JOURNAL OF CATALYSIS 79, 466–469 (1983)

Oscillatory Instabilities in the Oxidation of Carbon Monoxide on Rhodium

In spite of the fact that rhodium is an active component in the "three-way" catalysts (*1*) used in automotive exhaust control, the elementary kinetics of oxidation reactions are much less studied on rhodium than on platinum. As we are interested in the so-called technological gap, i.e., the question as to how far high-vacuum kinetic results may be extrapolated to normal pressure, we need experimental data on the CO oxidation on rhodium. Thus we started an investigation of this reaction in excess air at atmospheric pressure.

We began the study by using an impregnation-type catalyst. It contained 2.5 wt% Rh on γ-Al_2O_3 (Pechiney CR 240, BET surface 240 m^2/g), as determined by spectrophotometry (*2*). The reaction was studied by use of a simple flow reactor in the temperature range $400 < T/K < 500$. The mole fraction of CO at the reactor inlet varied in the domain $0.01 < X_{CO} < 0.1$. The concentrations of CO and CO_2 were determined by nondispersive infrared spectroscopy. The results could be correlated by a global rate equation which was first order in CO taking into account that the reaction was inhibited by both CO and CO_2. At CO contents with $X_{CO} < 0.01$, oscillations of the reaction rate could be observed over the whole temperature range. However, it was not possible to give a satisfactory interpretation of the experimental results. Besides the interference of transport effects the main difficulty arose from the fact that even after a period of more than 6 months the activity of the catalyst was still changing. A possible explanation of this behaviour could be the variation of the structure or the surface of the active component, since rhodium catalysts are strongly influenced by different pretreatments (*3*). We therefore decided to avoid these artefacts by using the metal in the form of a polycrystalline ribbon.

The reactor was given the special geometry shown in Fig. 1 to permit the possibility of calculating mass transfer coefficients. It consists mainly of two concentric tubes. The catalyst is spot-welded to form a ring which is drawn over the inner tube. Its position is far enough away from the reactor inlet to permit fully developed laminar flow of the entering gas mixture. As the inner tube is made of quartz the catalyst can be subjected to various heat treatments in defined atmospheres without removing it from the support. The active surface used in the experiments described below had an area of 0.75 cm^2.

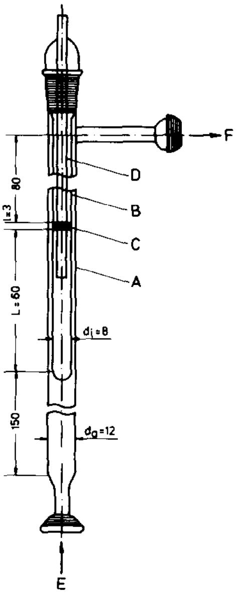

FIG. 1. Flow reactor with polycrystalline rhodium catalyst (all dimensions in mm): A, outer tube; B, inner tube; C, catalyst ring; D, thermocouple guide; E, gas inlet; F, gas outlet.

