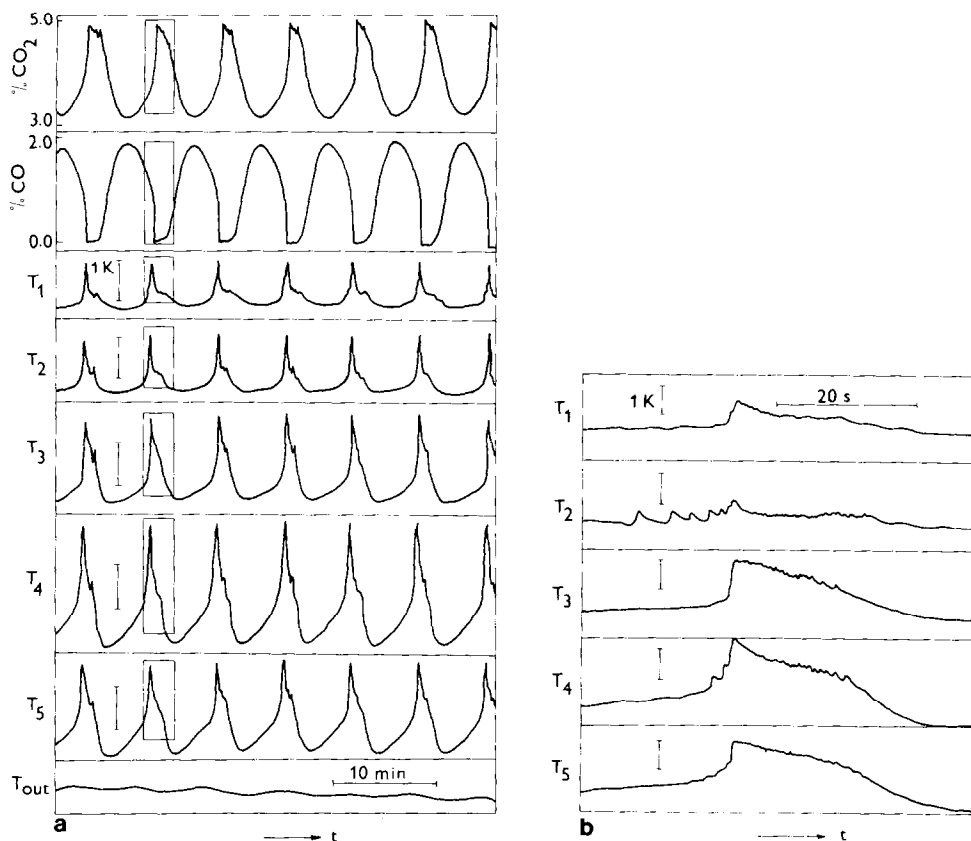


FIG. 2. (a) Synchronous periodic course of concentration and temperature signals on single pellets at 413 K, 5% CO in O<sub>2</sub>, flow rate 3 cm<sup>3</sup>/s, and recycle ratio 1/90. (b) Detailed recording of concentration and temperature signals from (a).

Fig. 4. The reactor was operated as an integral one (without recycle); hence the CO concentration along the bed decreases from the inlet concentration (5% CO) to the outlet values of the order of 0.1%. The oscillations on the pellets located close to the inlet (pellets 1 and 2) are synchronized (see Fig. 4a). However, the oscillations on pellet 3, located in the middle of the bed, are approximately in antiphase. The CO concentration at the end of the bed (pellets 4 and 5) is too low to provide distinct oscillations. Another case of the regime with concentrations and temperature gradients is depicted in Fig. 4b; it confirms the variation of the course of oscillations along the bed. When the recycle ratio was sequentially lowered

we observed that the amplitudes of temperature oscillations at first increased but the synchronization was preserved. When the recycle ratio was decreased to 1/16, then the gas phase started to be insufficiently mixed and the synchronization of oscillations also broke down.

The results confirm that both periodic and aperiodic oscillations observed under nongradient conditions in a bed containing a large number of catalytic particles have the same mechanistic causes and do not result from transport limitations in the bed or from a different course of the reaction on individual particles. The synchronization and desynchronization probably occurs via the gas phase. It is, however, still probable

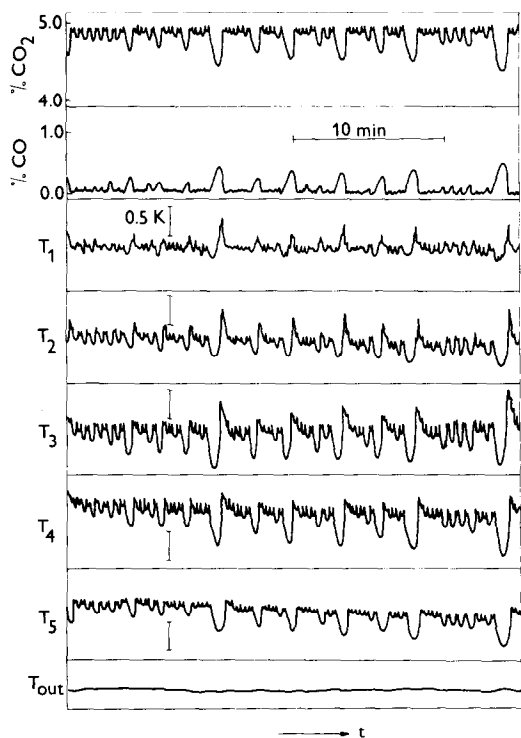


FIG. 3. Synchronous aperiodic course of concentration and temperature signals on single pellets at 443 K, 5% CO in O<sub>2</sub>, flow rate 3 cm<sup>3</sup>/s, recycle ratio 1/90.

that at the level of Pt crystallites large temperature and/or concentration gradients may exist (15, 16).

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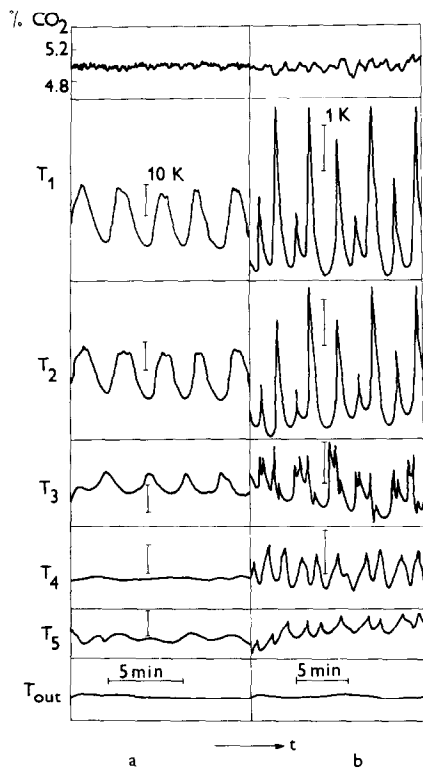


FIG. 4. Course of concentration and temperature signals on single pellets: (a) at 443 K, 5% CO in O<sub>2</sub>, flow rate 6 cm<sup>3</sup>/s, without recycle; (b) at 413 K, 5% CO in O<sub>2</sub>, flow rate 3 cm<sup>3</sup>/s, without recycle.