JOURNAL OF CATALYSIS 61, 289–290 (1980)

Influence of Inerts on Kinetic Oscillations during the Isothermal Oxidation of Hydrogen on Platinum Wires

In a recent experimental study of oscillations in the reaction rate during the isothermal oxidation of hydrogen on platinum wires the oscillations always disappeared when helium replaced nitrogen as the carrier gas (*1*). Recent experiments with the same equipment indicate that oscillations in the rate may be attained even when helium is the carrier gas. The reason that the oscillations were not observed previously is that under the operating conditions used in (*1*) either a stable or an oscillatory state may be attained depending on the start-up policy. The shift from nitrogen to helium always caused a very short transient reduction in the hydrogen concentration and a transition to the stable steady state.

This surprising behavior can be understood better by examining Figs. 1 and 2 which describe the dependence of the isothermal reaction rate on the hydrogen concentration using either nitrogen or helium as a carrier gas for two different linear gas velocities. The graphs indicate that at 95°C a unique stable state exists for low hydrogen concentrations (<0.2% v/v) while either a stable or oscillatory state exists for hydrogen concentration in the range of 0.2–1% (v/v). For higher hydrogen concentrations a unique oscillatory state exists.

For linear gas velocity of 1 cm/s the mass transfer resistance was not negligible and as seen from Fig. 1 the reaction rates for mixtures containing nitrogen as a carrier were lower than those containing helium as the carrier. However, for linear gas velocities of 3 cm/s the rates were identical for both reaction mixtures (Fig. 2). The magnitude, frequency, and shape of the oscillations were essentially the same with both inert diluents. The slight differences are probably insignificant as they are about equal to those obtained when one tries to reproduce a previous experiment. The period of the oscillations was usually in the range of 20–50 min.

The data indicate that for hydrogen concentrations in the range of 0.2–1% (v/v) transient fluctuations in either the hydrogen concentration or other operating conditions may cause a transition from one state to the other. Thus, extreme care should be taken in the search for oscillatory states in this region in order to guarantee that the system will converge to such a state.

It should be noted that the electrothermic method used to measure the isothermal rate can be used only if the heat generated by the reaction is smaller than that transferred from a nonreactive wire, kept at the same surface temperature, to the reaction mixture. Thus, at 95°C it was not possible to measure accurately oscillations in the reaction rate of mixtures with a hydrogen concentration exceeding 1.1% (v/v) when nitrogen was the carrier. However, when helium was used as the carrier, the increased rate of heat transfer enabled reliable measurements with mixtures containing up to 2% (v/v) hydrogen.

It was suggested by Eigenberger (*2*, *3*) that kinetic oscillations are caused by some inert species which drives the system between two stable states. The coexistence of an oscillatory and stable state with nonover-

0021-9517/80/010289-02$02.00/0

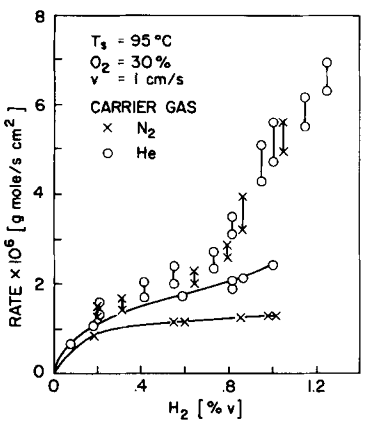

FIG. 1. Dependence of the oxidation rate on hydrogen concentration. Endpoints of vertical lines represent peak to peak amplitude of the oscillation.

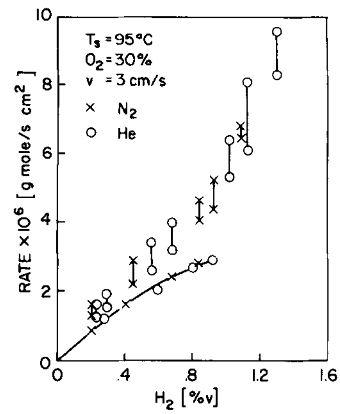

FIG. 2. Dependence of the oxidation rate on hydrogen concentration.

lapping rates indicates that a different mechanism is responsible for the behavior in this case.

Varghese *et al.* (*4*) have reported recently that impurities in the feed were responsible for spurious oscillations during the oxidation of CO on supported platinum. The experiments reported here were carried out using extra-dry grade hydrogen and oxygen (Linde) and high-purity grade nitrogen and helium.

According to the manufacturer's specification the hydrocarbon content of these hydrogen, oxygen, nitrogen, and helium cylinders is less than 1, 30, 1, and 1 ppm, respectively. Thus, the hydrocarbon content of the mixture is less than 9 ppm.

A separate series of experiments were conducted using a mixture of ultrahigh-purity grade hydrogen and nitrogen and zero grade oxygen. According to the specifications the hydrocarbon content of the cylinders of these gases is less than 1, 1, and 0.5 ppm, respectively. The behavior observed with this mixture, which contains less than 1 ppm hydrocarbons, was the same as that observed with the mixture of lower purity. Thus, we believe that the oscillations observed in this work for hydrogen oxidation are not affected by the purity of the gases used. Obviously, our experiments cannot preclude the possibility that impurities at the level of ppb are causing the oscillations.

ACKNOWLEDGMENTS

We wish to acknowledge helpful discussions with Dr. M. Sheintuch and are grateful to the Welch Foundation for financial support of this research.

REFERENCES

1. Zuniga, J. E., and Luss, D., *J. Catal.* **53**, 312 (1978).
2. Eigenberger, G., "Proc. 4th Int. Symp. Chem. React. Eng." Dechema, Heidelberg, 1976.
3. Eigenberger, G., *Chem. Eng. Sci.* **33**, 1255 (1978).
4. Varghese, P., Carberry, J. J., and Wolf, E. E., *J. Catal.* **55**, 76 (1978).

KUPPUSWAMY RAJAGOPALAN
DAN LUSS

Department of Chemical Engineering
University of Houston
Houston, Texas 77004

Received March 27, 1979; revised August 9, 1979