0021-9517/83/020466-04$03.00/0

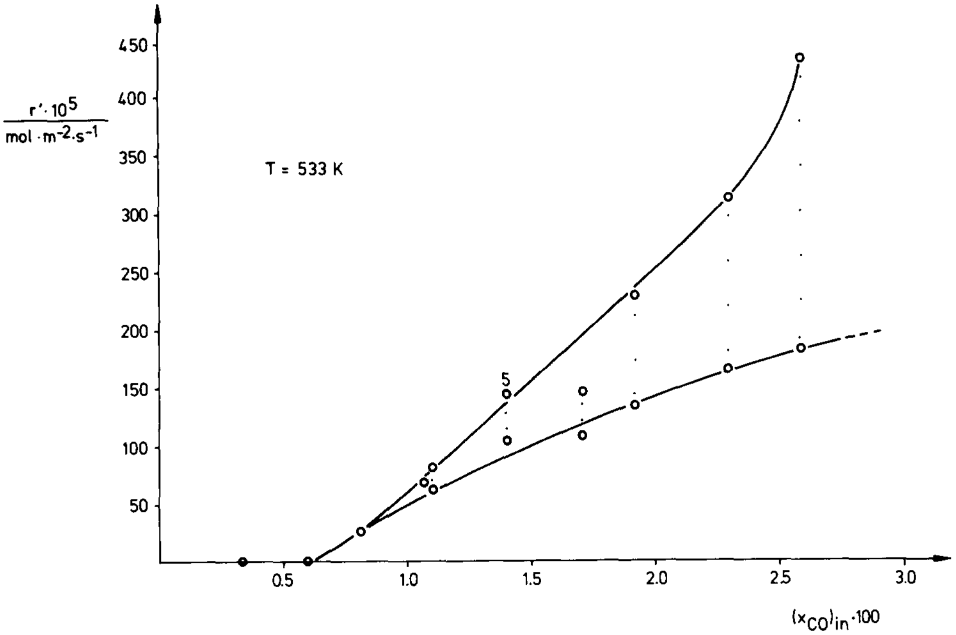

FIG. 2. Reaction rate as a function of CO mole fraction at the reactor inlet, $\dot{v}$ = 100 cm^3/min. The two curves represent the two envelopes of the oscillating reaction rate.

The first results showed that as in the case of supported catalysts (*4*) polycrystalline rhodium is subject to pronounced memory effects. This concerns not only the pretreatment of the metal before a complete experimental run but also its whole history before every single measurement. The memory can be erased and reproducibility of the results can be attained if the metal is heated before each measurement at 670°C for 1.5 h in hydrogen at 1 atm. A typical result obtained in this way is shown in Fig. 2. In this figure the variation of the specific rate r' is represented as a function of the CO content at the reactor inlet at constant temperature. Even so, time-independent values were obtained only after the catalyst had been under reaction conditions for up to 8 h. Above about X_{CO} = 0.01 we observe oscillations of the reaction rate, the amplitudes of which are represented by the points drawn in Fig. 2. Figure 3 shows the typical forms of these oscillations: they are certainly not isothermal as the adiabatic temperature variation in the gas phase cor-

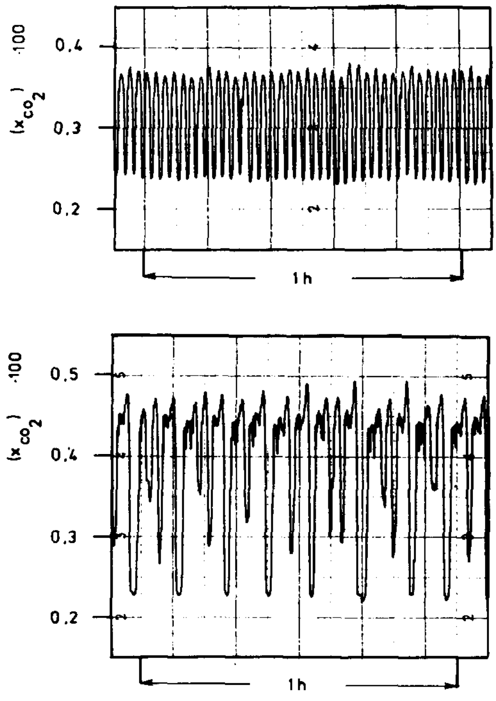

FIG. 3. Examples of rate oscillations: original drawing of CO$_2$ mole fraction at reactor outlet. Experimental conditions as in Fig. 2. Upper part: point 5 of Fig. 2. Lower part: $X_{CO,in}$ = 0.021.

responding to the fluctuations of conversion would be more than 40 K in the case shown in the lower part of the figure. However, due to the experimental setup temperature fluctuations of the catalyst could not be measured.

In recent years considerable attention has been paid to oscillatory instabilities in heterogeneous reactions. The pertinent literature has been reviewed recently by Eigenberger (*5*), by Hlavácek and Votruba (*6*), and especially for platinum by Wicke *et al.* (*7*). To our knowledge the present work reports for the first time the observation of oscillations on rhodium.

There are two interesting aspects of these preliminary results. First we can compare the behavior of the two noble metals platinum and rhodium with respect to oscillatory instabilities in CO oxidation. In the case of platinum they have been observed by several authors and studied in detail (*7*). They arise, as in the case of rhodium, both for supported catalysts (*7*) and polycrystalline foil (*8*). The phenomenon has been observed mainly under atmospheric pressure conditions; however, Barkowski *et al.* (*9*) have recently measured oscillations in the oxidation of CO on a polycrystalline Pt foil at pressures of about 16 mbar. Up to now no observations had been reported in the literature concerning oscillatory instabilities under high-vacuum conditions. However, in the case of CO oxidation by NO on platinum, isothermal oscillations of the reaction rate arise under high-vacuum conditions (*10*), which is not the case for rhodium (*11*). This striking difference points out that the reasons for the phenomena cannot be the same in both pressure regions.

Second, Riekert (*12*) has recently proposed an explanation of oscillatory instabilities based on thermodynamics. He has shown that multiplicity is to be expected if thermodynamics permits the existence of a metal as well as that of an oxide on the surface of a catalyst in contact with the reactants. Oscillations in the kinetic regime may be the result if neither of these two phases is kinetically stable. We will conclude this note by showing that the thermodynamic conditions are fulfilled in our case. For the temperature (533 K) given in Fig. 3 we can calculate from tabulated thermodynamic data (*13*) the dissociation pressure of Rh_2O_3; $p^*_{O_2} = 2 \times 10^{-10}$ bar. This is substantially less than the oxygen pressure in the gas phase, $p_g = 0.2$ bar, but much higher than the extremely low value of the equivalent oxygen pressure of the oxygen acceptor system $p_e = 4 \times 10^{-47}$ bar, calculated for a presumed CO conversion of 50%, that is, $p_{CO} = p_{CO_2}$.

We thus obtain the inequality

$$p_e < p^*_{O_2} < p_g$$

which is the necessary condition for a kinetically determined phase composition of the solid. In spite of the limited precision of thermodynamic data we can thus conclude that the proposed explanation (*12*) may be valid in the case of rhodium.

ACKNOWLEDGMENT

A fellowship from the 15th International Seminar at the University of Karlsruhe is gratefully acknowledged by one of us (G.T.).

REFERENCES

1. Schlatter, J. C., and Taylor, K. C., *J. Catal.* **49,** 42 (1977); Koberstein, E., and Völker, H., *Chem. Ing. Tech.* **50,** 905 (1978); Hegedus, L. L., Summers, J. C., Schlatter, J. C., and Baron, K., *J. Catal.* **56,** 321 (1979).
2. George, U., and Bogenschütz, A. F., *Galvanotechnik* **68,** 485 (1977).
3. Wang, T., and Schmidt, L. D., *J. Catal.* **71,** 411 (1981).
4. Cant, W., Hicks, P. C., and Lennon, B. S., *J. Catal.* **54,** 372 (1978).
5. Eigenberger, G., *Chem. Ing. Tech.* **50,** 924 (1978).
6. Hlavácek, V., and Votruba, J., *in* "Advances in Catalysis and Related Subjects," Vol. 27, p. 59. Academic Press, New York/London, 1978.

7. Wicke, E., Kummann, P., Keil, W., and Schiefler, J., *Ber. Bunsenges. Phys. Chem.* **84,** 315 (1980).
8. Edelböck, W., and Lintz, H.-G., *Chem. Eng. Sci.* **37,** 1435 (1982).
9. Barkowski, D., Haul, R., and Kretschmer, U., *Surf. Sci.* **107,** L329 (1981).
10. Adlhoch, W., Lintz, H.-G., and Weisker, T., *Surf. Sci.* **103,** 576 (1981).
11. Lintz, H.-G., and Weisker, T., unpublished results.
12. Riekert, L., *Ber. Bunsenges. Phys. Chem.* **85,** 297 (1981).
13. Barin, I., Knacke, O., and Kubaschewski, O., "Thermochemical Properties of Inorganic Substances." Springer-Verlag, Berlin, 1973.

KLAUS R. FRANCK[1]
HANS-GÜNTHER LINTZ
GÖNÜL TUFAN[2]

Institut für Chemische Verfahrenstechnik der Universität (TH) Karlsruhe
D 7500 Karlsruhe, Germany

Received April 21, 1982; revised September 10, 1982

---

[1] Present address: Laboratoire des Sciences du Génie Chimique, E.N.S.I.C., 1 Rue Grandville, 54042 Nancy Cedex, France.

[2] Present address: Department of Chemical Engineering, Ege University, Izmir, Turkey.